DEVELOPMENTS IN SEDIMENTOLOGY

41

G.V. CHILINGARIAN and K.H. WOLF
(Editors)

DIAGENESIS, I

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DEDICATION

Dedicated to Chris Amstutz, Don F. Sangster, and the late Wolfgang Krebs for their important contributions to the field of ore-related diagenesis, and to Francis J. Pettijohn, Robert L. Folk, Hans Füchtbauer, Paul E. Potter, Raymond Siever, and German Müller for theirs in sandstone diagenesis.

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CONTENTS

XII

INTRODUCTION

Ubiquity of diagenesis – catagenesis – metamorphism — A brief review of complex interrelationships of variables and environments

KARL H. WOLF and GEORGE V. CHILINGARIAN

INTRODUCTION

Like the comprehensive, evaluative summaries-cum-synopses of many of the earlier volumes in Developments in Sedimentology, the presently offered volume (to be supplemented by others) of "Diagenesis" hopefully will become an equally popular vade-mecum for the busy researcher, consultant, teacher, and explorationist. The chapters serve as a continuum, or literary extension, of the contributions made in Volumes 8, 9, 12, 16, 18, 21, 24, 25A, B, 28, 29, 33 and 36 of Elsevier's Developments in Sedimentology series – and there is no logical end in sight to the evolving concepts on diagenesis. Consequently, periodic reviews are greatly needed.

COMPLEX INTERRELATIONSHIPS OF DIAGENETIC VARIABLES AND ENVIRONMENTS

Diagenesis is a highly developed, interdisciplinary field of study. It is reciprocal in that it borrows from numerous scientific or technological specialties and then, in turn, repays them with useful results. Too often, however, the information gained and concepts developed remain unintegrated instead of being utilized quickly by several related earth-science fraternities: the transition of ideas and methodologies is a very slow diffusion process!

Figure 1 is a so-called linkage or concatenation circular model[1] that highlights potential concrete and abstract (philosophical) interrelationships (see Wolf, 1987). Such a model can stress the actually existing as well as the possible interconnections and overlaps of the diagenetic data in those disciplines that are plotted on the circumference. The so-called "interrelations" or "interconnections" can be of several different types, depending on how one wishes to utilize these models: (a) genetic (unidirectional or reciprocal); (b) spatial (associative, distributional); (c)

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[1] Stebbins/Ayala (1985) have used a similar approach in biology by depicting complex relationships affecting biological evolution in their "crossing polygon" – but the writers prefer to call them "linkage" or "concatenation circles" or models.

time (sequential, paragenetic, stages – phases-type); and/or (d) abstract-style (e.g., comparative – contrastive-type). Thus, the circular linkage – concatenation models are also based on the concept of synergism, which depicts the combined effect of any variables – factors – parameters and/or environments that exceeds the sum of their individual effects.

It has long been known that comprehensive, creative, integrative reviews require special talents; such specialized intellectual activity, if well performed, does make a fundamental contribution that assists those engaged in the so-called more fundamental research. Good summaries actually "free the hands" of researchers and explorationists, allowing them "to do their own thing" by providing them with more time, identifying problems to be tackled, and by assembling data ready to be "manipulated by the electronic wunderkinder" (= computers). A few comments on some selectively chosen specifics are presented here.

In Chapter 1, dozens of parameters involved in diagenesis have been listed (in effect, a catalogue or checklist of nearly 350 diagenetic variables has been prepared, which is not offered here in its entirety). The macro-variables in any geological system, that also control diagenesis either obviously – directly or latently – indirectly (i.e., explicitly or implicitly), are complexly interrelated. Indeed, the total complexity is still beyond the grasp of geologists – conceptually and methodologically. Recently, however, an excellent start was made in unravelling the enormous intricacies.
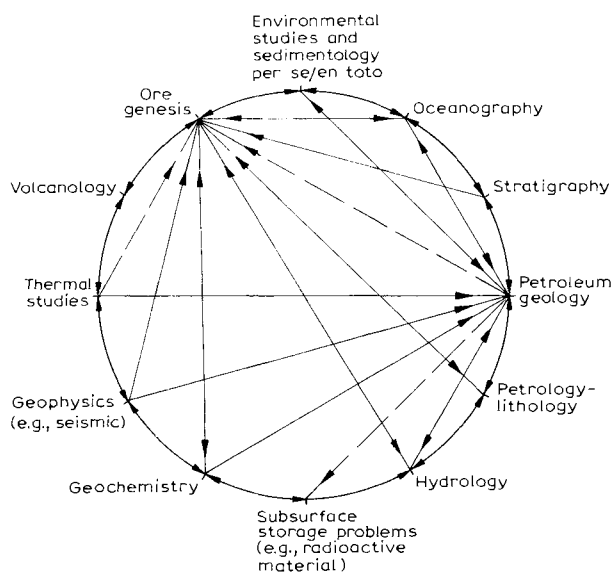
Fig. 1. Several earth-science disciplines which undertake diagenetic – catagenetic – burial metamorphic investigations by using an interdisciplinary integrative-style approach and, in turn, supply results to all other sister sciences and among themselves: a truly reciprocal intellectual – philosophical phenomenon among investigators. (This and the other four figures herein are after Wolf, 1978, periodically modified – unpublished.)

In Fig. 1, only two disciplines, i.e., ore genesis and petroleum geology, have been "related" to the other "variables" or fields of investigation in this particular model. The arrows around the circumference in this and all other figures stress the disciplines' (or "factors' ") transitions – gradations in respect to methodology, aims, contributions, data generated and utilized, etc. For example, ore genesis integrates the concepts and data from volcanology, thermal studies, geophysics, geochemistry, hydrology – paleohydrology, petrology – lithology, sedimentology – paleoenvironmental investigations, oceanography, stratigraphy and even petroleum geology (e.g., in the case of Missippippi Valley-type ores). As a "reciprocal gesture", the results can be applied in most instances to all other fields of endeavor.

Figure 2 depicts twenty macro-variables and the few imposed lines plus arrows highlight selectively chosen potential genetic – environmental unidirectional, reciprocal, and sequential inter- and intra-relationships between the variables and within environments. Again, only two variables have been "related" to most other parameters – factors (i.e., "depth of burial" and "mineralogy – geochemistry"). One can readily see that depth of burial is either controlled by the other variables [1] or it influences the others [e.g., No. 2] in a unidirectional fashion, or the relationship is reciprocal [3]. (For simplicity's sake no other arrows have been drawn, except around the circumference; these interrelationships can be examined as an excercise.)

"One of the greatest pains to human nature is the pain of a new idea."

Walter Bagehot
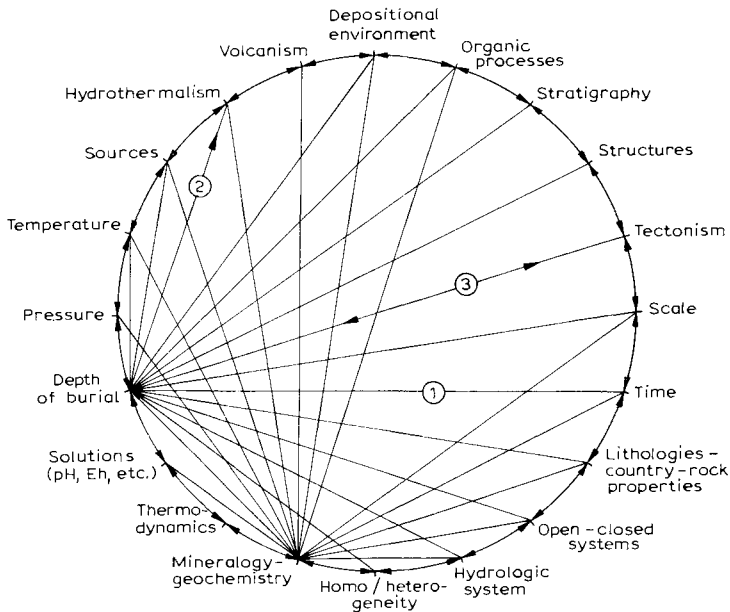
Fig. 2. Megavariables (selectively chosen for demonstration purpose) of a diagenetic – catagenetic – metamorphic system.

"There is nothing more difficult to take in hand, more perilous to conduct, or more uncertain in its success, than to take the lead in the introduction of a new order of things."

Niccolo Machiavelli (quoted in Rabbitt, 1980)

In deliberations on ore-genesis-related diagenesis (Ch. 1), the writers have listed in several tables the scope of diagenesis, e.g., Table 18 provides the specific sedimentary hostrocks of ore mineralization, each of which comprises its own environment for secondary processes. Insofar as the senior author (Wolf, 1987) has repeatedly emphasized that integrative investigations must also include the examination of transitions – gradations, continua – spectra possibilities, and overlapping phenomena, Fig. 3 has been given here to demonstrate this requirement.

In this figure, only the ores (for example, Mississippi Valley-type Pb – Zn – Ba – F concentrations in carbonates) are highlighted by lines + arrows. The following questions arise here:

(a) What are the genetic, source, (re)mobilization, and environmental interconnections between the ore, on one hand, and black shale (i.e., organic matter and source of metal and/or sulfur) [No. 1]; evaporite (as a supplier of saline ore-forming solution which dissolved metals from country rocks) [No. 2]; clays – shales [as metal supplier during compaction and dehydration(?) in some cases] [No. 3]; and dolomite (formed by epigenetic late-diagenetic – catagenetic dolomitization) as an ore hostrock [No. 4], on the other?
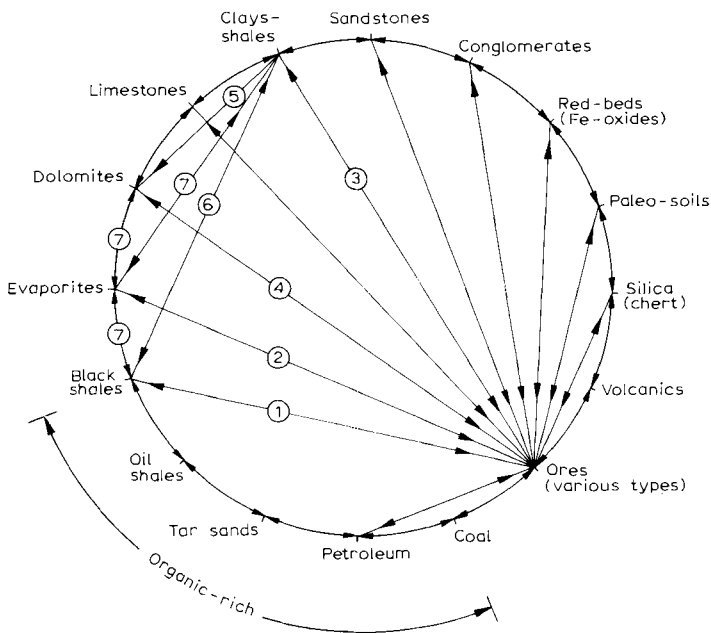
Fig. 3. Specific sedimentary – volcanic deposits which undergo diagenesis – catagenesis – metamorphism. The differences, similarities, overlaps, transitions – gradations, and continua – spectra in regard to secondary alteration mechanisms, environments and products ought to be clearly compared and contrasted.

(b) Did the clays supply Mg for dolomitization [No. 5]?

(c) Are black shales absolutely required for specific ore types to be formed, or can any clay – shale body, even one formed under an oxidizing milieu, furnish the necessary ingredients for ore genesis [No. 6]?

(d) What must be the "stratigraphic proximity" of evaporites, clay-shales – black shales and dolomites association to ascertain maximum potential for ore genesis and the presence of ores in a compacting sedimentary basin [No. 7]?

One can expand or supplement the above deliberations of the diagenetic characteristics of lithologic groups by being more specific, i.e., by considering mineral diagenesis – catagenesis (Fig. 4). From past observations (many reported in the literature), and founded on "pure geochemical – mineralogical logic", the existence of genetic and environmental interrelations, transitions, and overlaps between many minerals are known. These interconnected phenomena have been stressed by lines + arrows in Figs. 4 and 5.

The relationships between some mineralogical products in Fig. 4 need some elaboration, as supported by several preferential examples. Numerous clastic – detrital – "terrigenous" materials and chemical precipitory products in sedimentary – volcanic sequences (1) can undergo diagenesis – catagenesis – metamorphism, (2) can be the product of these secondary processes, and (3) can have a "mixed" origin (combination of the two above) (e.g., clastic feldspar is overgrown
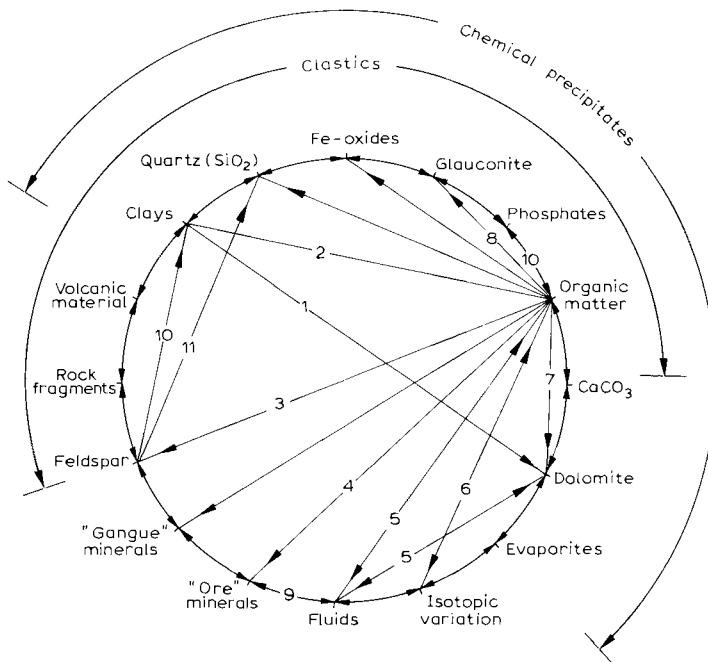
Fig. 4. Concatenation diagram depicting complex interrelationships among numerous clastic and chemically formed constituents. See text.

by authigenic feldspar which are subsequently both altered to chlorite), thus involving two separate groups of material.

As an exemplar of complex genetic (and potential space – time, paragenetic, and associative) interrelationships, the organic-matter-control (= OM) is preferentially stressed: Dolomite genesis may require the presence of clays and OM [Nos. 1 + 2]. The following questions should be answered: Does OM prevent or enhance the alteration of feldspar to some type of secondary mineral [Nos. 3 → 10]? The movement of OM by fluids into a dolomite hostrock may permit the precipitation of sulfides ("ore") [Nos. 7 → 5 → 9]. During this involvement in ore genesis, do the C-isotopes in OM change [No. 6]? Innumerable other complex interconnections can be "visualized" by examining at length such a diagram (additional numbers should be used).

Figure 5 is a more generalized model in contrast to Fig. 4. The former is based on three groups of parameters: (1) chemical – biological – physical processes; (2) sedimentary rock properties (like the components' composition, textures – fabrics, etc.); and (3) isochemical versus "metasomatic" (addition or removal of chemical constituents) phenomena.

The matrix variable can be considered next. The origin of matrices in many types of rocks (graywackes, volcaniclastics, pyroclastics – tuffs, etc.) has been controversial; and several schools-of-thought have developed, although a general concensus has been achieved. For exacting geochemical studies, however, several possibilities exist for any specific matrix case. Both chemical and physical processes control the
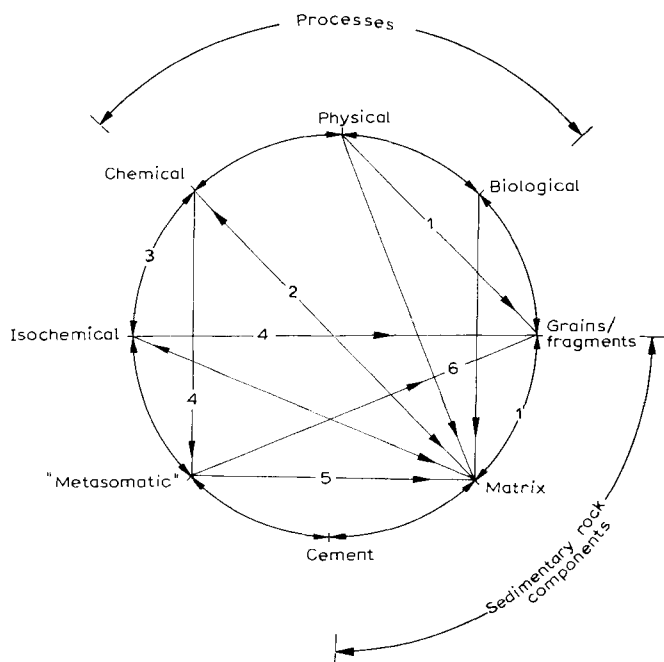
Fig. 5. A model comprising three processes, three sedimentary components, and two "chemical process variables". The origin of matrices is discussed in the text.

characteristics of matrix — and during the early stage of sedimentation, biological reworking is also present. Compaction of soft clay-rich fragments can produce a matrix [No. 1]. Burial metamorphism produces "chemically controlled" matrix [No. 2]. In some cases, the matrix formed under isochemical conditions (no change in the micro- meso-scale composition) [Nos. 3 → 4]; whereas under other circumstances the processes were "metasomatic" [Nos. 4 → 5]. A metasomatic attack on grains — fragments may also be involved [Nos. 6 → 1]. One may well agree that the above deliberations are "common-sense-based" and no such diagram is required for "logical reasoning". One should remember, however, that this model is merely a simple example. On adding 10 to 20 other variables related to specific geochemical settings (e.g., Eh, pH, solute composition, fluid mixing, rates of reactions, open- versus-closed system, homogeneity — heterogeneity), physical conditions (e.g., $T - P$, depth of burial) and some "abstract" variables (e.g. time), interrelating all these parameters becomes very complex!

Having demonstrated briefly the "power of conceptual resolution" in outlining natural complex genetic — environmental interrelationships, an appeal is made to continue and expand integrative studies in both theoretical and applied diagenesis (e.g., see Wolf, 1987).

"Deliberate over-generality and abstraction, . . . and the proliferation of concepts and terms have often done more harm than good in the sciences. It should be a matter of regret that the least exact among them, sciences whose very principles are the least certain, tend to be the most concerned with rigor, generality, and axiomatics."

B.B. Mandelbrot (1977, p. 14)

FUTURE RESEARCH NEEDS

As reiterated above, there is no end in sight to diagenetic research because of its wide practical and intellectual appeals. Gaping holes still exist in the present-day knowledge — and a final definitive word is never attained, so that our "present certainties" will be modified or replaced. All data and concepts need a caveat emphasizing its possible "dated nature"! Many new discoveries will be forthcoming more by accident than by design.

But what are the immediate and potential remote-future needs for information that the exploration geologists or practical operators can utilize? The research earth-scientist can help here by both field and laboratory studies in solving the innumerable enigmas. The list below offers merely a few haphazardly given questions and proposals related to potential future research topics. Thirty years ago, the American Association of Petroleum Geologists' Research Committee (1957) outlined research needs; similar lists on the whole spectrum of earth-science needs ought to be published by specialists' journals and books.

The following topics related to diagenesis — catagenesis — metamorphism must be given consideration in future research programs:

(1) A classification of all natural fluid types is required which can be utilized by research geologists; all geological, geochemical, and hydrological characteristics of these fluids ought to be reviewed. (Even specialist researchers lack such a check-list.)

Several classification schemes are required as the approach will vary according to needs and variables used: descriptive (several) and genetic (numerous) schemes, geochemical and environmental schemes, etc., are to be contemplated – not in isolation but in association. Synonyms and analogous terms must be identified among the many names in wide use already.

(2) What are the fluid and solute mass-balance (and numerous other) requirements in a regional diagenetic – catagenetic complex ranging from the source area via the transportation – aquifer passage system to the precipitation – depositional – reconcentration locality? (See Wood/Low, 1986, among others.)

(3) What are the fluid release and generation mechanisms [including processes of (re)mobilization] during diagenesis – catagenesis – metamorphism? What are the precise interplays between compaction – tectonism – mineral neoformation in controlling the various "types" or compositional ranges of solutions? (See Oliver, 1986, among many others. Much data are available, but a comprehensive review is needed.)

(4) What are the diagenesis-established micro → meso → macro-scaled hydrologic patterns; or conversely, what are the hydrologic flow patterns that cause variations in diagenetic facies in the various types of sedimentary basins? (Are fractal studies needed to solve the problem? See below.)

(5) What types of diagenetic, meteoric, catagenetic and metamorphic conductive and convective phenomena exist in the various types of basins? What are their characteristics, differences, similarities, among others? (See Episodes, 1986c.) To what extent are convective flow processes within sedimentary – volcanic deposits part of and control diagenesis on the micro- to meso-scale, independent from those convection flows on the macro-scale or regional scale? How does convection (re)mobilize fluids, elements and heat or energy? (See Thibodeaux/Boyle, 1987.)

(6) The study of fluid composition – evolution must be undertaken by using multidisciplinary approaches, including mineralogical – geochemical space – time paragenetic investigation. (See Schmidt/McDonald, 1979a, b.)

(7) How can one establish absolute and relative ages of fluids involved in diagenesis, catagenesis, and metamorphism?

(8) An attempt must be made to identify – discriminate subsurface fluid-movement directions by utilizing structural, textural, alteration, mineralogical, isotopic and trace-elemental criteria – guides that reflect or are formed by the passage of diagenetic – catagenetic – metamorphic solutions (with or without heat – energy exchange?). The western geological fraternity ought to develop their own "Ontogeny of Minerals" (?). [See Grigor'ev (1965) and Lebedev (1967) for textural features.]

(9) How do abnormal fluid pressures control diagenesis? Does diagenesis actually create abnormal fluid pressures in the various lithologies? (See Episodes, 1986c.)

(10) What are the precise boundary phenomena that affect diagenesis?

(11) How did geochemical and physical (e.g., permeability) barriers, that can change an open to a closed system, for example, form during diagenesis?

(12) How can one recognize the long-distance, hidden influences of igneous intrusions on diagenesis (in this case "induced" diagenesis?) as well as catagenesis and "regional" metamorphism, in contrast to basin-derived hot fluid-induced secondary controls?

(13) How can one recognize the influence of hydrothermal – exhalative processes superimposed on surface or near-surface "normal" ones? Or how can one recognize products formed by mixing of hydrothermal and marine fluids during diagenesis? (See Kalogeropoulos/Dabitzias, 1986.)

(14) How do hydrothermally vented gases (e.g., helium and methane) influence diagenesis (see Episodes, 1986a)? Or do these gases escape? Are any gases trapped in sediments or volcanics? Can organisms utilize certain gases?

(15) As to dating sediments and pyroclastic deposits, there are many remaining problems. The following questions are deliberately based on some older publications to demonstrate that some early-recognized problems have as yet not been fully solved. What are the processes of isotopic separation of elements in the ^{238}U series? What are the effects of biological mixing, etc., including residence time and other time-dependent phenomena, on the control of isotopes used in absolute and relative age-dating of sedimentary detrital and biological material? (See Holmes, 1981.)

(16) In regard to dating contemporaneous and other younger sediments and ancient, lithified sedimentary rocks (and pyroclastics), one should determine the influences of (a) diagenesis; (b) the presence of organically absorbed C and U (among others) (Cobb, 1961); (c) differential C-distribution in organic versus skeletal components and rates of sedimentation (Emery/Bray, 1962); (d) base-exchange and thermal controls (Kulp/Engels, 1963); (e) rate of sedimentation (Goldberg et al., 1963/64); (f) inheritance history of isotopes (e.g., Whitney/Hurley, 1964); (g) authigenic and diagenetic – catagenetic versus clastic mineral origins (e.g., Pasteels, 1968); (h) sampling techniques and selectivity of specimens (Kulp, 1961) from different interbedded lithologies (bentonites, tuffs, volcanic sediments exposed to metasomatism) (Fitch/Miller, 1964); (i) open- versus closed-system alteration (Kulp, 1963; Miller/Fitch, 1964); and (j) atmospheric – hydrospheric variations in isotopes during the earth's history. The items listed above apply to the following dating methods: K – Ar, Th – Pb, U – He, Rb – Sr, C, Io – excess, Io – Th and Pa – Th.

(17) How can one measure the "simultaneity" of geological events, including those of diagenesis, catagenesis, metamorphism, etc.? Many problems remain; see Kitts (1966), among others.

(18) What are the applications of fission-track methods (e.g., of apatite) in diagenetic studies? (See Episodes, 1986c.)

(19) How does neoformation of magnetite (and other minerals) during diagenesis – catagenesis – etc. remagnetize earlier-formed magnetization? (See Bogen, 1986.) Middleton/Schmidt (1982) presented a unifying hypothesis comprising the relationship between burial metamorphism, depth of burial, coalification rank, thermal activation of magnetization, and paleotemperatures.

(20) How have the geomagnetic polarity reversals affected diagenesis – catagenesis – metamorphism? (See, among others, Simpson, 1966, for "evolutionary pulsations", which increased ionization radiation and enhanced general mutation rate of organisms. Is one to assume that these "geophysical" processes did not affect diagenesis, for example?)

(21) What are the changes in isotopic geochemical processes during diagenetic to metamorphic evolution of, or in, various types of lithologies in a basin? (See Hunziker, 1986.) More than one isotopic method has to be applied to solve such questions.

(22) During the evolution (in both time and space) of diagenetic – catagenetic systems, are there (a) environmental "trigger" or "initiator" mechanisms (Hallam, 1986), and (b) geochemical, biological, physical, hydrological (including thermal) "thresholds" or "barriers" that must be crossed or overcome before one diagenetic – catagenetic system can be succeeded by another one?

(23) What are the controls of the "four fundamental forces of nature", namely the strong, electromagnetic, weak, and gravitational forces (based on Wolf, 1974; unpublished list of future research problems; see also Di Francia, 1976/1981, among others)? How do these forces correlate with the 12 energy types discussed by Wolf (1987) and in Wolf's chapter in Vol. III. This is an entirely new research problem, in geology in general as well as in studies of secondary phenomena such as diagenesis to metamorphism.

(24) All exo- and endothermal processes operative during diagenesis to metamorphism must be identified.

(25) What are the kinetics of the numerous secondary mechanisms during diagenesis to metamorphism? How do the kinetics relate to energy requirements, for example?

(26) What are the heat or energy sources, "conductors" or "dissipators", etc., in any natural system?

(27) What are the energy budgets of diagenetic to metamorphic complexes under various geological settings?

(28) What is the thermal evolution within specific lithologic types and how is the migration of fluids influenced? How does differential heat-transfer influence secondary geochemical – mineralogical processes in closed and open systems? Experience has shown that several potential thermal history scenarios for each specific case have to be established to find the correct one by trial-and-error on a comparative – contrastive-type basis.

(29) What are the changes in thermal conductivity during compaction of a basin, which in turn influences diagenesis – catagenesis. (See Episodes, 1986c.) Paleotemperature reconstructions have to be made by using several methods that measure temperature, because the information obtained is often inconsistent and contradictory. For instance, depth-versus-temperature studies are frequently inconsistent; different methods provide different data; and depth does not directly correlate with pressure. In any study of secondary mineral assemblages, the geochemical model must be coupled with several others, e.g., thermal and geodynamic models, among others. (See Episodes, 1986c.)

(30) What are the residence-time requirements for various diagenetic – catagenetic systems? Mass-balance needs must be taken into consideration. (See also rate of sedimentation controls; Gebelein, 1977.)

(31) What are the differences between active and passive diagenesis (Milliken et al., 1981)?

(32) How do diagenetic to metamorphic heterogeneitic systems form in contrast to homogeneous ones?

(33) Which diagenetic – catagenetic – metamorphic processes (and products as well as whole environmental systems) are reversible in contrast to those that are irreversible, unidirectional in time and space? Which processes can be cyclical in geologic history from the Precambrian to the Present?

(34) For all deep boreholes drilled into the Earth's crust, an all-inclusive diagenetic to metamorphic investigation ought to be carefully planned. For example, in the Soviet Union a borehole up to 15 km in depth will be drilled that reaches zones of very high pressures with temperatures up to 250°C in a sedimentary basin (Episodes, 1986b). During the study of rocks of such deep boreholes, can one recognize isochemically formed material in contrast to those that originated by metasomatic ones? (See Stanton, 1982, for related, interesting concepts that require future examination.) Can one obtain data related to (re)mobilization mechanisms and environments from such deep boreholes (see Wolf, 1987)?

(35) What are the biological, chemical and physical – mechanical (re)mobilization processes that cause diagenetic movements or transfer to produce diagenetic – catagenetic-type veins? For example, Cu-detritus can undergo diagenetic leaching – dissolution to form authigenic reprecipitation in small, early-formed, diagenetic fissures: the open mechanical system was succeeded by a closed geochemical system, the latter characterized by a closed bacterial sulfate reduction process. This setting has also been (alternatively) explained by mixing of diagenetically derived Cu-rich brines and S-rich hydrothermal fluids. Flint et al. (1986) suggested that a full integration of sedimentary, diagenetic and hydrothermal models must be achieved.

(36) Establishment of a list of "comparative preservation potentials" of all biological, chemical and physical diagenetic to metamorphic products. Thus, a corresponding (converse?) list or spectrum of "processes of destruction" would be the result. One can then, perhaps, answer the question as to whether the alteration of illite by mild-burial metamorphism can also be achieved by some other mechanism.

(37) Identification of the still-required geochemical data to unravel diagenetic versus catagenetic versus metamorphic versus hydrothermal enigmas (see Brookins, 1986).

(38) Additional studies based on analyses of both metallic and non-metallic elements, because too many investigations concentrate on one or the other and no correlation between various groups of elements in the Periodic Table is possible.

(39) Studies of the reliability – degree of accuracy. For example, investigations of diagenetic-to-metamorphic changes merely employ isotopic and fluid-inclusion analytical methods in paleoenvironmental reconstructions. Lately, it has been clearly demonstrated that several other methods must be integrated to ascertain plausible, useful results.

(40) What are the combinations of several geological and geochemical methods to enhance the reliability, accuracy, and thus applicability of data? (See Hunziker, 1986, and Frey, 1986, for an integration of illite crystallinity, index mineral data, coal rank and fluid inclusion in the study of burial metamorphism to unravel "zoneography" of secondary facies.)

(41) The theories – laws of thixotropy and related concepts ought to be given more serious consideration in the study of diagenesis – catagenesis (see Elliston, 1984, 1985; his ideas can be extrapolated to diagenesis, for example).

(42) What are the differential – preferential – selective diagenetic to metamorphic trends? For example, this phenomenon is operative during the origin of matrix in so-called graywackes, as discussed above.

(43) Much remains to be done on unravelling mineral and geochemical parageneses in both space and time. See, for example, the problems related to diagenetic versus "epigenetic" products in Mississippi Valley-type ore deposits described in Ch. 1.

(44) Identification of the many chemically and genetically related mineral species and groups, which are transitional – gradational, overlapping, and form continua – spectra in regard to elemental and isotopic composition and environment of formation. The mechanisms of origin, compositional boundary relations, and potential conversion, inversion, transformation processes, among others must be investigated. (See Murowchick/Barnes, 1986, for marcasite – pyrite formation in roll-front U, Mississippi Valley Pb – Zn, submarine hydrothermal vent, and epithermal deposits – all diagenetically influenced.)

(45) What are the pathfinder elements for specific diagenetic processes in particular environments? (See Brookins, 1986, among many others.)

(46) What are the physicochemical and biochemical capture mechanisms allowing As and many other elements to be concentrated in pyrite and other minerals? (See Belzile/Lebel, 1986.) What are the differences between diagenetic, catagenetic and metamorphic capture processes?

(47) What are the syngenetic – diagenetic – supergenetic processes that form REE anomalies (of various patterns) in shales and other sedimentary – volcanic rocks. (See Schieber, 1986.)

(48) How can one discriminate between the many types of processes and environments (and classify them meaningfully in order to obtain a check-list) that result in trace-element anomalies in a particular lithology-forming setting? (For a specific problem, see Orth et al., 1986, for four alternative hypotheses of Os, Ir, Pl, Cr anomalies: comet impact, increased ocean upwelling, stagnation, and volcanic-exhalation – in all four hypotheses diagenesis will, or can, be influential during or after the event, depending on various factors.)

(49) What are the "geochemical signatures" of former meteoritic (and other) impacts, in contrast to other types of geochemical anomalies? Are there diagenetic (even if rare) processes that can produce geochemical concentrations similar to those formed by an "outerspace" source? What syngenetic – diagenetic environments are needed to preserve highly unusual geochemical signatures? (More than 100 craters larger than 1 km in diameter have been found around the world; see *New Scientist*, 1987, p. 19.)

(50) How can one distinguish between outcrop contamination products and genuine natural sedimentary – volcanic and diagenetic materials? (See Montanari, 1986.) To put it differently: what are the criteria to separate genuine "natural" authigenic – diagenetic products from anthropogenic pollution material? (See El Ghobary/Latouche, 1986, and many others, for natural and man-induced diagenesis. See Wolf, 1986, for intricate relationships beyond diagenesis.)

(51) Comparative – contrastive study must be conducted on the secondary organic versus inorganic minerals. How do they mutually control each other during diagenesis?

(52) How can one eventually correlate – compare environment-sensitive fossils with inorganic, physicochemically formed diagenetic, surface-produced minerals?

(See, for instance, Vella, 1962, regarding "depth paleoecology"; Sylvester-Bradley, 1971, for "animal paleogeography" and discussions on organic versus geologic – geochemical evolution.) Are there "diagenetic provinces" in addition to, or comparable to, ecologic ones? Can their boundaries coincide? (See also Dorf, 1963, for climatic controls on fossils.) Is there an identifiable associated diagenetic control? Do the areas of preservation during burial of biological and physicochemical components differ?

(53) Which diagenetic systems affect organisms to cause dwarfism in micro- and macro-organisms?

(54) What are the types of diagenetic – catagenetic – metamorphic dubiofossils, pseudofossils and other physicochemically produced particles in contrast to those of genuine organic – biological origin. (See Hofman, 1972, for example, and the Precambrian-chert enclosed "fossils".)

(55) More use of the scanning electron microscope in "cathodoluminescence petrology" should be made in unravelling microscopic diagenetic – catagenetic – metamorphic features. This methodology has been employed to investigate the following (albeit haphazardly listed) exemplars: very small changes in crystal chemistry, intra-particle porosity-type delineation, outlining of pore geometry (micro-joints, cracks, channels, pin-point, tortuosity), anisotropy identification, chalk pore geometry in physical and engineering property studies (diagenetic history of a rock used in applied geology), clay microstructural alteration during burial metamorphism, coagulation feature recognition, unravelling of cementation history, surface features of grains to establish flow direction of corroding or mineral-precipitating solutions, nucleation mechanisms, recognition of minute inter- and intra-particle remnants, differentiation of various types of shearing features and stress – movement patterns, tracing of history of individual grain types (reworked, fragmented, abraded, transported, leached, etc.), recognition of micrite types and their alterations (see chalk problem), recognition of micromixtures of minerals (and organic material) of matter previously believed to be one specific mineral (e.g., phosphatic, glauconitic, clayey components, among many others), discrimination of framboidal pyrite types and their multiple genetic origins.

One rare practical application of cathodoluminescence petrology was described by Basham/Shilston (1978), who have recognized the following features in a U – V sandstone-hosted ore deposit: compaction, pressure solution, framboidal pyrite pore linings, crystallization, adsorption-replacement, stylolitization, deformation – bending – fracturing, dissolution, corrosion, cementation, micro-distribution (micro-dissemination), overgrowth, abrasion, and alteration features.

(56) How does intense chemical leaching in a source area control the chemical composition of sediments in a basin? Are the leached – dissolved elements supplied to the area of precipitation by surface waters and suspended particles only, or can subsurface fluids supply such chemicals as well? What are the differential – preferential diagenetic concentration mechanisms? (See Kronberg et al., 1986.)

(57) What are the differences, similarities, gradations and overlaps in mineralogy, geochemistry, and textures of primary (unaltered) weathering – supergene products in contrast to those that have undergone diagenesis and/or are of marine origin? (See Stubendorff, 1986, among many others.)

(58) What are the relationships between the dynamics of an environment and diagenesis? For example, the average turbulence may control certain diagenetic variables, such as rate of sedimentation, preservation of organic matter, and thus subsequent Eh − pH conditions, secondary alterations along diastems or micro-unconformities (Gebelein, 1977), maturation of pore fluids, and many more.

(59) "Suspension diagenesis" requires to be investigated, i.e., organic and inorganic particles may undergo alteration while suspended in a body of water before final incorporation in sediments. The derivation or origin of these suspended particles must also be identified: (a) supplied to oceans by rivers; (b) neoformed due to mixing of river and ocean waters; (c) resuspended material owing to reworking of bottom sediments; and (d) hydrothermal − exhalative supply from the subsurface. (See Ch. 1 for Suspension Diagenesis.)

(60) How can one recognize reworked (mechanically − physically) syngenetic − diagenetic sulfide grains in sedimentary − volcanic − exhalative-type deposits? (See Baird/Brett, 1986.) Diagenetic pyrite − marcasite, phosphorite, glauconite, and Cu, Pb − Zn, etc., concentrations have been reworked and resedimented along diastems and unconformities.

(61) There are certain regional to local processes that affect directly or indirectly diagenesis − burial catagenesis, of which there is only little information. For example, rapid sedimentation may prevent certain geochemical equilibria to be established that are required for cementation − lithification which, in turn, will result in episodic catastrophic sediment failure, vertical mixing and upward discharge (across "impermeable" layers) of fluids, gases and dissolved material. (See Hanor, 1981; and Episodes, 1986c.) Fluids can migrate along faults to cause sediment diapirism during such catastrophic events. These solutions (derived from buried marine pore waters, for instance) have been extensively altered by clay-base exchange, and bacteria, and cause mineral precipitation and further base exchange.

(62) What are the differences, similarities, transitions − gradations, overlaps and spectra possibilities in the processes and products in the formation of diagenetic (soft-sediment) and tectonic (lithified rock) deformation features on all scales? (See problems related to distinguishing structural and textural features in many stratabound − stratiform ore deposits.)

(63) What are the criteria to discriminate between very early diagenetic and late diagenetic, catagenetic and metamorphic "epigenetic-type" fracture systems that, when filled, form vein complexes? What are the processes that can form micro → meso → macro-scaled fracture (vein) systems during the various diagenetic stages? (See Schieber/Katsura, 1986; and Dill/Nielsen, 1987.)

(64) How important are "internal" sedimentation systems in syngenetic − diagenetic and later-formed "epigenetic" fracture (vein) complexes? (See Schieber/Katsura, 1986.)

(65) Many diagenetic − catagenetic problems exist related to the numerous types of ore deposits (cf. Kisvarsanyi et al., 1983; Gautier et al., 1985).

(66) More studies must be undertaken on diagenetic facies ranging from the local to the regional and worldwide extent. (See Schmidt/McDonald, 1979a, b, for an approach or methodology that could be fruitful to ore-hostrock studies.)

(67) What are the "diagenetic interdependencies"? For example, evaporite in-

fluence on diagenesis of surrounding lithologies due to release of saline solutions; evaporite control on the generation of ore-forming fluids during catagenesis – metamorphism; etc.?

(68) Although there is much data on maturation, the oil + gas versus metal ion release – transportation – (re)precipitation is still poorly understood [see Wolf, 1987, regarding (re)mobilization]. In regard to ore genesis related to basin evolution, including maturation, see Gautier et al. (1985) and Kisvarsanyi et al. (1983). Many so-called maturation data are as yet unreliable and contradictory, depending on the methods used.

(69) How does coal diagenesis affect the diagenesis of associated or circumjacent lithologies, such as mudstone – shale, sandstone, and carbonate, for example? Can, for example, the fluids released from compacting maturing coals control or even override processes in adjacent (even remote) lithologic units? (See also Hallam, 1986.)

(70) What are the differences in diagenetic – catagenetic – metamorphic alterations in mono-lithologic in contrast to poly-lithologic systems? (See De Lange, 1986, for diagenetic reactions in interbedded pelagic muddy and turbiditic sand sediments, and Hallam, 1986, for limestone – shale cycles.) What types of lithologic associations give which types of diagenetic results? What types of expelled fluids are provided by which types of lithologic associations?

(71) A totally new approach in the earth-sciences en toto rests on the application of "fractals" to, say, regional diagenetic facies and other irregularly shaped and irregularly distributed secondary alteration bodies, or any other space – time distribution phenomena. Its practical application to the search for "hidden" oil pools may be a possibility by utilizing complex computer models based on equally complex conceptual models.

Mandelbrot's (1977, 1982) concept of "Fractals, Form, Chance and Dimension", which he has applied to certain scientific enigmas (e.g., to Brownian movement in solutions, as part of a physicochemical utilization, and to geomorphology, among others) stated: "Many important spatial patterns of Nature are either irregular or fragmented to such an extreme degree that EUCLID – a term used in this Essay to denote all classical geometry – is hardly of any help in describing their form. The coastline of a typical oceanic island, to take an example, is neither straight, nor circular, nor elliptical, and no other classical curve can serve without undue artificiality in the presentation and the organization of empirical measurements and in the search for explanations . . . it is possible to remedy this absence of geometric representation by using a family of shapes I propose to call 'fractals' – or 'fractal sets'. The most useful among them involve chance and their irregularities are statistical in nature. A central role is played in this study by the concept of fractal (or Hausdorff-Besicovitch) dimension".

In the present writers' estimation, the "fractals" theory ("hypothesis" at present?) is applicable, it seems, to the study of "spatial homogeneity – inhomogeneity – heterogeneity" and "self-similarity", approximation and "the limit of decreasing approximation", "physical dimension", "isotropy of motion – movement – transportation", among others, in the earth-sciences. "Fractals" might well be applied to the sometimes irregular and fragmented products of diagenesis and

reservoir properties, ore-body distribution, among dozens one can propose. For example, the fractal patterns of diagenetic chemical dissolution, (re)mobilization and (re)precipitation complexes ought to be examined (see Daccord/Lenormand, 1987, for a related investigation).

(72) What are the variations in diagenetic – catagenetic – metamorphic systems in the numerous types of sedimentary basins now recognized (for a classification of basins, see Mason, 1980)? What are the source bed, aquifer rock, reservoir rock, and caprock diagenetic – catagenetic differential evolutions in the eight basin types (see Mason, 1980, figs. 8-3 to 8-5, pp. 104 – 106)? What are the porosity evolution trends of reservoir rocks as controlled by provenance, depositional environment and diagenesis. (See fig. 13-8 in Mason, 1980, p. 178.)

(73) How can one differentiate between diagenetically formed cycles from those controlled by climate, and other variables? (See Hallam, 1986, for study of limestone – shale cycles. Many other types of lithologic cycles ought to be examined, including those of sediment-associated ore deposits.) Hallam concluded that only a multi-disciplinary approach can be successful as some methods supply answers to only narrow specific problems; field, experimental and conceptual methods are needed in combination with each other.

(74) What diagenetic (and associated syngenetic – depositional) features in the various types of "sedimentary" breccia can be used to differentiate them from the many other varieties of post-sedimentation, post-lithification breccias, e.g., in carbonate rocks?

(75) What are the differences between spring-related, lacustrine – playa – sabkha-type limestones and dolomites versus the marine varieties? (See Hay et al., 1986; for several problems, see Mylroie, 1986.) Carbonate paleosols ought to be studied in this context, because how can these be discriminated from more recent (e.g. Pleistocene) ones?

(76) As to the diagenesis – catagenesis – metamorphism of salt (evaporite) deposits, the following selective questions can be posed (see Schreiber/Harner, 1985, for examples – the page numbers below refer to those in this publication): (a) What are the criteria that permit the distinction between gypsum and anhydrite formed by syndepositional and burial diagenetic processes (pp. 11, 41, 161, 171, 257)? (b) How are fluid inclusions in salt minerals changed during diagenesis – burial catagenesis (pp. 41, 11, 217, 231, 247) because many inaccurate temperature measurements have been made (p. 247)? (c) What is the effect of "impurities" (such as clays) on the diagenesis – catagenesis of evaporite minerals (p. 267)? (d) Are there any differences in the genetic mechanisms of gypsum nodules in contrast to other types (e.g., limestone and siliceous nodules or concretions) – the former may have formed early diagenetically by capillary fluids (p. 171)? (e) What is the diagenetic system of borate minerals in salt lakes? How does the "sulfate problem" related to S-availability affect sulfide ore genesis and the Pb – Zn sulfide mineralization in dolomite hostrocks, among others (see p. 217)? (f) How do pore – intercrystalline fluids "lubricate", enhance – promote, or retard – prevent diagenesis in evaporitic basins (and other types, of course) (see also p. 231)? (g) How can pore-fluid data (in association with hydrologic information, of course) be used to "pinpoint' diagenetic reactions in evaporitic and other basins (p. 231)? (h) To

what extent is the mixing of marine brines and continental waters along the surface mirrored by associated subsurface fluids (see also p. 257)? (i) What are the secondary changes that occur during burial of diagenetic talc, serpentine, chlorite and smectite formed in evaporite rocks (p. 267)? (j) Why are nitrate deposits so rare in the geologic sedimentary – volcanic column? The diagenetic system of the Chilean nitrate deposits must have been extremely complex and rare (p. 285). (k) Were very unusual secondary processes required to ascertain preservation of these nitrates?

(78) What are the global event responses preserved in sedimentary rocks? To study these responses all regional diagenetic phenomena have to be considered – see Fraser and Suttner (1985) and Clifton et al. (1985).

(79) What are the evolutionary trends in diagenetic systems from the Precambrian to the Recent?

(80) To what extent, and under what conditions, can one apply the Law of Uniformitarianism to diagenetic – catagenetic – metamorphic (– anatexic – magmatic remelting) systems?

(81) Can one formulate a "Law of Minimum in Diagenesis" in regard to biological, chemical and physical – mechanical processes? (From Wolf, list of future research problems, 1974, unpublished.) "The Law of Minimum in Environmental Reconstructions" (see Wolf, 1965) is a general one, but can be made specific by applying it to particular systems, such as diagenetic complexes. The "Law" states, that the environmental factor for which an organic group, biochemical and/or physicochemical process – system – product has the narrowest range of tolerance acts as the limiting factor (or environmental setting) regardless of the fact that the other associated members of the system can withstand a wider range of the factors. In applying the "minimum range", all available data has to be compared and contrasted.

(82) What are the most "meaningfull" parameters – variables – factors of any specific diagenetic system, in contrast to those that are less significant, in characterizing that system?

(83) Comparative – contrastive studies must be made of the numerous recognized diagenetic environments (cf. Dickinson, 1970, 1974; Galloway, 1979; Blokh/Dagayeva, 1984; Fontana et al., 1986).

(84) Investigation of the many complex interrelationships between numerous factors so far not given proper attention: chemical + biological, physical + chemical, chemical + biological + physical diagenetic processes and environments must be studied in unison (see Tillman/Almon's 1979 study of paragenetic sequences in reworked versus non-reworked marine bar facies; many other studies should be undertaken on an integrated basis).

(85) Diagenetic continua – spectra ranging from initiation phases to mature stages as based on textures (including evolution of porosity), regional mineralogical trends, fluid-inclusion and isotopic composition, organic matter, etc., must be studied. (The "maturity" is different for various lithologies and environments.)

(86) Preparation of a list of all known environments and types of diagenetic milieus, e.g., hot spring, supergene, terrestrial, evaporative-lacustrine, evaporative-marine, nearshore and deep-water setting, "normal" marine and hydrothermal – exhalative – marine-mixed, and many more. All diagnostic features ought to be

identified for these diagenetic settings. The environmental gradations – transitions, overlaps, degrees of importance of variables (see Law of Minimum in Geochemistry) and other characteristics must be recognized for future progress.

(87) All methods that attempt to determine paleotemperatures, pressures, salinities, fluid compositions (including isotopes), and their space – time evolutions must be compared and contrasted. It must be noted that no universal calibration scale for methods of the evolution of basin maturity is available; each method reacts differently to different thermal histories! (See Episodes, 1986c.) A single-method approach is disastrous, although we too frequently do not realize it until much later!

(88) Many "remote-parameter-interrelationships" (= RCP-type; a phrase coined by the senior author in 1984, unpublished) phenomena remain to be investigated, such as the influence of tectonism through many intermediaries controlling, in turn, diagenesis (cf. Hayes, 1979; the mega-thinker's approach).

(89) What are the needs of the operational, practically inclined explorationists for hydrocarbons, metalliferous deposits and water resources, for example, in regard to the application of diagenetic to metamorphic phenomena?

"Entrepreneurs of Ideas" are the guides of "Mundaner Fact Gatherers."

Karl H. Wolf, Aug. 10, 1986, Canberra, A.C.T.

DIAGENETIC CONTROL OF POROSITY AND PERMEABILITY IN SANDSTONES

As pointed out by Knut Bjørlykke in Ch. 2, diagenetic processes in sandstones determine the rate at which porosity and permeability are lost or gained as a function of burial depth. Mechanical compaction and pressure solution are functions of the effective stress acting on the grain framework. High pore pressures (over-pressures) are effective in reducing the net stress at the grain contacts and thereby preserving porosity. Quartz cement may be derived from pressure solution of quartz amorphous silica or from kaolinitization of feldspar. The low solubility of quartz in porewater makes it necessary to assume very large fluxes of porewater to explain introduction of quartz cement from outside a sandstone body. According to Bjørlykke, compacting shales contain in most cases insufficient water to provide a porewater flux capable of transporting significant amounts of silica into thicker sandstones (> 100 m). Leaching of clastic minerals and cements to increase the porosity significantly in thicker sandstones also requires very large fluxes of porewater. Calculations by Bjørlykke show that in order to gain 10% secondary porosity by dissolution of silicate minerals in a 100 m thick sandstone, a flux of $10^7 - 10^8$ cm^3 cm^{-2} of undersaturated porewater must flow through the sandstone. This is a requirement which probably is rarely met except very locally in sedimentary basins. Recent studies indicate that low-salinity meteoric porewater is widespread, underlying continental shelves, and may cause leaching. Unlike the upward flow of porewater due to compaction, which is limited to the volume of porewater buried with the sediments, the meteoric water is fed from a renewable groundwater source.

The potential for leaching by groundwater is, therefore, greater[1].

Bjørlykke also pointed out that chemical reaction in the subsurface, such as release of CO_2 from kerogen and clay mineral reactions, may cause late diagenetic leaching. Calculations by Bjørlykke suggest that in most basins the amount of CO_2 produced from kerogen is insufficient to explain the formation of large-scale secondary porosity in thicker sandstones. The amounts of deep subsurface leaching that can take place is limited by the amount of acids produced and the flux of porewater which is necessary to dissolve feldspar or carbonate. In some cases, secondary porosity observed in thin-sections may be offset by the volume lost due to precipitation of authigenic minerals in the same sandstone but not always the same sample, perhaps redistributed by convection currents.

Diagenetic processes which control porosity and permeability are very complex and depend primarily on the primary clastic composition of the grains, subsurface pressures, and porewater circulation. All these factors may be related to the stratigraphic and plate-tectonic setting of the basin.

CONCLUSION – BRIEF NOTE

In conclusion, one can state that the overwhelming mass of diagenetic data already available, in combination with the future research output which will add further "packages of knowledge" will, no doubt, impose a strain on any earth-science generalist as well as on the diagenetic specialist. To connect and interrelate (put into full context or perspective) the material, one must continually switch from the general to the particular and then reverse the philosophy and go from the specific to the general in our theoretical and applied research and exploration attempts[2]. Still too frequently, "one either cannot see the leaves for the forest or one cannot see the forest for the leaves" – depending on whether one looks at natural phenomena from the viewpoint of a "generalist" or a "specialist" (and substituting the "leaves" for the proverbial "trees"!). In one case, one may be hampered by not knowing enough specific details in comparison to the other situation where a broad overview is lacking that does not permit integration. Specialization can indeed be an intellectual straight jacket or blindfold extra ordinum!

The above situation merely reflects the individualistic human limitation in attempting to grasp all available data and in engaging in more than one or two scientific and/or humanistic disciplines. Hopefully, the present volumes of "Diagenesis" will assist the individual and the research group in keeping up with the data explosion.

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[1] The senior editor (GVC), however, believes that Dr. Bjørlykke underestimates the role of compaction fluids.

[2] As exemplars of specific, narrowly-defined diagenetic systems that have been examined, see Nissenbaum, 1980; Weaver/Beck, 1977; Iijma et al., 1983; Gautier et al., 1985; MacDonald, 1983; Fontana et al., 1986; Zenger et al., 1980; Cook/Enos, 1977; Schneidermann/Harris, 1985; Schmidt/McDonald, 1979a, b; Kisvarsanyi et al., 1983; and Chilingarian/Wolf, 1975, 1976.

20

Vive la research et vive la laboratoire et la librairie.

Inasmuch as "geologists prepare to study global processes" (Fraser and Suttner, 1985) during the International Decade of Sedimentary Geology (Clifton et al., 1985), the "ubiquitism" of diagenesis and, in particular, the complex interconnections of all variables must be emphasized.

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Chapter 1

ORE-RELATED DIAGENESIS — AN ENCYCLOPEDIC REVIEW

K.H. WOLF and G.V. CHILINGARIAN

Part I — General aspects of ore diagenesis

Dedicated to the Australian geologists who have made many contributions to the geology of their continent as well as to the world in general.

"The geological data are a consequence of our methodology (techniques, instrumentation, concepts); and the methodology is a reflection of our experiences, preferences, and abilities."

K.H. Wolf, Sydney, N.S.W., January 25, 1983

"Knowledge is of two kinds; we know a subject ourselves or we know where we can get information upon it."

Samuel Johnson (1709 – 1784)

GENERAL COMMENTS

Diagenesis is today a mature petrological and geochemical discipline concerned with a multitude of theoretical and applied problems encountered in the study of rocks which range in age from the Precambrian to the Recent. This progressive development of diagenesis is manifested in several books, as well as in the few thousand papers that have dealt specifically with this wide-ranging sub-discipline. Inasmuch as it is primarily concerned with sedimentary and volcanic deposits, diagenesis has made fundamental contributions to the understanding of the origin of petroleum and stratabound/stratiform ore deposits. In the present chapter, diagenesis is treated only in the context of ore genesis.

In the first (1967) edition of *Diagenesis in Sediments,* the chapter on "Sedimentary Mineral Deposits" by Amstutz/Bubenicek has covered several preferentially chosen topics which are not repeated here. Instead a different approach has been used: after discussing general aspects in some detail, the numerous variables involved in diagenesis of metalliferous deposits are each briefly examined as based on a (predominantly English-language) literature survey. Only a very general and superficial overview, however, is presented. As discussed in the section on Terminologies – Classifications, diagenesis has been defined by numerous researchers in variable ways, so that for that reason alone, a wide spectrum of geological and geochemical processes and environments are deliberated on here.

It is rather illuminating to examine the history of diagenesis as applied to ore

genesis. In general, hypotheses or theories[1] are often developed in a particular country or are circulated within the literature of one language without being either noticed or accepted by "outsiders" and "uninitiated". As pointed out by Wolf (1981, vol. 8, table CXXVII) certain "philosophical" (nation-, language-, culture-, time-, discipline-preferential) barriers have existed in the sciences that isolated countries and schools-of-thought from each other (Table 1). This also applies to diagenesis of ores. It was employed much earlier in Europe to explain certain types of ores in contrast to countries where more classical hypotheses still prevailed. The gradual worldwide acceptance of syngenesis – diagenesis in the investigation and interpretation of sediment- and volcanic-hosted ores has been reviewed by Amstutz (1964a,b) (Fig. 1) and Amstutz/Bubenicek (1967; see also Amstutz' conceptual

TABLE 1

Static and dynamic scientific knowledge (after Wolf, 1981b, p. 325)

(1) Static, stationary, out-of-circulation information in specific areas in the world because of preferential use.
    Reason (a): – nation/country-preferential information
                 – language-preferential
                 – culture-preferential
                 – time (in human history)-preferential
                 – institutional-preferential (especially if confidential)
                 – "school-of-thought"-preferential*
                 – topic/problem-preferential* (i.e., no cross-fertilization even within same broad discipline)
                 – discipline-preferential* (i.e., no cross-fertilization across boundaries of disciplines)
    Reason (b): information proven wrong, hence shelved
[* Interim note: Differences are made between "disciplines" (physics, chemistry, mathematics vs. geology), "school-of-thought" (e.g., drifters vs. non-drifters which is not discipline-confirmed), and "topic/problem" (i.e., within one discipline, e.g., in geology: sedimentology and biology vs. ore petrology).]

(2) Dynamic, moving, in-circulation information.
    Pattern (a): moving *within* above-set (see 1a) boundaries.
    Pattern (b): transgressing one, several or all above-set boundaries (most ideal system in a worldwide, across-all-boundaries circulation, except for confidential data).

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[1] A distinction ought to be maintained between scientific hypotheses, theories and laws. Too frequently, the first two terms are used synonymously in formal discussions and writings. The differences, however, are as follows (cf. Webster's New Dictionary of Synonyms, 1984, p. 410): ". . . *hypothesis* implies tentativeness . . because of insufficient evidence and applies to a well-founded conjecture that serves as a point of departure for scientific discussion or as a tentative guide for further investigation or as the most reasonable explanation of an imperfectly comprehended phenomenon . . . *Theory* . . . in precise technical use presupposes more supporting evidence than 'hypothesis' does, a wider range of application, and greater likelihood of truth . . . *Law* . . . emphasizes certainty and proof and therefore applies to a statement of an order or relation in phenomena that has been found to be invariable under the same conditions".
   A triangular diagram could be drawn with the term hypothesis, theory and law at its apices; thus depicting the transitional/gradational and overlapping characteristics of these three concepts (cf. Wolf, 1985, for a similar diagram).

diagram in Wolf, 1976a, vol. 1, fig. 35). The development of syngenetic and diagenetic ideas in Australia and in North America were outlined by King (1976) and Ridge (1976), respectively; whereas Bernard/Samama (1976) discussed epigenesis versus syngenesis of the French school-of-thought. Vokes' (1976) survey of the history of genetic concepts is even more specific insofar as he outlined in a diagram (see his fig. 7, p. 101) "the cycle of thought" regarding the Scandinavian massive sulphide deposits. The "evolution of diagenesis" in general and in the study of mineralization, as part of the German, Russian, Chinese, Japanese, and other schools, has yet to be summarized — the senior writer was unable to find authors for this task (Wolf, 1976, 1981, 1984, 1985, 1987).

PURPOSE AND AIM OF AN ENCYCLOPEDIC SUMMARY

In the first stage of any research or exploration project an initial review ought to be undertaken to obtain a comprehension of what has been done in the past and, consequently, what remains to be done in the future. To prepare a nearly all-inclusive synopsis of any subject is quite a challenge, and the narrower one preferentially selects a topic, the less time is needed to do the summary. Diagenesis, however, is now far from being a narrow concept because it is applied in the study of all varieties of exogenic (and some endogenic), earth surface-related phenomena and deposits; hundreds of variables/parameters/factors are involved. How can we best summarize the information?

The usual text or reference book approach is too cumbersome to list, discusses and integrates a vast amount of data and would result in a very thick compendium. It seems preferable, therefore, to organize the data according to the *major variables* and list them alphabetically. They provide the titles of the sections in which some relevant publications are mentioned briefly in the approximate sequence of their year of publication.

Certain difficulties and inherent disadvantages present themselves is using *one* variable as an umbrella term, for virtually all research deals with more parameters, so that an extensively cross-referenced approach would be the ideal. This is not possible, however, in a relatively short chapter. Thus, only a convenient starting point is offered to the reader to assist him in expanding the information made available here — he can supplement the embryonic encyclopedia ad infinitum to suit his special requirements.

Of some concern to "informational purists" is that the topics dealt with in this chapter are of a mixed categorical nature and, consequently, are not neatly grouped or classified into mutually exclusive varieties: there is no separation between descriptive (petrographic, non-genetic) and interpretive (petrologic, genetic) information, microscopic and macroscopic data, geologic and geochemical or biochemial discussions, for example. Any classificatory structuring would have imposed a deleterious restriction upon the generalized treatment of diagenesis.
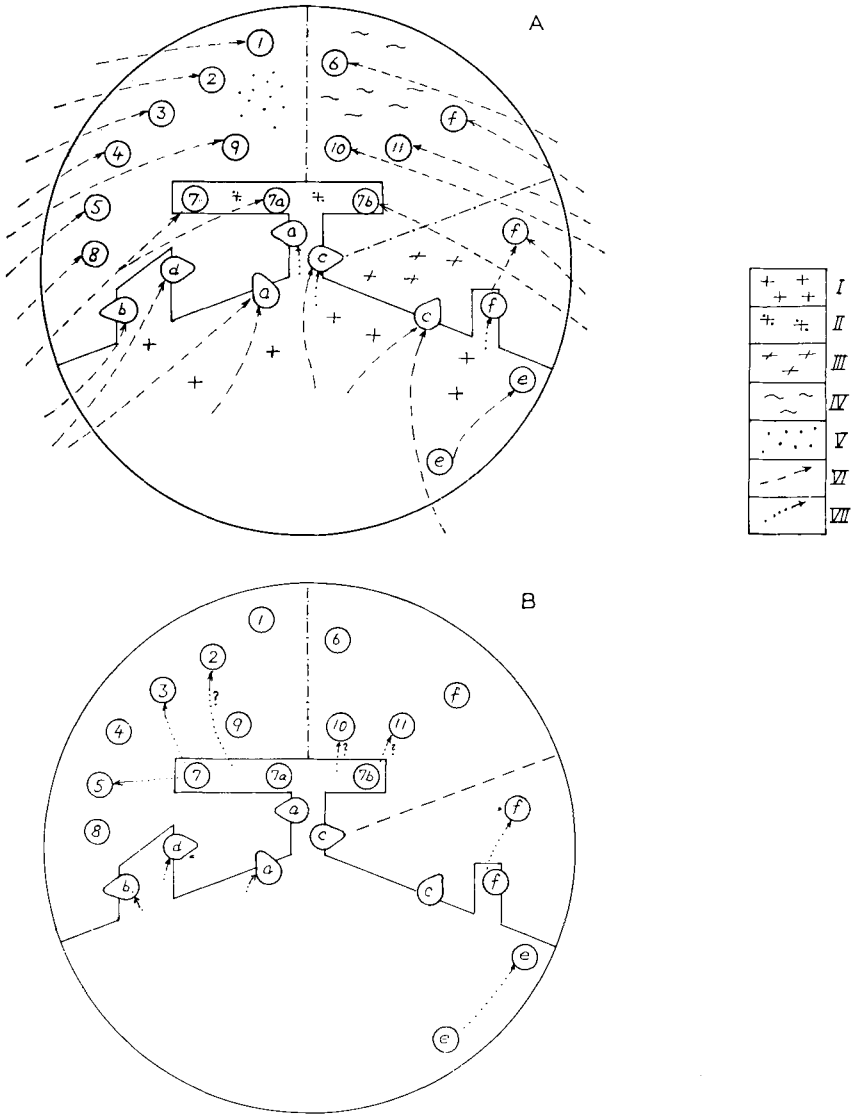
Fig. 1. Schematic representation of ore genesis according to the conventional and the new patterns of thought. (After Amstutz, 1964a, b; see also Wolf, 1981b, p. 62.)

A. The domination of the myth of epigenetic replacement and of the unknown depth ("deep-seated sources"). Epigenetic introduction from the outside is an axiomatic condition for the formation of most ore deposits. This pattern corresponds essentially to the creationistic, pre-Darwinian beliefs in paleontology.

B. The pattern of ore genesis theories according to the new "petrographic" or integrated theory, according to which ore deposits normally formed at the same time and essentially within or very near the observed host rock. Just as man and animals in the evolution theory of paleontology, ore deposits are, in the new theory, considered a normal integral part of rock evolution.

DIAGENESIS: PART OF METHODOLOGICAL MODELS AND RESEARCH AND
EXPLORATION ANALOGUES

Research and exploration not only require a compilation of existing information,
but the variables need to be modeled to expose natural complexities and to highlight
the multifarious interrelationships. Consequently, a few selected models are prof-
fered here — models or analogues that have been formulized by the quoted resear-
chers to suit their respective narrowly defined purposes. These particularized models
are both explicitly and implicitly piecemeal or fragmentary, so that extrapolation or
transference to other natural systems is difficult insofar as many variables have been
ignored — often by necessity and with the full awareness of the researcher.

The present encyclopedic data-bank, although of low-level coverage as a conse-
quence of the space limitations, will hopefully be useful in the following situations:

(a) In the preparation of general, all-inclusive idealistic conceptual models. Such
broader-scope analogues provide a neat overview comprising as many parameters
as possible against which less-ambitious, more restrictive models can be tested or
compared. To put it conversely: smaller models can be put into a meaningful con-
text within mega-models (assuming they are available!) to check which variables
needs further attention. For instance, how often have petrologists asked about the
energy sources for certain processes? There are dozens of factors that are frequently
left unconsidered!

(b) Models ought to be prepared both prior and subsequent to an investigation.
In the former case the model assists in selecting logically those variables that appear
to be most promising. In the latter situation, where a model (or several) is (are) for-

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I = igneous intrusive rocks (known!); *II* = igneous extrusive or subvolcanic rocks (known); *III* =
metamorphic igneous rocks or migmatites; *IV* = metamorphic sedimentary rocks; *V* = sedimentary
rocks (non-, or partly metamorphic); *VI* = introduction from the (unknown) outside assumed; *VII* =
some migration probable, possible, or(?) questionable.

List of major types of ore deposits for which a syn-endo[1] as well as an epi-exo[1] origin has been pro-
posed. In sediments and volcanic rocks: *1* = Arkansas-type barite deposits; *2* = Mississippi Valley-type
deposits (including the barite and fluorspar deposits in the same type of sediments); *3* = Rammelsberg
and similar deposits; *4* = magnesite, rhodochrosite and siderite deposits of the Alps and elsewhere; *5*
= Kupferschiefer and/or Red Bed copper deposits as well as various disseminated to massive
copper – lead – zinc deposits, for example of the Kuroko type; *6* = Blind River, Witwatersrand and
similar deposits; *7* = propylitic deposits of copper, gold, and other metals; *7a* and *7b* = deposits of
sulfides, oxides and native elements (Cu, Ag, Au) in or near volcanic rocks (often with spilitic phases);
8 = Mina Ragra-type vanadium deposits; *9* = Colorado Plateau or "sandstone-type" uranium deposits;
10 = iron deposits of the Lake Superior type; *11* = Ducktown, Broken Hill, Outukumpu, Falun, and
similar deposits in metamorphic belts. In and adjacent to igneous rocks: *a* = porphyry copper deposits
in and around intrusions (including the Climax molybdenum deposit); *b* = Granite Mt., Utah, deposits
of magnetite, and similar deposits; *c* = tin deposits in and around intrusions; *d* = contact deposits, pipe
deposits, perimagmatic vein deposits; *e* = chromite deposits; *f* = pegmatites.

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[1] Endogenous = from within (the hostrock or its own source). Exogenous = from outside (the
hostrock or its own source). Syngenetic = at the same time as the hostrock. Epigenetic = at any later
time than the hostrock.

mulated after the information is on hand, it will assist in the interpretation of the environment, for example, and point out many complex interconnections and alternatives.

At present, most conceptual models (diagrammatic, pictorial, cartoon-like or of the flow-chart-like or spider-web types) are qualitative, but increasingly are quantitative, as expected. The following lists merely a few publications where models are or could have been utilized: Lewis (1981), D.E. White (1981), Aubagne et al. (1982), Callahan (1982), Carpenter (1982), Bertranen (1982), Ridge (1983), and Bigot (1983). See also Wolf (1973a,b, 1976a,b, 1981).

GENERAL VERSUS PARTICULAR

"Nature operates holistically, whereas human endeavours are fragmentary."
K.H. Wolf, Sydney, N.S.W., February 8, 1983

"Deduction: The process of deducing from something known or assumed; specifically in LOGIC, inference by reasoning from generals to particulars."
The Shorter Oxford English Dictionary, Vol. I, 1975

"Induction: In LOGIC, the process of inferring a general law or principle from observation of particular instances (opposite to deduction)."
The Shorter Oxford English Dictionary, Vol. I, 1975

"Diagenesis is an all-embracing complex earth-surface phenomenon: the investigation thereof is open-ended and nobody has 'the monopoly of the obvious'."
K.H. Wolf, March 18, 1985

"The 'Concept of Triage' (= principle of selectivity) is a universal law applicable to science and all other human endeavours – including in specific investigations of diagenesis: a total coverage is never attained so that the methods used as well as the diagenetic processes and materials examined are preferentially or selectively isolated."
K.H. Wolf, Jan. 1985 (cf. Wolf, 1985b, and Time, Dec. 10, 1984)

Any scientific (as well as humanistic, philosophic, and artistic) endeavour consists of, what one may call euphemistically, "general" in contrast to "particular" or "specific" information and concepts. Many data, by necessity, come from investigations of *specific* problems, and inasmuch as these have been *preferentially or selectively isolated out of context* from their complex surroundings in order to *simplify the study,* the resulting information is, of course, simple also and certainly *does not convey intricate holistic interrelationships* with other variables and environments.

The presently available information on diagenesis (both the general and the specific) is given in isolated, disconnected "packages" or entities from: (1) low-temperature laboratory studies; (2) petrological – geochemical examinations of oil reservoir and source carbonate, sandstone, shale, and other rocks and from their burial metamorphic histories; (3) investigations of "sedimentary" syngenetic – diagenetic $U-V$, $Cu-Ag$, Au, $Pb-Zn-Fe-Ba$, Mg, Mn, W, P, etc., concentrations; and (4) research on volcanic – pyroclastic and sedimentary – exhalative

deposits. All of these data appear to remain restricted to their fields of endeavour, and little cross-fertilization occurs. For example, hardly any comparative/contrastive-type reviews are undertaken; consequently, similarities and differences remain unnoticed and, therefore, unused. Investigators of one particular diagenetic sub-discipline may be unaware of the data and concepts of another field, so that work may be duplicated and/or already-known principles are not applied. Due to the disciplinary isolation there is an absence of a common data bank from which researchers and explorationists can draw information. Even those aware of this situation, who conscientiously collect all the somehow-related information to be able to sift out what they can utilize, do so at great cost of time and money.

Once all the particular information of the interconnected disciplines has been collated to form a data bank (step 1), the data can be (a) sifted out, sorted, grouped, structured and classified (step 2); (b) compared and contrasted, and possibly reclassified and restructured (step 3); and (c) interpreted, modelized (genetically), and a hypothesis formulized (step 4). This eventually may lead to extrapolations and suggestions for future studies (step 5). These phases or stages of compiling and utilizing data reflects simplistically the "Scientific Method" and are, of course, applicable to diagenesis.

To elaborate on the above, one may consider the numerous applications of diagenesis in the study of ores hosted by sandstones, pyroclastics, red-beds, shales, and carbonate rocks (see the section on the types and division of diagenesis) originating in umpteens different sedimentary environments. Although the *detailed* investigation of each of these deposits is in its infancy, sufficient data is available to permit us to reconstruct an approximation of the genetic factors involved. The origin of each type of ore mineralization and its host rocks was controlled or influenced by (1) physical/mechanical, chemical and biological variables; (2) the sources of the anions and cations; and (3) the tectonic and depositional environments, burial history, remobilization, etc. Literally thousands of specific studies have considered these parameters or factors for ore deposits, but (as in the earlier-cited cases) only a few comparative/contrastive studies have been made – and these are commonly superficial: they may cover merely a few obvious variables, some of which may not even be of fundamental, but only of incidental or remote "academic" importance.

Once a mass of data is available on the parameters that control the origin of *specific* types of ores, one can ask about the *general* application of this information to other types of mineralization. For example, in regard to the volcanic – exhalative (= sedimentary – hydrothermal – exhalative) ores, one should enquire about the source, the transportation mechanism and depositional milieu, and which one has the *greatest general fundamental control?* Insofar as many ore deposits are classified or grouped according to their host-rock types, one might unthinkingly conclude that the depositional environment is most significant, because it determines the host lithology (conglomerate, sandstone, dolomite, etc.). But if one decides that the source is more fundamental and that the hydrothermal – exhalative metal-bearing fluids debouch onto the seafloor and then spread over *several types* of milieus, and thus over *several* sedimentary facies, then the rock hosting the ore becomes "a little less" significant (see Finlow-Bates, 1980, p. 159).

Of course, in each case there are several geological – geochemical – biological variables of subsidiary or auxiliary importance, such as topography (controlling ore distribution and trapping of fluids), pH – Eh zoning according to water depth, presence or absence of bacteria, etc., which also have to be taken into account. To conclude: each *specific* ore deposit is unique and can be placed into a *generalized, averaged-out* class only by ignoring numerous differences. But what are the possible *common descriptive and genetic denominators?*

By comparing and contrasting the parameters of the ore deposits which are genetically related, one may be able to identify the most significant controlling variables. One may also succeed eventually in listing the so-called auxiliary factors in *order of importance* or according to the *degree/extent* to which they influence ore formation (several publications on exploration guides or on recognition criteria have attempted this already). Once this has been accomplished for *genetically related* ores, one can attempt to compare/contrast the deposits from *different* genetic groups. Within each *genetic group* one should then compare the various ore types with different *observational information.*

Upon determining all the factors that control the origin of the numerous ore varieties (and, thus, by eliminating those parameters that have no influence), the ore types can be *classified* on the basis of the *most crucial* variables. Of these factors, there are at least two kinds: (1) those that are characterized by the "presence-versus-absence" mode of control, as in the case of the metal source. Either the hydrothermal source is present or it is not, and either organic matter, adsorption, etc., is influential or not – there is no other alternative [at least not in the present simplistic argument, although the quantitative factor (i.e., the "how much" question) should not be forgotten]. (2) The "maximum – minimum threshold"-type of controls, as exemplified by the maximum – minimum ranges of values of pH – Eh, temperature, solubility, etc., between or within which the ore-forming system can operate, but beyond which no mineralization can be produced. It must be stressed that the parameters of the "presence-versus-absence" mode are not as useful (?) as those of the "maximum – minimum threshold" variety, because the former are qualitative in nature, whereas the latter are quantitative. Consequently, whenever possible the former ought to be converted to the latter, so that at least a semi-quantitative approach is made possible.

The above deliberations apply in general to the whole continuum of syngenesis – diagenesis – catagenesis systems, as well as to the more restricted, or more specific, field of diagenesis. And it is the purpose of the present chapter to consider as many variables as space allows and put them into an overall context or perspective, although discussions of their complex mutual interrelationships cannot be undertaken here.

OVERVIEW OF ORE-RELATED DIAGENESIS IN TERMS OF CHECK-LISTS AND CATALOGUES

"Synthesis and analysis of our man-made terminologies and classifications are a prerequisite to the synthetic – analytic and deductive – inductive study of nature."

K.H. Wolf, Sydney, N.S.W., February 20, 1983

"In an attempt to 'put some practical sense' into any complex system we must search for the (common?) *'lowest denominator(s)'* by adhering to the LAW OF MINIMUM: understand those variables which have such an overriding control over all other factors that the latter can be ignored in first-approximation comprehension of that system."

K.H. Wolf, 1963 (cf. Palaeogeogr., Palaeoclimatol., Palaeoecol., 1: p. 220, 1965)

In the previous section on general versus particular information, the writers opined that most diagenetic investigations described in the literature are based on *selectively* chosen environmental situations and on the examination of *preferentially* selected materials and processes. The methodology employed is equally preferentially chosen from a plethora of possibilities. With the enormous amount of widely dispersed data on diagenesis available from dozens of publications, preparation of a *general, all-inclusive inventory* of all types of inorganic and organic materials, genetic mechanisms, environmental settings, and results obtained seems of paramount importance. In the first instance, such an inventory is based merely on several check-lists of the catalogue-type in order "to know what we are dealing with". Concomitantly, by establishing such lists, one is taking the first step towards putting some order into the highly complex natural system(s) of diagenesis by sorting out and grouping those variables that are "somehow" related. The resulting catalogues offer, therefore, a crude but effective first-order type of mega-division

TABLE 2

Variables used in establishing classifications of diagenesis (Wolf, 1973, unpublished)

1. Applications of diagenesis
2. Chemical diagenetic reactions
3. Parameters in chemical diagenetic systems
4. Chemical and physical barriers
5. Factors causing diagenetic potentials
6. Miscellaneous variables
7. Methods utilized in investigating diagenesis
8. Diagenetic processes
9. Factors influencing diagenesis
10. Sources of fluids and materials involved in diagenesis
11. Types of ore deposits in which diagenesis is operative
12. Specific-mineral diagenesis
13. Transition possibilities of specific-mineral diagenesis
14. Diagenetic processes based on mineralogic processes and changes
15. Eh-dependencies of individual minerals and parageneses
16. Major lithology-based classification of diagenesis
17. Specific-hostrock-based diagenesis
18. Transitions of hostrock diagenesis
19. Metal associations of diagenesis
20. Sedimentary-environments-based diagenesis
21. Natural-water-based diagenesis
22. Chemical classification of submarine volcanic and diagenetic/metamorphic processes
23. Submarine volcanism – diagenesis – metamorphism
24. Relationships, transitions, overlaps of hydrothermalism and diagenesis
25. Facies types of hydrothermalism (e.g., Atlantis-II Deep)

or mega-classification (to be continually updated in the future). In any study of diagenesis, whatever its purpose, such check-lists are of great value during the planing, implementation, execution, and final evaluation – interpretation of the project. In what other manner can one explain the assumptions made, the aims set, the preferences chosen, as well as the limitations, advantages/disadvantages of the investigation; and how else is it possible to put the narrowly defined system into a broader context without knowing the total intricate natural system? In addition, no models of diagenesis can be prepared, unless *all* the materials, processes and controls have been catalogued first. Once the summary lists are available, one can proceed to examine which ones of the parameters are deterministically and holistically interrelated by using flow-chart-like conceptual diagrams and/or pigeon-hole-type

TABLE 3

Applications of diagenesis in geological disciplines (Wolf, 1973, unpublished)

1. Metalliferous ore genesis: e.g., source of anions, cations, etc.; origin of the hostrocks; bacterial influences
2. Non-metalliferous/industrial mineral investigations: origin of clays, zeolites, coal, sulfur, evaporites, barite, phosphorites, etc.
3. Petroleum/gas investigations: research of and exploration for source, conductor/transmitter/aquifer, reservoir and cap rocks; maturation studies
4. Hydrology: study of aquifer, for example, regional variations of fluids due to diagenesis/catagenesis/burial metamorphism
5. Petrology: modifications of lithology, permeability, etc.
6. Mineralogy, geochemistry: trace – minor – major elemental changes; alterations of isotopic compositions
7. Oceanography: halmyrolysis, hydrothermal – exhalative metasomatism
8. Environmental-pollution studies

Note: (a) Many of the above are directly interrelated – a clear separation is not possible. (b) Many of the data, methods and concepts from groups 2 – 8 can be utilized in group 1, i.e., in the study of ore deposits.

TABLE 4

General chemical classification of diagenetic reactions (Wolf, 1973, unpublished)

Reactions involving:
(1) Fluid + solid (minerals, rocks)
(2) Fluid + suspensate (Hartmann, 1973)
(3) Fluid + fluid (mixing of solutions)
(4) Fluid + gas/vapour
(5) Solid + solid
(6) Solid + gas
(7) Fluid + organisms (e.g., bacteria)
(8) Solid + organisms
(9) Gas + organisms
(10) Fluid + organic matter[1]
(11) Gas + organic matter

[1] Note the difference between reactions with living organisms in contrast with dead organic matter.

tables in preliminary qualitative work, or by finding a formula as a first step towards quantification. The present section will list in numerous tables the components, variables and factors involved in diagenesis. It will be obvious that there are both intra-table and inter-table duplications, overlaps and transitions. These interdependencies in and between *man-made* catalogue-like and pigeon-hole-type tables also reflect the complexities in *nature* (albeit in a very simplistic fashion), as one will encounter repeatedly in this chapter. Systems analysis techniques (with or without the assistance of a computer) will be applied in the future to unravel the less-obvious interrelationships of the many variables in diagenesis.

What is the most logical division of the parameters upon which the check-lists of diagenesis can be based? Table 2 gives a total of twenty-five such variables, most of which are self-explanatory. Table 3 lists the geological disciplines which have employed diagenetic investigations. Of course, there is a transition and an overlap between them inasmuch as the techniques and concepts developed in the petroleum and non-metalliferous industrial mineral research, as well as in oceanography, for example, are applied in the study of metalliferous ore deposits.

Table 4 offers a generalized chemical classification comprising the five major constituents that may be involved in diagenesis, namely fluids, solids, gas/vapour, organic matter, and organisms. Of course, numerous combinations are possible, some of which are listed as well. What is the reason for preparing such a "self-evident" table? Well, even the simplest guide can turn one's thinking into the right direction! For example, what are the *precise* conditions needed for adsorption, desorption and diffusion to occur? In which of the eleven systems can these processes take place? Which system(s) is (are) the most efficacious? What are the organic processes affecting solid particles, e.g., increasing or decreasing their solubility in a direct manner, not just by indirectly changing the pH – Eh of the surrounding milieu? How do organisms desorb metal ions? How do the many possibilities of fluid mixing affect adsorption and desorption? (If one does not ask the right questions, one does not get the correct answers!)

Table 5 summarizes the factors that control geochemical systems, either directly or indirectly. Although these variables are listed under three umbrella terms (chemical, physical + miscellaneous, and geological), no other systematic grouping was attempted. It is high time that the interrelationships of many of these variables, especially those chemical and physical ones of which much data is available, are modelized (by specialized geochemists for geologists). Both qualitative and quantitative procedures can be employed as in particular the former types are useful to geologists in their "daily routine" work. As a first step, numerous parameters (say, 10 – 20) can be conceptually related by utilizing the spider-web-type of diagram (e.g., Wolf, 1976, ch. 2, fig. 1). Such models can be general or specific (e.g., in the latter case all variables that influence solubility or coprecipitation or those that control the pH, or isotopic composition, can be modelized). An example is provided in Fig. 280 and Table 83.

Table 6 is a classification of the biochemical, physicochemical and mechanical (e.g., placer-type) barriers that result in the "fixation", concentration or accumulation of certain chemical elements. The diagenetic (as well as the syngenetic,

TABLE 5

Parameters that control and/or are controlled by diagenesis; alphabetically listed (Wolf, 1973, unpublished)

(1) *Chemical parameters*
- alteration
- anion activity
- cation activity
- chemical fronts
- common-ion effect
- complexing
  - organic
  - inorganic
- concentration
- concentration gradients
- coordination
- coprecipitation
- decomposition (e.g., of organics)
- degassing
- dissolution
- Eh
- electric potential
- electronegativity
- elements (chemical)
- energy
  - inorganic
  - organic
- enthalpy
- entropy
- enzymes
- equilibrium/disequilibrium
- exothermic/endothermic reactions
- fugacity
- interionic effects
- ionic radius
- ion-exchange
- ionization potential
- isotopes
- kinetics
- lattice energy
- lattice geometry
- ligands
- mass-action effect
- mobility (of elements)
- oxidation
- pH
- polarization
- precipitation
- radioactivity
- rate of change
- reduction
- salinity
- saturation/supersaturation
- solubility
- solutions (numerous properties)
- Soret effect (Barnes, 1979)
- stability (e.g., thermal)
- steady-state condition
- surface-reaction-controlled dissolution + precipitation + redistribution (cf. Berner, 1980)
- transportation-controlled dissolution + precipitation + redistribution (cf. Berner, 1980)
- valency

(2) *Pysicochemical, physical, biological, and miscellaneous factors*
- abrasion
- accretion
- advection (cf. Berner, 1980)
- age/aging
- agglutination
- aggregation
- algal processes
- bacterial processes
- barriers (several) (see text):
  - biological
  - chemical
  - physical
- biodiffusion (cf. Berner, 1980)
- boiling
- borers (organic)
- brines
- burrowers (organic)
- coagulation
- coating of surfaces (protective)
- colloidal properties
- contamination
- crystal growth
- crystallinity
- crystallization/recrystallization
- decomposition
- differentiation (various types)
- diffusion (various types)
- dilution
- dispersion (various types)
- dwarfism (of organisms)
- evaporation
- exhalations
  - compaction fluids reaching surface
  - volcanic fluids and/or gases
- fermentation
- flocculation
- flow versus diffusion systems (cf. Berner 1980)

- flushing
- fluxing/refluxing
- food supply (for organisms)
- gases/vapours
- heat
- hiatus
- hydrocarbons (presence or absence)
- immobilization/fixation (!)
- inclusions
- inhibitions (e.g., by organisms)
- interfaces (e.g., water – sediment)
- interfacial free energy (cf. Berner, 1980)
- interstitial fluids (presence/absence, type, etc.)
- isomorphism
- leaching
- metabolism
- mixing
  - fluids
  - sediments
- molecular diffusion
- nucleation/nuclei
- open vs. closed systems
- organic matter (presence or absence)
  - properties
  - active versus passive participation
- organisms
  - active versus passive
  - properties/processes
- particulate matter
- partial pressure
- pelletization
- pressure
- rates (numerous);
  - chemical reactions
  - crystallization
  - fluid flow
  - influx/reflux
  - mixing
- replacement (various types)
- reversibility/irreversibility
- segregation
- sorption (ad-, ab-, de-)
- surface-free energy
- surface reactions
- suspensate (Hartman, 1973)
- temperature
- toxicity (regarding organisms)
- transportation – diffusion (cf. Berner, 1980)
- water properties (numerous)
- water content
  - crystals
  - lava
  - magma
  - rocks

(3) *Geological variables*
- amount/proportion of fluids
- associations (several):
  - elements
  - facies
  - isotopes
  - rocks/lithologies
  - tectonic units
- authigenesis
- bioturbation (cf. Berner, 1980)
- brecciation
- burial
- bypassing
- cementation
- clay minerals (presence or absence, type, etc.)
- climate (numerous factors)
- concretionary action
- condensation
- consolidation
- currents
- cycles (numerous types, scales, etc.)
- depth of burial
- depth of water (pressure)
- degassing
- diagenesis within versus below zone of bioturbation (cf. Berner, 1980)
- diastems
- eolian processes
- erosion
- evolution
  - inorganic
  - organic
- fabrics
- facies
- fluid-flow direction
- fractionation
  - chemical
  - physical
- geothermal gradient
- grains (numerous properties)
- halmyrolysis
- history
- hydrology
- hydrostatic pressure
- influx (numerous)/reflux:
  - fluids
  - minerals
  - particulates
  - suspensates
- inversion
- karstification
- lithification (various types)
- localization (numerous factors)
- magmatism

38

TABLE 5 *(continued)*

- maturation (of various materials):
  - inorganic
  - organic
- melting temperature
- metamorphism/metasomatism
- mineral transformations (various types)
- mobilization/remobilization
- multi-factorial systems
- multi-stage systems
- ore/gangue mineral associations
- overturning (hydrologic)
- parageneses
- porosity – permeability – transmissivity (various relationships)
- productivity (organic)
- pumping:
  - osmotic
  - seismic
- pyroclastics (presence or absence)
- rate (numerous):
  - burial
  - influx/reflux
  - mixing
  - sedimentation
  - volcanism
- ratio (numerous):
  - clay/matrix/cement
  - grains/matrix/cement
  - clastic/chemical material
  - volcanic/non-volcanic material
  - ore/non-ore material
- reactivity (chemical):
  - minerals
  - rocks
- red-beds (presence or absence)
- reflux
  - surface
  - subsurface
- replacement
  - molecule-by-molecule
  - volume-by-volume
- reworking (numerous types)
- river influx
- scale/size/proportions
- scavengers
- sedimentation (numerous factors)
- seismicity
- seismic pumping

- shock (seismic)
- silicification (presence or absence)
- size (numerous):
  - particles
  - water body
  - source area
  - etc.
- sorting
- source (numerous variables):
  - anions
  - cations
  - fluids
  - clastics
  - conditions of area, etc.
- stratigraphy (numerous variables)
- stability
  - complexes
  - minerals
  - organics
- subsurface alteration
- sulfuritization
- surface alteration
- surface area:
  - depositional area
  - source area
  - particles (reaction surfaces)
- structures:
  - primary versus secondary
  - alteration haloes, etc.
  - depositional
  - tectonic/deformational
- thixotropy
- time
- traps (several types):
  - barriers
  - chemical
  - structural
- turbidity
- turbulence
- unconformities/diastems
- uniformitarianism (applicable versus non-applicable situations)
- upwelling (oceanic)
- volcanism
- waves
- weathering
- winnowing
- zoning

Note: (a) The complex interrelationships (namely those of the various parameters *within* each group 1, 2 and 3, and *between* 1 + 2, 1 + 3, 2 + 3, 1 + 2 + 3) have to be studied before natural phenomena are fully understood. (b) Some of the parameters could have been listed in two rather than in one of the columns. There is no sharp division between the three columns. (c) Diagrammatic conceptual models are to be prepared to depict the complex interconnections of the variables in this table.

catagenetic, metamorphic, volcanic) processes, or the conditions under which they operate, can be classified accordingly, i.e., based on the barrier influencing the system. These barriers can be effective either along the Earth's surface or in the subsurface. What are the depth/pressure and temperature limits of certain of the barriers? Table 7 then lists some "diagenetic potentials" and "trends" that must be given more future consideration in regional studies, for example of metal zoning. These potentials ought to be identified in our theoretical deliberations before one can expect geologists to make attempts to find criteria or guides to recognize the geological – geochemical products in the field and laboratory.

Table 8 presents miscellaneous variables that are difficult to place into any

TABLE 6

Classification of geochemical barriers of the elements fixed in them (after Perel'man, 1967)

I. Biogeochemical barrier
    O, Si, Fe, Ca, Na, K, Mg, H, Mn, P, F, Ba, S, Sr, Cl, Rb, V, Zn, Cu, Ni, C, N, Co, B, As, Ge, Mo, I, Se, Ra

II. Physicochemical barrier
    1. Oxidation barrier (oxygen barrier)
       Fe, Mn, S, Co
    2. Reduction hydrogen sulphide barrier
       Fe, V, Zn, Ni, Cu, Co, Pb, U, As, Cd, Hg, Ag, Se
    3. Sulphate and carbonate barrier
       Ca, Ba, Sr
    4. Alkaline barrier
       Fe, Ga, Mn, Sr, V, Cr, Zn, Cu, Ni, Co, Pb, Cd, Ca, Mg
    5. Acid barrier
       SiO_2
    6. Vaporization (evaporation) barrier
       Ca, Na, K, Mg, F, S, Sr, Cl, (Pb), Zn, U, (Ni), Li, Mo, N, V, Rb, I
    7. Adsorption barrier
       Ca, K, Mg, P, S, Rb, V, Cr, Zn, Ni, Cu, Co, Pb, U, As, Mo, Hg, Ra

III. Mechanical barrier
     Zr, Cr, Nb, Th, Sn, W, Hg, Pt, Pd, Os, Au, Ru, Ir, Rh, and others

TABLE 7

Factors causing "diagenetic potentials" (or "diagenetic potential trends")[1] (Wolf, 1973, unpublished)

1. Along lithologic boundaries, e.g., carbonate to shale
2. Along boundaries differing in petrophysical properties, e.g., porosity/permeability
3. Along contacts differing in reactivity, e.g., shale to evaporite, carbonate to evaporite, siltstone to carbonate, quartzite to red-beds
4. Along boundaries of different fluids, e.g., varying in Eh, pH, common ions, concentration, temperature, salinity, . . .
5. Variation in pressure
6. See Table 6 for various "barriers"

[1] Attempts should be made to map these "potential trends" during very detailed studies.

classificatory scheme — many of these parameters, however, are of utmost importance in any geological study. Although they too appear "so self-evident", there are several that are usually not conscientiously treated in the literature as, for example, (1) open versus closed systems, (2) exothermic versus endothermic reactions, and (3) the influence of thixotrophy on the stability of a mass of sediments and on their bound or trapped anions and cations. In addition, often abstract ideas are presented as concrete ones, and differences and reliability of in vitro experimental data in contrast to natural settings are ignored.

The methods or procedures employed in diagenesis can be divided (albeit artificially) into general and specific approaches (Table 9). The analytical and interpretive techniques are applied on all scales, both in the field and in the laboratory, covering the whole spectrum of geological and geochemical materials and features. However, many specific or individual diagenetic studies concentrate on those constituents that fall into the pre-designated realm of *secondary* processes and products. Thus, they are preferentially or selectively oriented investigations. Again it can be said that Table 9 is rather an obvious one. On picking any publication on diagenesis, however, one can determine the parameters that have been examined in that study and tick them off on a well-prepared check-list. In other words, the aims and results of "what has been done and obtained" can be put *into context* of the actualistic complex natural system. If the researchers had done that as part of their publica-

TABLE 8

Miscellaneous variables of diagenesis as a possible basis for grouping or classifying systems, processes and products (Wolf, 1973, unpublished)

1. Aqueous versus non-aqueous systems
2. Thixotropic versus non-thixotropic systems
3. Open versus closed chemical systems
4. Exothermic versus endothermic reactions
5. Surface versus subsurface systems and conditions[1]
6. Qualitative versus quantitative data and methods
7. Organic versus inorganic systems
8. Bioturbated versus non-bioturbated systems (cf. Berner, 1980b)
9. Natural versus in vitro (laboratory) systems
10. Natural (uncontaminated) versus man-polluted milieus
11. Concrete (observational, reconstructable, descriptive) versus abstract (concepts, hypotheses, opinions, genetic, interpretive, extrapolative) information
12. Range or coverage of diagenetic changes: (a) textural only, (b) compositional only (trace + minor elements, organic matter, minerals), (c) texture + composition
13. Intensity: incipient (embryonic) through pervasive to totally destructive diagenetic alteration (no numerical or verbal scale for the intensity seems to be available as yet)
14. Mineralogical (and other types of) zoning formed during progressive diagenesis: zoning based on modern basin maturation concepts of zeolites — clays — organic maturity — reflectivity — textural, and other variations
15. Facies based on pH — Eh, pressure or water depth, temperature, oxygen fugacity, and other parameters

[1] This includes the controls of both *time* and *space*. For example two different paragenetic relationships can exist: (1) diagenetic — exhalative (*surface*) hydrothermal spectrum; and (2) diagenetic — burial metamorphic (*subsurface*) — catagenetic or regional metamorphic spectrum.

tion, the reader at least would know the reasons used for the selectively chosen parameters that were investigated. The often extremely simplistic studies performed seem to suggest that many researchers did not attempt to obtain such a perspective in planning their project, aside from the limitations set by a lack of equipment, finances, time, and the likes. This ought not to be construed as a destructive criticism of any researcher's intentions and abilities – we are merely pointing out the present limitations which should be clearly stated in each publication and that every individual investigation is "isolated" and must be put into its proper perspective.

Table 10 summarizes many of the physicochemical, biogenic and physical processes that have been invoked for diagenesis – the reader may wish to add a few more. A voluminous literature, though widely dispersed, is available on these processes, but many problems remain to be resolved, especially in regard to complex interrelationships between two or more of them. In this regard it should be emphasized that many of the chemical processes are biologically induced or controlled. Holistic conceptual models are needed.

Table 11 comprises the factors that influence diagenesis over a wide range of

TABLE 9

Methods utilized in diagenetic investigations (Wolf, 1973, unpublished)

General
1. Micro-, meso-, macro- and mega-scaled
   Microscaled: microprobe, electron microscope, petrographic microscope, X-ray diffraction, isotope studies, etc.
   Mesoscaled: handspecimen studies – similar to microscaled techniques for the study of textures/fabrics, microstructures, and compositions
   Macroscopic: "outcrop-sized" investigations – in addition to the above the macrodepositional and tectonic structures plus stratigraphic features are examined
   Megascopic: regional studies – as the macroscopic approach, but on a larger scale to reconstruct the three-dimensional geology and evolution thereof; e.g., facies-control on diagenesis and diagenetic regional zoning
2. Field versus laboratory studies
3. Petrographic – petrologic/petrogenetic studies

Specific studies and techniques used
1. Mineralogic
2. Paragenetic
3. Geochemical: bulk composition, trace – minor – major elements, isotopes, age determinations, and organic matter
4. Maturation: inorganic and organic (burial history)
5. Textures to microstructures
6. Petrophysical properties
7. Chronology (relative and absolute; see Geochemistry)
8. Depositional features, including top-and-bottom criteria of syngenetic – diagenetic origin in ores
9. Tectonic – deformational features
10. Facies/lithologic associations; stratigraphy
11. Basin analysis and environments
12. Evolution

42

TABLE 10

Diagenetic processes (Chilingar et al., 1967, pp. 183 – 184)

Physicochemical mechanisms
Solution – dissolution
Corrosion
Leaching
Bleaching
Oxidation – reduction
Precipitation – coprecipitation
Mobilization – remobilization
Dewatering – dehydration
Inversion
Reversible (vs. irreversible)
Crystallization – recrystallization
Grain growth – grain diminution
Cementation – decementation
Lithification, consolidation
Authigenesis, neomorphism
Replacement
Sorption: adsorption, absorption, desorption
Accretion, aggregation
Chemical internal sedimentation
Open-space fillings
Diffusion
Evaporization
Sulfurization, etc.
"Suspensate diagenesis" (Hartman, 1973; see this chapter)
Thixotropic changes

Biochemical/organic processes
Many of the above-listed physicochemical processes are controlled by or are entirely due to biogenic mechanisms.
(a) Bacterial processes
(b) Metabolic influences
(c) Indirect controls by changing the pH, Eh, ion-concentration, and addition of organic matter and acids
(d) Biotic reworking (mud-eaters, borers)

Physical/mechanical processes
Compaction
Drying – desiccation – syneresis – shrinkage
Soft-sediment deformation
Abrasion – corrosion
Mechanical internal sedimentation
Mixing – reworking
Thixotropic changes

---

scales or distances, i.e., by "remote (long-distance) – indirect" and by "immediate (short-distance) – direct" controls. For obvious reasons, more is known about the latter because they are easier to study in nature and in the laboratory, although here too numerous enigmas remain to be tackled. The "long-distance – indirect" influences become increasingly more difficult to examine with an increase in distance

and with an increase in variables involved. However remote and complex the situation may appear, these "remotely indirect" controls on the sources, transportation mechanisms, depositional environments do exist and, consequently, influence also syngenesis and diagenesis. Hence, the "long-distance" controls must not be ignored in geological reports merely because we were not able to obtain information on them. Let it suffice to propose here the simplistic Table 11 as one of numerous possible sequential natural settings.

For the sake of completeness, the sources of materials involved in diagenesis are listed in Table 12. The next section on "Definitions, Classifications, . . ." deals more fully with the stages or phases, time concepts, direction of supply, etc., in their proper context (see, for example, the Glossary at the end of the chapter with definitions-cum-explanations).

TABLE 11

Factors influencing diagenesis of sediments (either remote – indirectly or immediate – direct; Wolf, 1967, modified from Chilingar et al., 1967, p. 183)

1. Geographic factors (e.g., climate, humidity, rainfall, type of terrestrial weathering, and surface-water chemistry)
2. Geotectonism (e.g., rate of erosion and accumulation, geomorphology, basin versus platform, and emergence and subsidence)
3. Geomorphology (e.g., type, position of basin; basin configuration; stratigraphy, hydrology, sedimentation)
4. Depositional environment (e.g., type and distribution of specific milieus, e.g., basinal versus lagoonal versus fluvial, etc.; currents, particle size, sorting, transportation)
5. Rate of sediment accumulation (e.g., influences halmyrolysis, preservation of organic matter, biochemical zoning, and ion-transfer)
6. Initial composition of sediments (e.g., aragonite versus high-Mg calcite, and isotopic and trace-element content)
7. Grain size (e.g., influences content of organic matter, number of bacteria, and rates of diffusion)
8. Sorting and differentiation of sediments (e.g., percentage of clay and organic matter, base exchange of clays altering interstitial fluids; and porosity – permeability)
9. Interstitial fluids and gases (e.g., exchange of ions, diffusion, fluid mixing, and rate of flow)
10. Physicochemical conditions (e.g., pH, Eh, and partial pressure)
11. Previous diagenetic history (e.g., earlier expulsion of fluids and recrystallization of clays with elemental expulsion)
12. Example of complex interrelationships:

Climate

```
                    particle        type of         rate of         pH            type of
           ──────►  size of   ───►  bacteria  ───►  diagenesis  ───► and   ─────►  replace-
                    sediments                                       Eh            ment
```
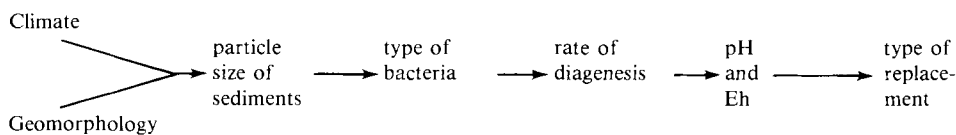
Geomorphology

In the above system, the regionally influential *climate* and *geomorphology* control the *particle size* of material eroded from the source area as well as the differentiation, sorting, etc., during transportation and accumulation at the depositional site, all of which control the particle *size of sediments*. The latter, in turn, control the *types of bacteria* and *biogenic mechanisms*, which, then, control the *rate of diagenesis*. The latter determines the *chemistry* of the interstitial fluids, and consequently, the type of *mineral replacement*. The above is only one setting illustrating the influence of mega- through macro- and mesoscaled factors on the micro-environments.

The classification of mineralizations or ore deposits has been based on a number of different parameters, as reviewed by Gabelman (1967a,b; cf. his tables I – XI), Wolf (1981), and Guilbert (1981). Table 13 merely lists these parameters, whereas succeeding tables provide additional subdivisions, with the exception of the tectonic type (see Wolf, 1981, and Guilbert, 1981, for these). Tables that depict the types of ores that may have been influenced by diagenesis ought to be accompanied by

TABLE 12

Sources of fluids and materials involved in diagenesis (and catagenesis – burial metamorphism) (This system is expanded in tables provided below)

1. Diagenetic – endogenous
2. Diagenetic – exogenous
   (a) Diagenetic – exogenous – hypogene
   (b) Diagenetic – exogenous – supergene
   (c) Diagenetic – exogenous – stratifugic

TABLE 13

Parameters for classifying ore deposits in which diagenesis may have occurred (Wolf, 1973, unpublished; see also Gabelman, 1976a)

Metallization grouped according to:
1. Metal or metals: e.g., Cu, U, Au, Ag, Pb, Zn, . . .
2. Metal associations (paragenesis) – by "type": U – V, Cu – Mo, Cu – Au, Pb – Zn – F – Ba
3. Chemical composition or mineral groups and classes: e.g., sulfides, oxides, carbonates, silicates, and phosphorites
4. Hostrock type(s): conglomerate-, sandstone-, red-bed, shale-, carbonate-, ignimbrite-, pyroclastic-, BIF-, and jaspilite-hosted
5. Major geological process: "sedimentary – chemical", clastic/placer, volcanic – exhalative, etc.
6. Direct emplacement mechanism: clastic settling, chemical precipitation (authigenesis), chemical weathering in situ, cavity (open-space) filling, etc.
7. Hostrock reactivity: very low to very high, depending on textures, permeability, competence, composition, etc.
8. Source of metals: endo- versus exogenetic; seawater – connate water – hydrothermal fluids, etc.; basement – intrabasinal volcanics – arkoses – organic matter + clay-bounded elements
9. Source of transportation solutions: diagenetically – catagenetically – metamorphically released; connate – sea – meteoric – hydrothermal fluids
10. Direction of transportation fluids: hypogene – laterogene (intrafugic) – supergene
11. Relative age of hostrock and deposit: syngenetic – diagenetic – catagenetic (epigenetic) – metamorphic
12. Degree of stratigraphic confinement: conformable versus disconformable (with variable size, scale, degree, intensity, distribution, and type of mineralization, such as disseminations, concretionary, vein-like, open-space fillings, etc., to be considered)
13. Diverse gradients: e.g., temperature, pressure, etc., during early diagenetic versus late diagenetic/ burial metamorphic and catagenetic stages
14. Environmental setting: e.g., fresh and marine water, saline and evaporative milieus (lakes, lagoons, and shallow seas); oxidizing and reducing (euxinic, Black-Sea type); fluvial, lacustrine, coral – algal reefs; and mid-oceanic ridge
15. Tectonic setting: platform, geosyncline, aulacogen basins, and intramontane depressions

a list of the types that are not controlled by it. Gabelman's (1976a) eleven classificatory schemes accomodate many ore types, and it would be interesting to comparatively examine each one as to possible diagenetic controls involved. Every parameter used by Gabelman to classify the ores can be employed also to classify diagenetic mineralizations.

In a follow-up, complementary contribution, Gabelman (1976b) reviewed the "strata-binding mineral processes" in which he listed the mechanisms related to physical dissemination and sedimentational concentration, inorganic and organic precipitation (e.g., phosphates, iron-formations, sulfates, Mn − Fe nodules, metal-rich shales, and metalliferous limestones), organic adsorption, hypogene exhalation, and evaporation. He also considered continental sedimentation (volcanism, placer concentration, karstification), fluid-secretion epigenesis (supergenesis, laterogenesis, hypogenesis), volcanism (lava extrusion, pyroclastic explosion, fumarolic activity) and many others related to plutonism and high-grade metamorphism, which are unrelated to the present leitmotif of diagenesis. As to diagenesis, treated by Gabelman in a brief separate section, he stated that the division, range and applica-

TABLE 14

Division of specific-mineral diagenesis[1] (Wolf, 1973, unpublished)

Ore minerals	"Gangue" minerals
Groups	*Groups*
sulfides	clays
oxides	silicates
silicates	oxides
carbonates	carbonates
bauxites	evaporites/halogens
arsenides	sulfates
sulfosalts	nitrates
elements	borates
Classes	*Classes*
iron oxides	chlorites
manganese oxides	silica
aluminium oxides	carbonates
Pb, Zn, and Cu oxides, etc.	mica
	zeolites
	iron oxides
Species	*Species*
pyrite, pyrrhotite	quartz, chalcedony
all Cu, Fe, Zn, Pb, U, Ag, etc. minerals	calcite, dolomite, siderite
	gypsum, anhydrite
	barite

Paragenetic specific ore + gangue mineral diagenesis
Pb − Zn − F − Ba + calcite/dolomite/ankerite

[1] This table, like many others presented here, is incomplete − it is merely a guide for the reader to prepare his own fully comprehensive summaries.

tion of diagenesis depends very much on its definition, and what some call diagenetic is epigenetic to others, to name only one of the possible confusions. Nevertheless, once a suitable definition has been found for a specific situation, one can proceed to examine which of the above-listed variables fall into the realm of diagenesis and attempt to modelize them, find quantitative data, etc.

Tables 14 – 16 list, respectively, (1) the ore and gangue mineral groups, classes and species involved in diagenesis; (2) the transitional possibilities (only examples) between them; and (3) a division of diagenesis according to mineralogical processes and changes involved. The geochemical system required to form each of the minerals in Table 14 differs, so that the diagenetic processes possibly involved

TABLE 15

Transitional possibilities of specific-mineral diagenesis to be locally or regionally (facies) affected[1] (Wolf, 1973, unpublished)

Based on ore-mineral groups:
Sulfides → carbonates → silicates → oxides

Based on ore-mineral classes:
Fe-oxides → Mn-oxides
Fe-sulfides → Mn-sulfides → Mn-oxides

Based on ore-mineral species:
Zn → Zn + Pb → Zn + Pb + F → Ba

Based on "gangue" mineral groups/classes/species:
Carbonates → silicates → oxides
Evaporites → iron oxides → carbonates → clays
Iron oxides → chlorites → micas → zeolites
Barite → gypsum → anhydrite → calcite → dolomite → ankerite

[1] (a) This table provides only examples and is, therefore, incomplete. (b) Each facies may have several textural varieties; e.g., similar composition but different diagenetic fabrics. (c) Specific-mineral facies may be divisible on the basis of minor- and trace-element variations.

TABLE 16

Division of diagenesis based on mineralogic processes and changes involved (Wolf, 1973, unpublished)

Dolomitization, dedolomitization
Carbonatization, decarbonatization
Silicification
Sideritization, ankeritization
Pyritization
Chloritization
Hematitization, limonitization, magnetization (note double meaning)
Glauconitization
Magnesitization
Baritization
Phosphoritization

should also vary. A useful summary of the geochemical controls for each mineral group, class and species as required by the ore petrologist would be very advantageous and save a lot of research time. It would assist in determining which mineral associations and parageneses are genetically related and possible. What changes in the ore-mineral-forming and gangue-mineral-forming solutions are needed to produce specific associations and parageneses?

In regard to the mineral-based diagenesis, it must be remembered that they may or may not be independent of the lithologies (= rock types) in which they occur. To take a simple example: although calcite cement is most common in carbonate rocks (limestones), this cement is also very widespread in conglomerate – sandstone sequences. Indeed, just about any sedimentary – volcanic rock may have secondary (diagenetic) calcite because the components for carbonate diagenesis are readily available from multiple sources and are easily dissolved – transported – precipitated – remobilized – replaced. To illustrate the utilization of the tables presented here, consider the following questions: Of the long list of diagenetic processes and variables in Tables 5 – 8 and 10, which ones apply to calcite (as cement in general and as a gangue mineral in association with ores)? Which variables have to be considered for the source area or source rock; which parameters control transportation of metals, and which are operative during precipitation? Which barriers have to be overcome in the source locality in contrast to the precipitation environment? Which barrier correlates with which associated ore types? All these questions, and many more, must be answered for both the ore and gangue minerals, before comparative/contrastive-type mineralogical-cum-geochemical models can be formulized to allow, for example, meaningful paragenetic interpretations. A few additional queries: Which diagenetic processes and conditions are more prevalent in which types of lithologies, or which ones are totally independent of the rock type? Among the diagenetic mechanisms, which ones are exclusive of each other; which ones can occur simultaneously or in some (paragenetic) succession? Once the geochemical constraints for each of a group of associated minerals are tabulized, these constraints can then be compared and contrasted to find the minimum and maximum tolerance limits of a mineral association and paragenetic group. For example, the temperature, pressure, Eh, pH, fugacity, common-ion effects, etc., can be compared to establish the limits within which minerals *coprecipitate* in contrast to those minerals that must have formed as *sequential precipitates.*

With sufficient data of this nature, one eventually ought to be able to formulate a *"Law of Minimum – Maximum Tolerance Limits in Environmental Reconstructions",* as proposed by the senior author more than twenty years ago (Wolf, 1965a, p. 220, table VI). Such a law has first been used in ecology, where each organism has a tolerance to the environmental factors to which it is exposed, i.e., there is a maximum and minimum value (e.g., pH and Eh) for each factor within which the organism can exist. In some instances, however, this tolerance may be so broad that it is of little value to precisely delineate a specific environment. For example, if an organism can tolerate a water depth ranging from 10 m above high tide to 150 m below low tide, the presence of this organism as a fossil in a rock could not be used to define intertidal conditions. However, if a second organism (read fossil) is associated with the above-mentioned one and has a tolerance that lies between high

tide and 300 m below low tide, at least the high-tide level is demarcated. A third associated fossil may have had a tolerance falling in the range of low tide and 150 m above sealevel, which would then allow one to delineate the low-tide level. Consequently, examining the tolerances of a *group* of organisms permits one to establish the *shared* tolerance range within which they *co-existed*. For example, in the above-cited case, the *maximum – minimum spectrum* of that particular environmental factor became clear.

It is hoped that this "Law of Minimum – Maximum . . ." can be extended to non-biological geological – geochemical conditions, systems, processes, and their products. The origin of particular minerals and coprecipitated trace elements, isotopes, sedimentary textures and structures, etc., may take place within a range of environmental minima and maxima tolerances that can provide guides or criteria indicative of water depth, salinity, temperature, hydrology, fluid composition, and so on. The following example demonstrates the Law by relating the origin of several minerals to Eh conditions. In Fig. 2, Case No. 1, the range of Eh values within which minerals X, Y and Z can form are depicted by three bars. The bars overlap, as outlined by the dashed vertical lines. Thus, if one can prove that the three minerals originated simultaneously (more-or-less) from the same solution, then the environment of mineral precipitation must lie between the minimum – maximum Eh-spectrum shown in Fig. 2 (which is negative in this case). In Case No. 2, minerals a and b cannot even be assumed to have formed from the same solution; at least a change in Eh (increase) must have occurred. Minerals b and c could have formed in association from the same fluid, because their Eh-spectrum overlaps (or coincides). It is clear, however, that overlap is *no absolute* proof that they actually did originate from the same solution, because *other variables* related to the solution control the origin of minerals, and they may have changed from the time b was
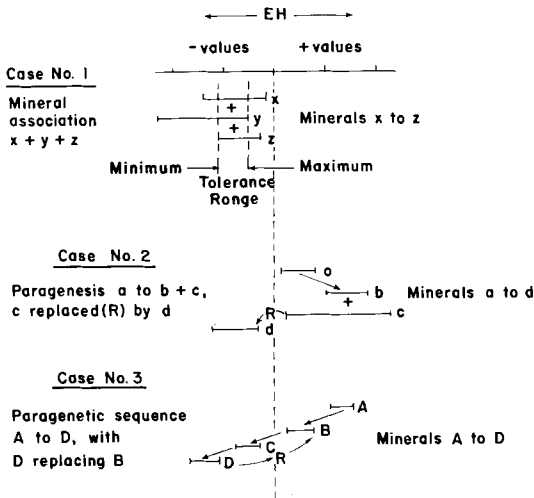
Fig. 2. Eh-dependencies of individual minerals, mineral associations, and parageneses. (After Wolf, 1980, unpublished.)

precipitated in contrast to the stage when c formed. An overlap merely suggests the *possibility* that b and c could have originated from the same solution; the absence of an overlap rules it out. Other data, therefore, is required. Mineral d formed under a reducing milieu, replacing c. Once the above is clarified, Case No. 3 is self-explanatory.

The approach used in Fig. 2, based on the Law of Minimum – Maximum, ought to be applied to both ore and gangue minerals, to determine as many geochemical constraints or limitations as possible. The data obtained for all sulfide minerals, for example, are then compared and contrasted. Such studies done on particular ore "types" may throw light on, for instance, the geochemical constraints of the Mississippi Valley-type Pb – Zn – F – Ba paragenesis (which sometimes passes into Fe – Cu varieties). What are the maximum – minimum constraints on these minerals in isolation (i.e., when they occur alone), in contrast when the minerals are associated? Were they formed in succession, and how did the fluid composition alter? Similar studies ought to be attempted on Cu – V, U – V, Cu – Ag, Mn – Fe metal associations and their gangue minerals to predict local and regional parageneses as well as elemental and mineralogical differentiations and zoning.

One of the most popular modes of classifying stratabound/stratiform ores is by hostrock type (although recently its limitations and "dangers" in exploration have been realized; Finlow-Bates, 1980). Consequently, it is necessary to attempt to understand as much as possible about the origin of the various hostrock varieties, and the whole geological history, from syngenesis onwards, has to be reconstructed. For example, diagenesis can increase or decrease the *"receptability"* of a rock in regard to ore-forming fluids and mineral precipitation. It stands to reason that the type of diagenesis is different in each of the various lithologies, so that we can speak of the respective types of diagenesis as based on lithology, e.g., sandstone-, clay-,

TABLE 17

Major-lithology-based division of diagenesis[1] (Wolf, 1973, unpublished)

Sedimentary diagenesis
– Water – sediment interface diagenesis, including halmyrolysis
– Intrasediment diagenesis

Pyroclastic diagenesis
– As above

Volcanic-flow-rock diagenesis
– Water-flow interface diagenesis, including halmyrolysis
– Intraflow diagenesis

Volcanic – chemical exhalite diagenesis
– Water – exhalite interface diagenesis
– Intra-exhalite diagenesis
– Sediment – exhalite interface diagenesis

[1] All horizontal and vertical, as well as intradeposit, transitions and gradations are possible.

50

limestone-, etc., diageneses. Table 17 lists the four major lithology-based diageneses, namely sedimentary, pyroclastic, volcanic-flow-rock, and chemical exhalative types. Table 18, on the other hand, merely provides an expansion of the numerous varieties of sedimentary host lithologies. Although there are many similarities and transitions or overlaps between the diagenetic systems from within one lithology to any adjacent ones, many important differences, not fully understood as yet, have been reported. The hostrock classifications of ore deposits, presented by Gabelman (1976a,b, table I), can be contrasted with the genetic – environmental scheme of Schneiderhöhn (1962) (see also Wolf, 1981, tables LXV, pp. 134 – 135, and LXIV, p. 133) and Baumann/Tischendorf (1976).

Transitions between mineral associations (Table 15) and hostrock facies (Table 19) have been pointed out here inasmuch as the complex interfingering, for example,

TABLE 18

Specific sedimentary hostrocks of stratabound/stratiform ore deposits, each of which has its own diagenetic milieu (Wolf, 1973, unpublished)

Claystones, mudstones, shales, argillites
Conglomerates
Sandstones/arenites (including siltstones)
  Quartzites
  Arkoses
  Greywackes (wackes, in general)
  Lithic clastics
  Red-beds
Coal, carbonaceous beds
Carbonates (evaporites associated?)
  Limestones
  Dolostones
Volcanic – pyroclastics, volcanoclastics
Volcanic – exhalatives: jaspilites and other silica deposits, iron deposits, barite, etc.

TABLE 19

Transitions between hostrock-based diageneses[1] (Wolf, 1973, unpublished)

General lithologies[2]:
 – Claystone/shale → carbonates → sandstones
 – Carbonates → silicates → evaporites → red-beds

Specific lithologies[2]
 – Organic-rich shale → limestone → dolostone → anhydrite → quartzite → arkose → lithic arenite → wacke → pyroclastics
 – Shale → micrite → bentonite → calcirudite (fore-reef talus) → biolithite (reef) → calcarenite (back-reef talus) → oolitic calcarenite → evaporite → quartzite

[1] This table provides only examples.
[2] It is logical to assume that diagenesis is pervasive or unvarying throughout these facies associations? Or does each lithologic unit have its own diagenetic characteristics?

of facies may have an effect on diagenesis, especially along the contacts or interfaces between various hydrologic, geochemical and mineralogical phases. For instance, the fluids in each sedimentary facies may vary, so that their mixing can provide characteristic diagenetic reactions.

The major sedimentary environments are outlined in Table 20 — ore deposits have been reported from all their "fossil" or ancient representatives as well as from some Recent environments. In some milieus, the mineralizations are of "sedimentary" chemical syngenetic origin, whereas in other instances the mineralization is of the exhalative or placer type. Each milieu is characterized by its own diagenetic (and syngenetic) system, but little comparative-type work has been done to establish the differences, similarities and overlaps. The sedimentary environments are quite frequently the basis of genetic classifications of ore deposits, usually in combination with hostrock, compositional, textural and other data (e.g., Gabelman, 1976a,b, table I; Schneiderhöhn, 1962, in Wolf, 1981, table LXV, pp. 134 – 135; Baumann/Tischendorf, 1976, in Wolf, 1981, table LXIV, p. 133; Bogdanov/

TABLE 20

Sedimentary environments, each of which may have its own type of diagenesis (Wolf, 1973, unpublished; based on the published literature)

Continental	fluvial – alluvial	braided / meandering
	karst	
	lacustrine	
	desert – eolian	
	glacial	
	volcanic	

Transitional (shoreline)
linear →
- clastic → beach – barrier / chenier – lagoon / estuary / tidal flat
- mixed carbonate – clastic
- carbonate
- arid shoreline + evaporite + tidal flat + sabkha

volcanic
lobate – delta complex (with numerous sub-environments)

Marine
- shallow siliciclastic sea → storm-wave dominated / tidal-dominated
- shallow-water carbonate shelf
- reef complex (with numerous sub-milieus)
- continental margin, slope
- pelagic
- deep oceanic (turbidite)
- volcanic
- hydrothermalism (Ridge axis)

Kutyrev, 1972, in Wolf, 1981, tables LXXIV and CI, pp. 160 and 254; Barnes/ Ruzicka, 1972, in Wolf, 1981, table XCV, pp. 226 – 227; and Quinlan, 1972, p. 160; these schemes covering three comprehensive classifications and Cu, Pb – Zn, U and karst-associated ores, respectively). One metal, or one type of metal association, can occur in several environments and, thus, in several hostrocks – and one en- vironmental setting can produce numerous varieties of mineralizations; it all depends on the specific combinations of several geological – geochemical variables. The karst-hosted types, for example, comprise five types of ores, some of which are late diagenetic or catagenetic in origin (see Quinlan, 1972).

Related to the division of sedimentary environments is the classification of natural waters, of which one of the simplest is that based on geographic/geomor- phologic distribution (Runnels, 1969; and Table 21). Such a scheme ought to be sup- plemented by a detailed compositional classification of waters (beyond merely "fresh" and 'saline"). For example, there is a whole spectrum of compositional lake waters that have been studied by hydrologists – geochemists (see Förstner, 1981a, among others), each of which offers a different early to late diagenetic set- ting. Some of these lacustrine environments are conducive to ore genesis; others are not, unless modified by hydrothermalism, influx of metal-bearing river water, etc. The descriptive classifications of waters can be supported by genetic divisions, as for instance by a scheme based on atmospheric precipitation, terrestrial runoff, evaporation, vadose, groundwater, diagenetic, catagenetic, connate, burial and compaction, and retrograde metamorphic, magmatic, etc., fluids. Another all- inclusive classification of waters useful to petrologists would be based on the mode of geological – mineralogical – petrophysical occurrence or genesis: adsorbed – absorbed – desorbed, intracrystalline, intercrystalline and interstitial, etc. (we have not seen any publication that offers the ore petrologist a practical summary of naturally occurring fluids; the book by Fyfe et al., 1978, covers only certain aspects). Once all the waters are known, one can then consider those that are in proximity from each other and can mix. Can *all* known types of fluids mix? Or are certain varieties geologically separated so that intermingling is impossible? In this case there would be no need to attempt to duplicate the non-existing mixing in the

TABLE 21

Classification of natural waters (after Runnels, 1969, table 1, p. 1189)

I. Meteoric waters

II. Surface waters
   A. Lakes: (1) fresh, (2) saline
   B. Streams: (1) fresh, (2) saline
   C. Swamps: (1) fresh, (2) saline
   D. Oceans

III. Subsurface waters
   A. Vadose: (1) fresh, (2) saline
   B. Phreatic: (1) normal formation water: (a) fresh, (b) saline
                 (2) ascending thermal water: (a) fresh, (b) saline

laboratory. Basically, the question is: Which fluids in nature mix and under what conditions?

Some of the types of solutions are depicted in the model in Fig. 3, and the numerous possible natural settings that allow mixing are deducible in the following possibilities:

seawater + meteoric water
meteoric water + magmatic fluids
seawater + meteoric + magmatic waters
seawater + hydrothermal − exhalative solutions
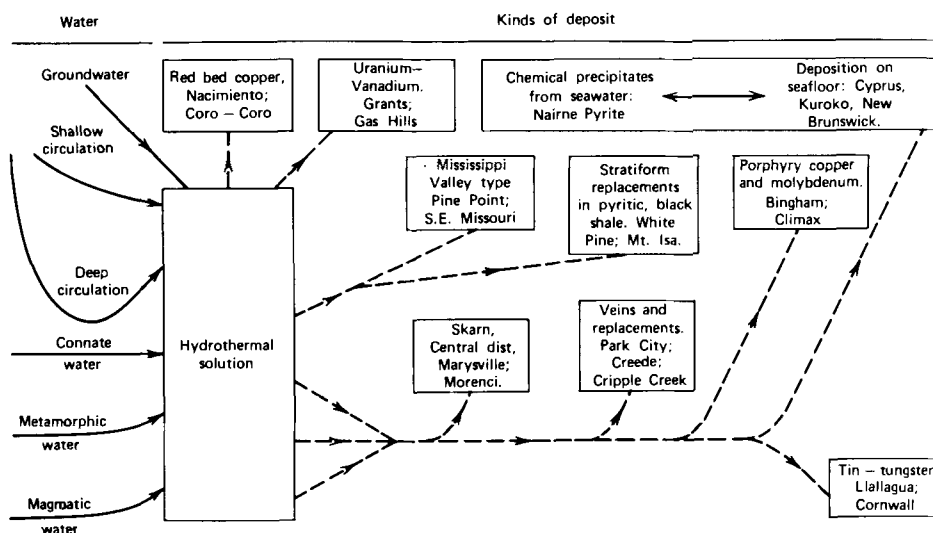
Fig. 3. Schematic diagram relating types of mineral deposits and sources of hydrothermal fluids. (After Barnes, 1979.)

TABLE 22

Chemical classification of submarine volcanic and diagenetic-cum-metamorphic/metasomatic processes (Boström, 1967, slightly modified; Wolf, 1973, unpublished)

Reactions between[1]:

1. Magmatic emanations and lava/pyroclastics
2. Seawater and lava/pyroclastics
3. Magmatic emanations and seawater
4. Magmatic emanations and sediments
5. Lava/pyroclastics and sediments
6. Magma and sediments
7. Combinations thereof
8. Hydrothermal − exhalative fluids and gases reacting with any of the above

[1] A similar table can be prepared for the various reactions with hydrothermal − exhalative material instead of with the lava − magma − water − sediment interactions.

connate waters with all the above
compaction fluids (reaching the surface) + seawater
metamorphic fluids + all the above.

All the cited fluid types, and all the mixing combinations, can be involved in ore genesis. Diagenesis takes part in many of the systems. Figure 3 provides an overview of the numerous fluids and the respective mineralizations that can form.

A special setting of diagenetic or metamorphic metasomatism occurs in association with submarine volcanism and/or exhalations, as described in numerous publications. A chemical classification of the potential reactions is given in Table 22. Many of the surface and near-surface alterations of the sediments, pyroclastic and volcanic flow rocks associated with the submarine volcanism are referred to as metamorphism by some and as diagenesis by others. It is in this "volcanic" environment where diagenesis (however defined), hydrothermalism and low-grade surface metamorphism/metasomatism are indistinguishable, transitional and overlapping. In such case, definitions of these terms merely depend on one's personal inclinations (guess what approach a metamorphic or igneous petrologist would choose, especially one supporting the usually unmentionable or unmentioned interdisciplinary rivalries?). However, whatever viewpoint one adopts, these three processes can be assigned to separate conditions as Fig. 4, for example, illustrates. Of the five proposed types of Kuroko ore deposits, three form at the surface: type III near the exhalative vent, type IV down-basin from the vent in a volcanic rock-dominated locality, and type V in the deeper part of the basin in a sediment-dominated environment. Subsequent to the accumulation of ore, numerous alterations take place – namely, chemical, biological and physical (e.g., mechanical reworking) alterations of the
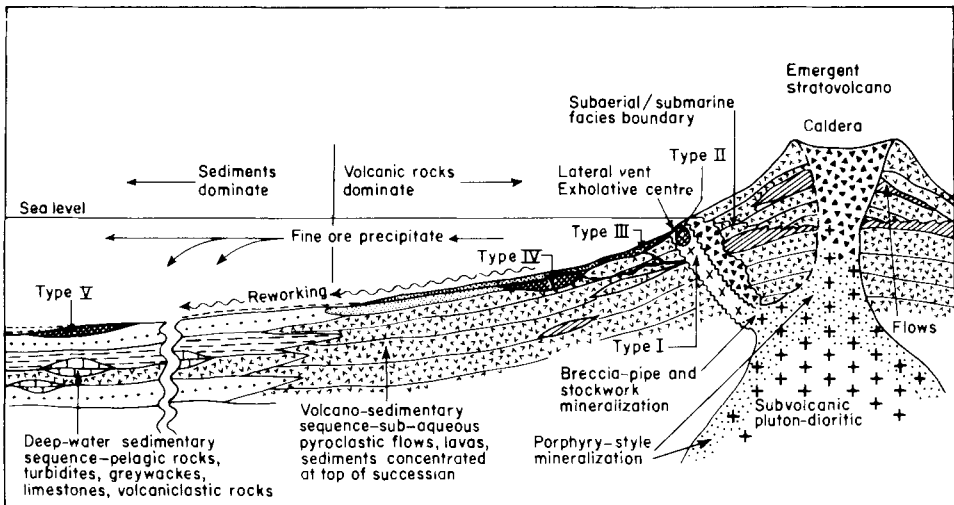
Fig. 4. Schematic model showing positions of various varieties of Kuroko-type sulphide deposits within a volcanic-sedimentary succession and their relation to island arc porphyry copper deposits. (After Colley, 1976; see also Govett, 1983, p. 143.)

rocks as well as of the surface and near-surface formed mineralizations. The altera-
tion fluids are either of hydrothermal, seawater, or intraformational derivation, or
a combination thereof. Where does one separate metamorphism from diagenesis
under such conditions? More important than the nomenclatural debate is to unravel
the geological and geochemical changes in both primary and secondary deposits that
took place in a zonal pattern away from the vent. With increasing distance from the
proximity of the exhalation center into the distal basin, the types of volcanic and
clastic plus chemical sedimentary rocks as well as the types of mineralizations
change, and with it the metamorphic-cum-diagenetic system(s) in both the near-
surface deposits and along the water – rock interface. Consequently, the secondary
zeolite – chlorite – silica – etc. facies (for example) vary both vertically and horizon-
tally, often in a characteristic fashion (see below for the Kuroko facies).
    It seems, then, that it is difficult to distinguish clearly between the following:
    sedimentary syngenesis → volcanic – exhalative syngenesis,
    sedimentary diagenesis → volcanic – exhalative diagenesis, and
    volcanic – exhalative diagenesis → volcanic – exhalative metasomatism.
Customarily, "diagenesis" has been used chiefly in sedimentology (including in the
study of volcanoclastic and pyroclastic rocks), but was less commonly applied to
volcanism in general (however, see Dimroth, 1980, for instance). The expression
"alteration" without any further genetic connotation, such as "diagenetic" or
"hydrothermal – exhalative", when applied to submarine chloritization, may be
sufficiently appropriate in a less precise study. However, the hydrothermally induc-
ed alterations are different from and are transitional into a number of low-
temperature sedimentary diagenetic modifications that may produce similar results.
A clear distinction, therefore, must be made wherever possible. Either one
distinguishes these different mechanisms by properly defining (or redefining) certain
terms, or one clearly describes the processes and parageneses, or both. The basic
rule has always been: attempt to eliminate confusion and misinterpretation. The
terms must be defined more carefully and the boundaries set more precisely as the
study becomes more detailed. A terminology that appears to be "artificially forced"
during a general study, may have to be unequivocally defined for more precise in-
vestigations.
    There are innumerable transitions and overlaps and each case has to be clearly
outlined. Table 23 depicts several possible gradations, namely between muddy (sha-
ly, clayey), carbonate and pyroclastic source rocks; and between these lithologies ac-
ting as a source, on one hand, and as reservoir (host) rocks, on the other. Different
diagenetic processes can release (mobilize, remobilize) metals from the various
source rocks; and different or similar mechanisms can *either* concentrate
(precipitate) the metals in the same rock from which they were released, or the
metals are allowed to move into another type of lithology where, upon encountering
the right conditions, the metals are precipitated. In the first case the source rock and
hostrock are the same, whereas in the second example they are different. On
remembering that different ore "types" have been established merely because they
are hosted by different lithologies, although these "types" can have in common
many (but not all) other geological and geochemical characteristics, one has to
realize that these "types" often are genetically not well founded. (Compare the

carbonate-hosted with the shale-hosted, and these in turn with the sandstone-hosted Pb – Zn – Cu deposits.) What is more significant in establishing types – the similarities or the differences, or a combination of both? But which similarities and which differences (of primary or secondary features, or both)? Insofar as some ore types are believed to have been formed chiefly by diagenesis, the presence or absence of secondary changes must be fully considered in the study of ore "types".

TABLE 23

Four types of ore deposits with several sub-varieties (for explanation, see text) (Wolf, 1976, Table 5-VIII, p. 571)

Type 1A	*Type 2*	*Type 3*	*Type 4*[1]	*Type 1C*[1]
Sedimentary muddy source rock, e.g., black shale	Transition zone between source and host rocks	Sedimentary host rock(s)	Volcanic host rock(s)	Fine-grained pyroclastic source rock(s)
Metals remain in the source rock, e.g., Kupferschiefer-type deposits	Metals move up into the shallower-water lithologies, up to the "host rocks"; but not into them because they are tight; example: sulfides in detrital sedimentary rocks adjacent to stromatolitic reefs, Mufulira, Rhodesia	Metals move into "reservoir" or host rocks, there are several types: (a) sandstones and conglomerates (b) carbonate rocks, e.g., Mississippi Valley-type Pb – Zn – Ba – F ores (according to Jackson-Beales hypothesis)	Metals move into other volcanic rocks (flows, breccias, pyroclastics)	Metals remain in the source rock
Type 1B Carbonate source rock	Two types of transition zone/ore occurrences:			
Metals remain in the source rock, e.g., Woodcutters Pb – Zn ore (Roberts, 1973)	(a) with a very sharp contact (b) with a gradational change in ore concentration, e.g., where breccia zone is present or where differential occlusion of permeable zones in limestones took place			

[1] Volcanic-exhalative and hydrothermal metal supply is not considered here.
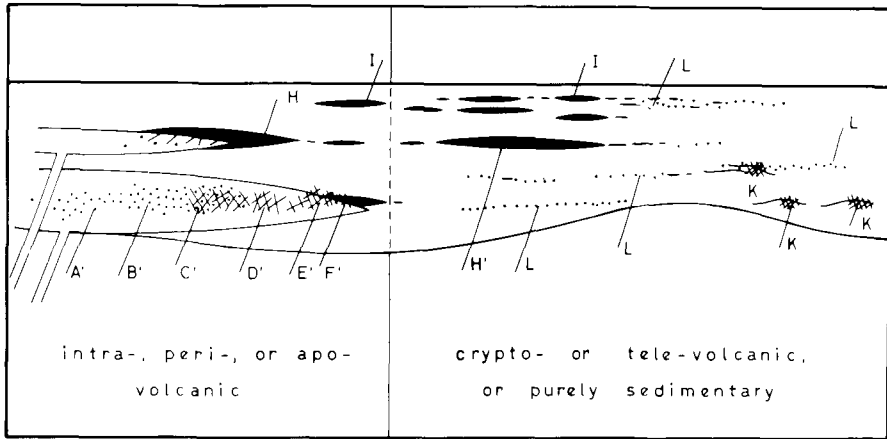
Fig. 5. Schematic drawing of types of mineral deposits. To the left ($A' - H$) are types of deposits clearly associated with volcanic rock; on the right ($H' - L$) are those which may or may not be connected with volcanic exhalative activity. K is largely contained in late-diagenetic compaction fractures in and near organic reefs. Types $A' - F'$ merely refer to common types of distribution patterns in lavas, whereas $H - L$ are located within sediments, with which they were formed. (After Amstutz/Bubenicek, 1967; see also Wolf, 1981, p. 34.)
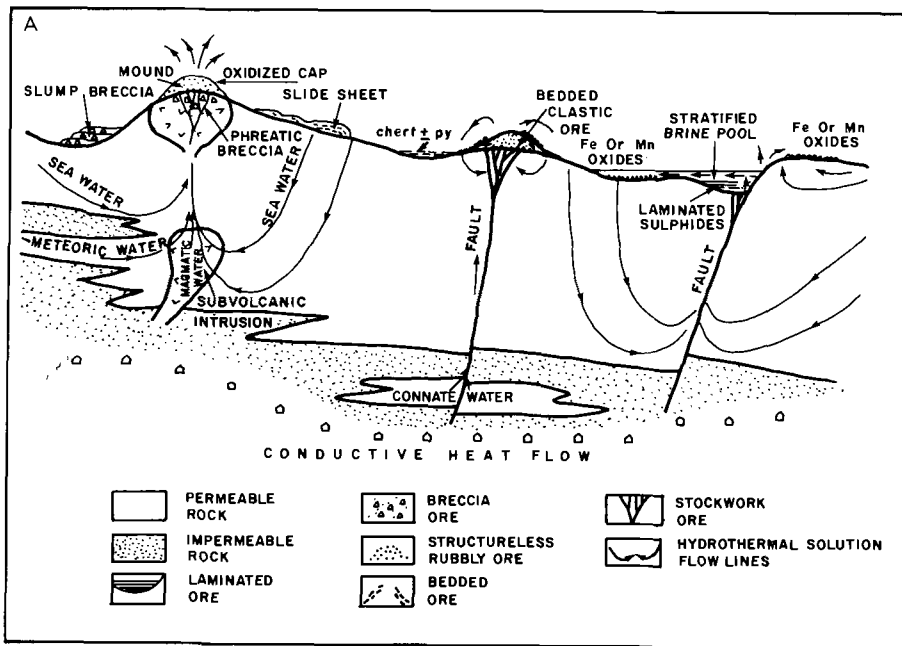
Fig. 6.A. Essential features of recent genetic models for volcanic-associated deposits. (After Franklin et al., 1981.)
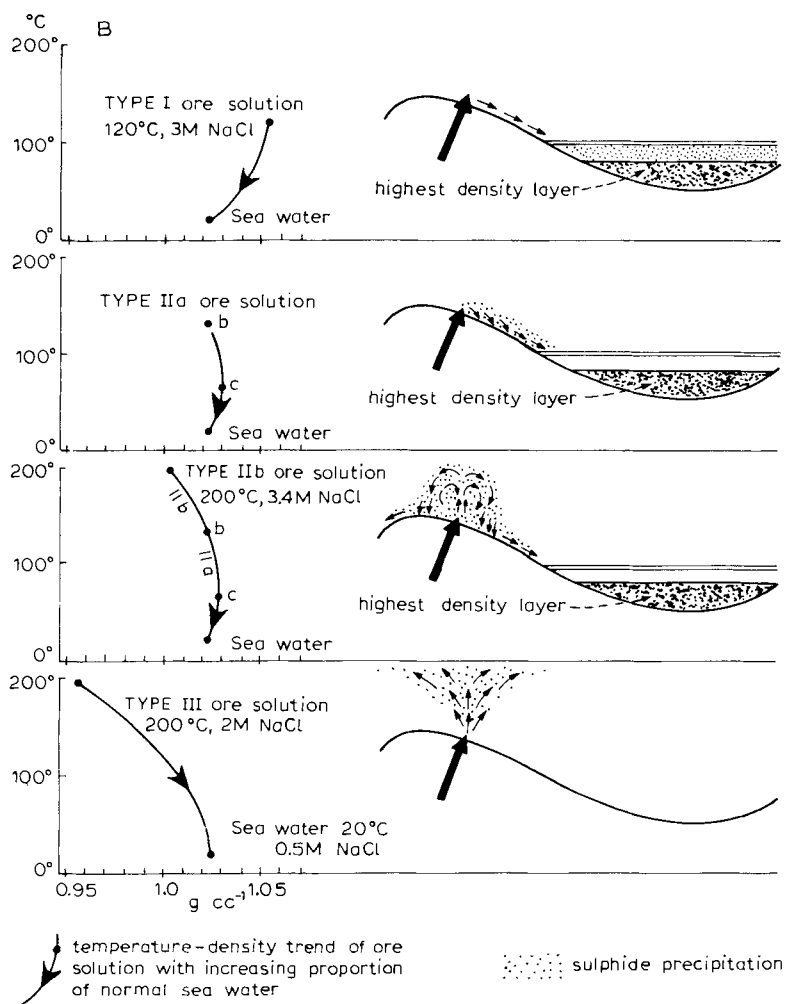
Fig. 6 *(continued)*. B. Possible behaviour of ascending ore solutions at the sea floor as a function of initial temperature and solubility of brine. (After Sato, 1972; see also Govett, 1983, p. 141.)

To return to the volcanic-associated mineralizations: Fig. 5 illustrates the types of ore that are formed in connection with volcanism as well as those that are unrelated to exhalatism (see also Fig. 6A). Several transitions plus overlaps can be visualized here also. The best example of the gradational or overlapping (Fig. 6B), and thus frequently inseparable, nature of hydrothermal and "normal" marine diagenetic conditions, processes and products is furnished by the Red Sea system (Table 24; see Degens/Ross, 1976; Bäcker, 1982; and many others). Diagenetic studies have been officially listed as being one among numerous geological, geochemical, paleontological, mineralogical, hydrological, geophysical, and other investigations of the Red Sea. The variability of the "Facies Types of Metalliferous

Sediments'' of the Atlantic-II Deep environment (also known from elsewhere in the world's oceans and from fossil metalliferous sedimentary rocks) leaves little doubt of the importance of sedimentary mechanical, chemical and biological syngenesis and diagenesis with or without a direct interplay of hydrothermalism. In some situations, hydrothermal processes only supplied the metals. Beyond acting as the source, however, they had no influence on the transportation, precipitation and mobilization, and diagenesis of the chemical constituents. Purely *sedimentary* syngenetic – diagenetic mechanisms took over once the hydrothermal metal-bearing fluids debouched into the sea. The precipitation of the minerals as oxides or as sulfides depended on the following variables in the Red Sea system: (1) pH, Eh, presence of organic matter, bacteria, etc., in the sedimentary milieu; (2) the salinity of interstitial brine within the various facies partly or wholly derived from

TABLE 24

Facies types of metalliferous sediments of the Atlantic-II Deep (Bäcker, 1982)

1. Detrital – biogenic group
   1.1   Marls
   1.2   Carbonates
   1.3   Pyroclastic material
2. Oxide group
   2.1   Limonite facies: iron hydroxides with Fe-contents over 40%; composed of amorphous Fe-hydroxides and goethite; lepidocrocite present in distinct layers
   2.2   Hematite facies: locally occurring as rather coarsely crystalline (sand-sized) grains, associated with magnetite, ilvaite and Mg-silicates
   2.3   Manganite facies: very fine grained; main minerals are manganite and todorokite
3. Sulfate group
   3.1   Anhydrite facies: mostly coarsely crystalline (sand-sized) material forming layers and thick lenses, locally contaminated with black sulphides
   3.2   Gypsum facies: less important than 3.1; small nodules and lenses in distinct stratigraphic positions.
   3.3   Barite facies: only minor occurrence in Atlantic-II Deep (but more widespread in other oceanic environments and more common in certain fossil ore districts)
4. Carbonate group
   4.1   Rhodochrosite facies: well-crystallized, as layers in other facies
   4.2   Manganosiderite facies: well-crystallized, as layer in other facies
5. Sulphide group
   5.1   Monosulphide facies of Zn and Fe with Cu (chalcopyrite) and Ag.
   5.2   Pyritic facies with Cu (chalcopyrite) and Ag. (Both facies are contaminated by carbonates and silicates. Up to 25% Zn and 2% Cu)
6. Silicate group
   6.1   Iron smectite facies: most common
   6.2   Talc, serpentinite, chlorite, vermiculite and palygorskite: occasionally reported constituents
   6.3   Authigenic cristobalite, feldspar and ilvaite facies: near the brine sources
7. Mixed facies
   7.1   Primary mixed facies: between limonite and manganite (= ferro-manganoan sediments), and between limonite/hematite and silicates (= iron – chert formation)
   7.2   Secondary mixed facies: caused by diagenetic and resedimentation/reworking processes
   7.3   Breccia and turbidite facies: caused by tectonic – vulcanic mechanism reworking of primary ore-bearing sediments; also some syndiagenetic fractures becoming filled by hydrothermal ore (= syndiagenetic vein-type)

evaporites (?); (3) adsorbing matter like clay minerals and organic matter; (4) circulating and overturning of waters of closed and open depressions or basins (regional to local in size); and (5) even the local higher thermal anomalies. All of these variables control the (a) solution, dissolution, and complexing of the metals; (b) dispersion and precipitation – coagulation; (c) gel-formation and crystallization; and (d) recrystallization of the "soft-sediment"-hosted ore mineralizations. The subsequent lithification – consolidation, compositional transformations, textures, structures, stratigraphy, distribution, etc., are, therefore, dependent on the syngenesis and early diagenesis.

The control of water depth on the hydrothermal fluids as they exhale onto the seafloor has been discussed by Haas (1971), Finlow-Bates/Large (1978) and Large (1979) (in this connection see also Large, 1980; Finlow-Bates, 1980; Klau/Large, 1980, for the genesis of submarine exhalative stratiform Cu – Pb – Zn ore deposits). The water depth controls the presence or absence, or intensity, of boiling of the hydrothermal solutions and, thus, the temperature (Fig. 6B), which influences the precipitation of metals. With progressive decrease of hydrostatic pressure, the boiling temperature decreases due to the loss by vaporization. Boiling occurs when vapor pressure exceeds the outside pressure. Explosive, in contrast to quieter, exhalative activity also controls the mixing of hydrothermal solutions with the seawater, the distribution of hydrothermal fluids along the surface, and, consequently, surface hydrothermal-cum-diagenetic alterations. It is interesting that the styles of mineralizations of the Rammelsberg, Mount Isa, McArthur and Tynagh/Silbermines have been plotted against water depth (respectively from deepest to the shallowest environment).

When one examines in detail the various models proposed for volcanic- and sediment-hosted submarine exhalative ore deposits, one appreciates the numerous depth-controlled (surface to subsurface) influences on the syngenetic and diagenetic systems: (1) structural (cross-cutting, massive and banded; concordant versus discordant; stockwork – vein/fracture – cavity – stratiform mineralizations); (2) textural/fabric (massive, disseminated, brecciated, etc.); and (3) facies (sulfide, chert, barite, BIF; oxide – silicate – carbonate – sulfide iron formations), etc.

Recognizing through "arm-chair" reasoning that hydrothermal and diagenetic processes are gradational (Table 25) with each other and, thus, can be confused, is one problem; to be able to successfully differentiate the hydrothermal and diagenetic products in the geological record, is another problem. In the exploration for ore deposits, it is particularly important to distinguish between hydrothermal rock alteration produced possibly by metal-carrying hot solutions from those alterations that were formed by non-metal-bearing basinal fluids. Although certain geological – mineralogical – geochemical criteria are available to make such a discrimination, the authors are not aware of any publication that has attempted to *compare/contrast* the various types of diagenetic, catagenetic, hydrothermal – metasomatic, burial metamorphic, contact metamorphic, etc., alteration styles in order to establish useful criteria or guides based on *differences and similarities*.

TABLE 25

Some relationships, transitions or gradations, and overlaps between hydrothermalism and diagenesis (Wolf, 1973, unpublished)

- Hydrothermal solutions debouching into normal sea or lake water can become layered or zoned according to temperature and composition, for example, with a transition zone (between the hydrothermal brines and normal sea or lake water) on the top. Metals occur in the zones as both suspensates[1] (e.g., sulfides and hydroxides) and in solution. The following diagenetic processes can occur (e.g., Hartmann, 1973, fig. 6):
    (a)   high-temperature (bottom) brine → low-temperature (overlying) brine
    (b)   low-temperature brine → transition (topmost) zone
    (c)   transition zone → normal sea or lake water
    (d)   high-temperature (bottom) brine → sedimentary/volcanic (underlying) rocks

- Hydrothermal solutions debouching into a body of water (sea or lake) with the metalliferous fluids passing *downwards* into the sediments and/or volcanic rocks until they encounter a favourable reducing layer, possibly with early-diagenetic, pre-ore pyrite/marcasite. The metals can replace the Fe-sulphide, because pyrite has a greater solubity than the Zn- and Pb-sulfide (galena, sphalerite) (see Finlow-Bates et al., 1977)

- Hydrothermal solutions debouching into a body of water (sea or lake) can choke the earlier established "sedimentary" diagenetic system and replace it by a new system

[1] This was called "suspensate diagenesis" by the senior author (KHW) during the preparation of this table.

DEFINITIONS, TERMINOLOGIES, CLASSIFICATIONS; RANGES, OVERLAPS, TRANSITIONS; LIMITATIONS; PARAGENESES

"Deductivism (i.e., in philosophy the preference for use of or belief in the superiority of deductive, as opposed to inductive, methods – according to the Shorter Oxford English Dictionary, Vol. 1, 1975) ought to be considered with suspicion, because we often 'deduce from something known or assumed'. Instead, science must be based on a continual balancing of and between synthesis – analysis and deduction – induction, for no one specific philosophy, method or concept has proven to be superior."
K.H. Wolf, Sydney, N.S.W., February 20, 1983

In this section a comprehensive overview of numerous aspects of diagenesis is presented. In order to allow the reader to obtain a quick orientation, these topics are indexed below:
(1)   Some introductory comments
(2)   Applications of diagenesis in ore petrology (Table 26)
(3)   Definitions-cum-explanations of terms (Glossary at end of chapter)
(4)   Uses of the prefix "syn-" (see Glossary)
(5)   Sedimentological continuum
(6)   Diagenetic stages (Fig. 7)
(7)   Influences on the hostrocks and ores (Table 27)
(8)   Parageneses (Table 28)
(9)   Hostrock – ore relationships in diagenesis (Table 29)
(10)   Basic patterns of rock – ore genesis (Table 30)
(11)   Time – space relations of syngenesis – epigenesis (Table 31)
(12)   Four basic hypotheses in origin of Mississippi Valley-type (=M.V.) ores (Fig. 8)

As summarized in Table 26, the term "diagenesis" has been employed during geological and geochemical studies to processes, relative-time stages, environments, products, components of a system, transportation and mobilization, concentration – precipitation, and sources. Holistically, they are all simply to complexly interrelated through time and space in any diagenetic – catagenetic system; but to use "diagenesis" for all of them, i.e., indiscriminantly as to whether one is referring to time, process, product or genetic class, or whether applied in the abstract or concrete, descriptive or interpretive, collective or specific sense, and to both causes and effects (Table 26, II), will invite "terminological" or "classificatory" confusion and disaster. In addition, the concept of diagenesis has been used in the study of a number of petrologic subdisciplines (Table 26, III), so that each makes its own preferential or selective demands upon "diagenesis", although many common elements are shared.

The above-mentioned nomenclatural confusion is not hopeless, as already pointed out in previous sections – just a bit of thoughtful rearranging and precise thinking and defining is required to obtain a logical system. The terms used in this chapter are defined as follows. Inasmuch as "diagenesis" is a member of a naturally occurring continuous or continual system (i.e., nature constitutes a continuum or spectrum), it cannot be examined in isolation but can only be appreciated in context with earlier and succeeding stages and processes (see below). In doing so, in addition to the terms related to diagenesis, quite a few other expressions that have been in circulation for some time and are familiar to all petrologists have to be taken into account. To avoid confusion, definitions-cum-explanations are repeated in the Glossary. As can be easily deduced, many of the names are based on the logical utilization of prefixes (mainly of Greek derivation), of which "syn-" is commonly encountered in other geological disciplines.

In addition to the definitions used here, there are numerous other variations of employing the terms, but they deviate only slightly (in precise work nevertheless importantly) from those given in the Glossary. The guiding rule ought to be that all the terms must be "explained" in accordance to the specific requirements or situation investigated. There may be *general or broad* problems of diagenesis that, correspondingly, require a generalized, less-precise definition. On the other hand, for detailed, *exacting studies of multi-phasial, multi-component diagenetic* systems that demand a three-to-five-fold division of the stages between syngenesis and catagenesis, a more meticulous approach is advisable. To be able to fulfill these

TABLE 26

Applications of diagenesis in ore petrology (Wolf, 1973, unpublished)

I. *"Diagenesis" has been used in petrology to denote:*
  1. Processes: i.e., mechanisms and mode(s) of origin
  2. Stage, phase, episode: i.e., time division, usually relative rather than absolute time; isolated or as part of a sequence (between syngenesis and catagenesis/epigenesis, for example)
  3. Environmental: e.g., diagenetic milieus (i.e., between syngenetic and catagenetic/burial metamorphism)
  4. Products: i.e., the result or consequential material of diagenetic processes operative during the diagenetic stage – e.g., mineralogical, chemical, isotopic, organic, transformational, textural, microstructural, and environmental changes such as in pH – Eh
  5. Ingredients, components, or members in a system: e.g., biochemical, physicochemical, and others involved in the early diagenetic bacterially formed pyrite
  6. Transportation, mobilization – remobilization mechanisms
  7. Concentration – precipitation/deposition mechanisms
  8. Reworking mechanisms
  9. Sources, i.e., derivation of components involved in diagenesis

II. *"Philosophical" uses of the term "Diagenesis":*
  1. In the "abstract" and/or "concrete" sense: e.g., applied to time and products of diagenesis, respectively
  2. To both "causes" and "effects" in petrology: e.g., the diagenetic environment and processes, on one hand, and the diagenetic mineral precipitation/concentration and transformation, on the other
  3. As a "descriptive – paragenetic" (though genetically flavoured) term in petrography, in contrast to a "genetic, interpretive, opinion-based, extrapolative" term in petrology – petrogenesis: e.g., "diagenetic carbonate cement" as a purely descriptive statement in contrast to the interpretation of the chemical environment of the cement's origin
  4. Used as a "collective/umbrella" in contrast to a "specific" term: describing a whole system versus particular parts or members thereof

III. *Geological sub-disciplines that use "diagenesis"*
  1. Petrology of all sedimentary and volcanic, including volcanic – exhalative, rocks
  2. Metalliferous and industrial mineral ore petrology
  3. Mineralogy: descriptive and genetic
  4. Inorganic geochemistry
  5. Organic geochemistry
  6. Isotope geochemistry (as part of 4 and 5)
  7. Hydrology
  8. Oceanography

varying requirements, Table 45 lists a number of simple to complex petrologic se-
quences from which the researcher can choose. They need not be contradictory to
or separate from each other — the complex sequences are based on an expansion
of the simpler ones by "fitting-in" additional terms to represent auxiliary phases or
stages. It is quite problematic to set the precise boundaries, however, as discussed
below. But we are getting ahead of ourselves — let us return to some fundamentals.

The sedimentary history of a basin consists of phases or stages that constitute a
continuum in both time and space. Once a chemical, biological, epiclastic or
pyroclastic accumulation has formed, there is a tendency for adjustments, altera-
tions, and disturbances to take place. A plethora of possible processes can act from
the first moment of deposition, and the same processes or, more likely, a combina-
tion of new mechanisms will continue to be operative on these accumulations for
millions of years throughout the whole rock pile. The influence of secondary pro-
cesses will be present as long as the rocks exist: where there are rocks, there are
secondary processes operative; and conversely, therefore: no rocks, no alterations.
It is a simple cause – effect relationship! The details, however, are complex — to
the extent that the unravelling of secondary changes has become a separate sub-
discipline of sedimentology.

As to the above-mentioned "spectrum" in regard to time: the collectively called
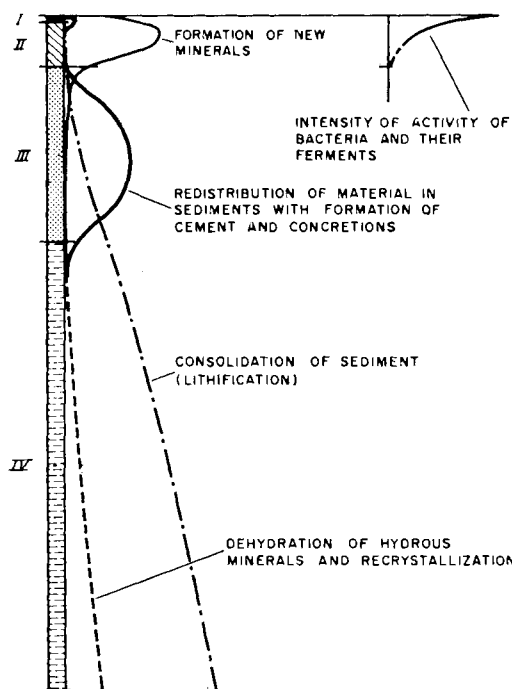
Fig. 7. Diagenetic stages in sediments. (After Strakhov et al., 1954, p. 596.)

secondary processes are active continually or continuously, although in detail, the type of mechanism, the degree of influence, intensity, etc., alter with both time and space. To be able to put some order into the studies of the multifarious secondary petrologic sequential systems, to enable one to record and communicate about them, and to systematically interpret them, nomenclatures and classification schemes have been developed that need to be properly outlined to avoid confusion and misunderstanding. As cumbersome or "boring" as the following section may seem, it is nevertheless necessary. Eventually, when all the "bugs" are recognized in the various (man-made) schemes, one will endeavour to establish a foolproof system without contradictions.

Figure 7, for example, depicts four diagenetic stages during which, among many others, the intensity of bacterial activities, the formation of new minerals, the remobilization of material within the sedimentary pile and their subsequent reprecipitation as cement and/or concretions, the compaction – consolidation – lithification, and the recrystallization – dehydration of hydrous minerals vary. These mechanisms, in combination with numerous additional ones, control directly and indirectly all sediment-associated economic earth resources (e.g., hydrocarbons, industrial minerals, certain types of metalliferous concentrations, and their hostrocks). The diagenetic controls on the (future) hostrocks during the *pre*-ore phase are given in Table 27, these generalities apply to the clastic, pyroclastic and carbonate hostrocks. Too frequently the *preparation* of the country rocks are not given their deserved attention in the study of ore mineralization.

TABLE 27

Diagenetic influences on the hostrocks of ores (Wolf, 1980, unpublished)

1. Preparatory-control (negative or positive) determining the "receptability" of the "aquifer" and "reservoir" or hostrock of the ore-forming fluids:
    (a)   Decreasing the "receptability", by decreasing the porosity – permeability – transmissivity through:
        (i)   compaction
        (ii)   cementation
        (iii) destruction/removal of organic matter
    (b)   Increasing the "receptability" by maintaining or increasing the porosity – permeability – transmissivity through:
        (i)   preventing or reducing compaction
        (ii)   preventing or reducing cementation
        (iii) decementation of earlier-formed cement
        (iv)   dissolution of soluble material from the framework of the rock (e.g., evaporite and carbonate) resulting in collapse breccia, diagenetic karstification, etc.
        (v)   prevention of destruction/removal of organic matter
        (vi)   influx/addition of carbonaceous fine-grained matter and/or hydrocarbons
2. Control on the "aquiclude" properties of the caprock in association with the aquifer and reservoir/hostrock to channel and trap the ore-forming solutions
3. Control of many factors that, in turn, determine the "source capabilities" of the sediments and volcanic rocks in a basin
4. Control on the formation and retention of both syngenetic and diagenetic non-economic constituents that are later replaced by economic components to form an ore deposit (e.g., pyrite replaced by Cu to form chalcopyrite)

The study of the origin of sediment-hosted metalliferous concentrations has to concern itself with at least three groups of components, namely the *hostrock* itself, and the *gangue* plus *ore* minerals. A clear comprehension of the mode of origin of these three involves also the unravelling of the mineral association(s) and their parageneses (= the space – time relationships, or the sequence in which they originated and their spatial distributions). Although there is a tendency to spend much time and money on high-falutin (e.g., probe and isotope[1]) analyses, too little effort is spent on regional paragenetic work (among others urgently needed). Most conclusions are based merely on a few thin- and polished-sections, and as a consequence many investigations are partial and incomplete, founded only on one or two of the four possible parageneses (Table 28). Insofar as certain syn-ore gangue minerals may also be prevalent in the hostrock and can there be of pre- and/or post-ore origin, all four combinations in Table 28 ought to be researched.

What are some of the "time connections" (or "sequential relationships") between hostrocks, ore and diagenesis? Two groups can be examined (I and II) in Table 29. Diagenesis affects both the hostrock and the ore in a continuum – but how can one split-up meaningfully that continual-cum-continuous geological sequence of secondary changes? The (partial?) answer lies in the utilization of the prefixes "pre-", "syn-" and "post-", and thus one obtains six classes of relationships (Table 29): three put the ore into context with the hostrock diagenesis, and three place the diagenesis into relationship with the ore mineralization.

The time – space relationships (combining the "hostrock – ore relative time of origin" and the "location of the source" or space of the metals, for example) have been used by many geologists to describe mineralizations. The four basic patterns are shown in Tables 30 and 31. As mentioned above, in a broader sense "syngenetic" often includes early diagenesis (indeed, in all natural systems there is no syngenesis without diagenesis; and vice versa?) Those who need no more detailed division can expand the scheme in the tables by adding "diagenetic", which then results in six basic patterns of genesis. These possible combinations, as they are called in Table 30, are then (as listed in table XXV by Wolf, 1981, p. 49): syn-endo, syn-exo, dia-endo, dia-exo, epi-endo or cata-endo, and epi-exo or cata-exo.

An application of the four basic hypotheses to the Mississippi Valley-type ore and

TABLE 28

Parageneses to be considered in the study of syngenetic – diagenetic – catagenetic ore deposits (Wolf, 1979, unpublished)

1. Hostrock + ore-mineral parageneses
2. Hostrock + gangue-mineral parageneses
3. Gangue mineral + ore-mineral parageneses
4. Hostrock + gangue mineral + ore-mineral parageneses

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[1] They are called "the be-with-it-bandwagon" because they are too frequently employed at the expense of and to replace more classical, more fundamental tools and concepts that should have been applied initially, prior to, or concomitantly with the modern approaches.

the Arkansas barite deposits were offered by Amstutz and his coworkers (1964, 1967) – they also could comprise in the future the two diagenetic schemes (Figs. 8 and 9).

As will be pointed out repeatedly, any of the two major above-mentioned phases can be divided into two or three sub-phases (rarely are more required at the present stage of knowledge) (see several tables near the end of this section). There are, for example, early and late diagenetic phases (or pre-, syn- and post-cementation diagenesis). That distinctions between early and late phases are quite marked and genetically significant, has been recently expounded by Amstutz/Fontboté (1982). During the sedimentation (= syngenetic) and early diagenetic (I in Fig. 10) phases ore matter accumulated in a "diagenetic open system with circulating interpore fluids", so that through circulation-related processes (e.g., "evaporate pumping", "seepage reflux", etc.) ore can be concentrated in conjunction with bacterial and/or

TABLE 29

Hostrock – ore time or sequential relationships related to diagenesis (Wolf, 1979, unpublished), based on the prefixes pre-, syn-, and post-

I. *Pre-, syn-, and post- used for hostrock diagenesis[1]; ore in context with hostrock diagenesis:*
  1. Prediagenetic ore: ore formed *prior* to the hostrock undergoing diagenesis (= syngenetic ore).
  2. Syndiagenetic ore: ore precipitated *during* the diagenesis of the hostrock. (The same diagenetic processes that affected the hostrock also gave rise to the ore – a question of "what-came-first-the chicken-or-the egg?"; Compare/contrast with 5a and 5c. Are they identical?)
  3. Postdiagenetic ore: ore formed *after* the hostrock underwent diagenesis.

II. *Pre-, syn-, and post- used for the ore[1]; diagenesis is in context with the ore mineralization:*
  4. Pre-ore diagenesis: diagenesis that occurred *prior* to the formation of the ore:
    (a) affecting the future ore hostrock system (see Table 27) or remaining neutral (i.e., having neither a positive nor a negative influence) in this respect;
    (b) making the milieu within the rock system conducive to the passage of fluids or precipitation of ore minerals by the influx of carbonaceous and/or hydrocarbon material, by bacterially changing the pH – Eh, etc.
  5. Syn-ore diagenesis: diagenesis that occurred *during* the formation of the ore – there are several important variations, namely:
    (a) diagenesis that is responsible for the origin of the ore and concomitantly affects the hostrock(s); (cf. 1 above – is it the same?);
    (b) diagenesis controlling the ore-forming processes but not the hostrock; and
    (c) diagenesis of the hostrock contemporaneously (i.e., coinciding in time) with the origin of the ore, but independent of the ore-forming chemical – biological – physical system.
  6. Post-ore diagenesis: diagenesis that takes place *after* the ore (the ore being of any origin, either syngenetic and/or early diagenetic) has formed. Several possibilities exist, namely, diagenesis affecting:
    (a) the hostrock, gangue and ore minerals,
    (b) the hostrock and gangue minerals,
    (c) the gangue and ore minerals,
    (d) the gangue minerals only, and
    (e) the ore minerals only.
    (Note that b – e represent selective or preferential diagenesis?)

[1] These two situations remind one of the possible confusing phrases "sedimentary ores" in contrast to "ores in sediments" – indeed two very different meanings.

hydrocarbon supply. These depositional environment-linked processes are succeeded by a diagenetic phase (II in Fig. 10) characterized by "fractional diagenetic crystallization and/or recrystallization differentiation" within a "partly closed diagenetic system". This fractional differentiation is part of the diagenetic evolution. During phase II, the typical diagenetic crystallization and recrystallization textures, fabrics and microstructures (e.g., rhythmites, geode-like features, syndiagenetic breccias, etc.) may form. It is important to realize, however that ore minerals are often involved in penecontemporaneous deformation textures and

TABLE 30

Basic patterns of genetic interpretations of rocks and ores (after Amstutz and Bubenicek, 1967; see also Wolf, 1981, p. 46)

Time	Space (of source)
Syngenetic formation = contemporaneous with the enclosing rock	*Endogenous formation* = origin same as, or from within the hostrock
Epigenetic formation = formation later than that of the hostrock	*Exogenous formation* = ore matter originates from outside the hostrock
Possible combinations: syn-endo syn-exo epi-endo epi-exo	

TABLE 31

Time – space relationships of mineralization of syngenetic or epigenetic (I or II) origin and of endogenous or exogenous (A or B) formations (after Amstutz, 1964, fig. 1; see also Wolf, 1981, p. 47)

Time[2] Δt Δs Space[1]	I Syngenetic formation $\Delta t = 0$	II Epigenetic formation $\Delta t = x$
A Endogenous formation $\Delta s = 0$	Possiblity Ia (or A1)	Possibility IIa (or A2)
B Exogenous formation $\Delta s = n$	Possibility Ib (or B1)	Possibility IIb (or B2)

[1] Endogenous = from within (the hostrock or its own source): exogenous = from outside (the hostrock or its own source).
[2] Syngenetic = at the same time as the hostrock; epigenetic = at any later time than the hostrock. For Ia to IIb see Fig. 9.

syngenetic	epigenetic
Ia Supergene: ore minerals deposited contemporaneously in and with the sediments; the ore matter, Ba,Pb,Zn,Fe,Cu,Ni,Co.S. etc., is of erosional and thus of supergene origin.	IIa Supergene: ore minerals deposited by supergene solution and replacement, i.e. by epigenetic lateral solution, migration and secretion caused by groundwater movements; the source of the ore matter is the same, or some adjacent sedimentary bed
Ib Hypogene: ore minerals deposited contemporaneously in and with the sediments; the ore matter is of exhalative-volcanic and thus of hypogene-hydrothermal origin.	IIb Hypogene: ore minerals deposited by solutions and replacements in the course of upwards percolations of telemagmatic hydrothermal or regenerative hydrothermal fluids or emanations, either along faults or fractures,or through pore spaces,along grain boundaries, both from unknown sources at depth.

Fig. 8. The four basic theories on the genesis of the Mississippi Valley-type ore deposits. (Diagenetic fabrics point to a syngenetic mode of formation, according to Amstutz/Bubenicek, 1967. See also Wolf, 1981, p. 48.)

Syngenetic $\Delta t=0$	Epigenetic $\Delta t=n$
Ia Sedimentation of material originating from erosion only; Ba, S, O endogenous to the rivers and to the ocean waters of the Mississippian sea.	IIa BaSO₄ endogenous to the sediments, but concentrated by circulating groundwater.
Ib Volcanic-exhalative Ba and/or S mixed and precipitated with normal sediments; thus, exogenous source for Ba and/or S.	IIb BaSO₄ exogenous to the sediments, introduced from the Cretac. Magnet Cove ring dike.

Fig. 9. The basic theories on the genesis of the Arkansas barite belt (S.S. = sandstone). (After Zimmermann/Amstutz, 1964; see also Wolf, 1981, p. 48.)

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                                    ┌──────────────────────────────────────────┐
                                  / │ PHASE I                                    │
                                 /  │                                            │
SEDIMENTATION                   /   │ ORE MATTER ACCUMULATION IN A               │
                               / \  │ "DIAGENETIC OPEN SYSTEM"                    │
   PHASE I                    /\ \  │ (DEPOSITION ENVIRONMENT-LINKED PROCESS)     │
                              / \ \ └──────────────────────────────────────────┘
                             /   \
─ ─ ─ ─ ─ ─              ᴸᴬᵀᴱ \   \  ┌──────────────────────────────────────────┐
                        DIAGENESIS\  │ PHASE II                              ₁    │
                                   \ │                                            │
                                    \│ DIAGENETIC CRYSTALLIZATION                  │
   PHASE II                         /│ DIFFERENTIATION IN A "PARTLY                │
                                   / │ CLOSED DIAGENETIC SYSTEM"                   │
                                  /  └──────────────────────────────────────────┘
                                 /
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Fig. 10. Genetic scheme applicable to most stratabound $Pb - Zn - (F - Ba)$ deposits in carbonate rocks.
[1] Note: Also called "fractional diagenetic crystallization/recrystallization differentiation". (After Amstutz/Fontboté, 1982.)

structures — some unequivocally indicating very early diagenesis, others late diagenesis.

When one adds as a third variable the source direction (= flow direction of the ore-forming solutions) to the above-cited two parameters (i.e., of time and space-of-source), then one has several additional genetic possibilities to consider in various interpretations (see Table 32). This table takes into account three time variables (syn-, dia-, and epigenetic), two space variables (endo- and exogenetic), and three source or fluid-flow directions (stratifugic, supergenic, hypogenic). As shown in the left-hand lower corner, the time-and-space combination results in six basic patterns (i.e., syn-endo to epi-exo or cata-exo). However, when the three-variable combinations of time – space –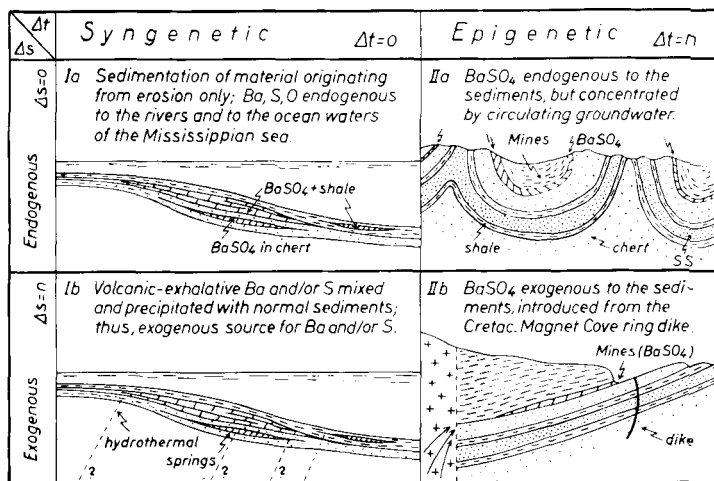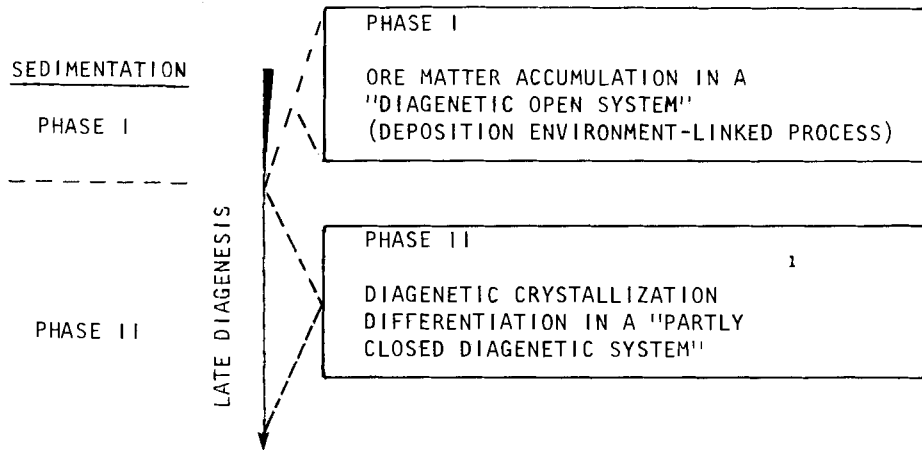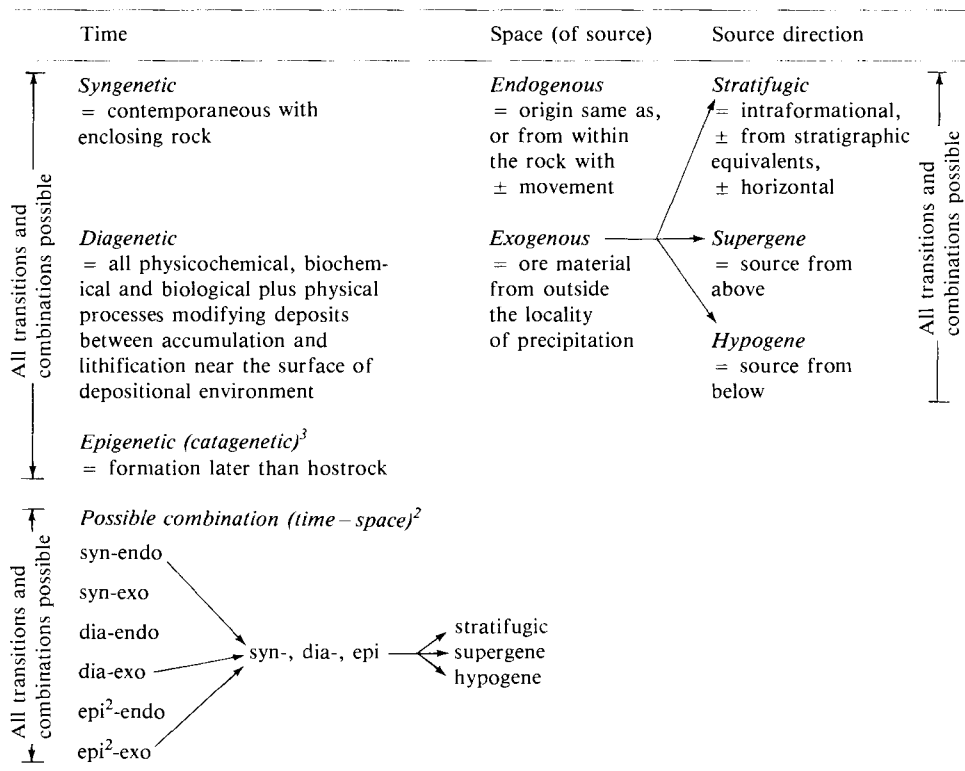 direction are examined, a fairly neat system arises for describing and classifying ore deposits (in a general fashion, that is). Each of the six basic types can be combined with the three "source directions"; so that we have dia-exo-stratifugic, dia-exo-supergene, dia-exo-hypogene, for example. In this example, all are diagenetic in origin and in all three cases the ore-forming components had an exogenous origin (i.e., outside the hostrock), but the fluid-flow pattern or the location of the sources were different.

Table 33 summarizes in a different fashion the above-said and offers a list of the "types" of the sedimentary and vulcanic/volcanic ores. In the above discussions, the terms syngenetic, diagenetic and epigenetic (= catagenetic) were used to represent time or phases. It must be remembered, however, that they also have been used, too often implicitly or by extrapolation, to represent other factors or parameters. For example, in Table 34 these terms are meant to group "modes of origin", i.e., in this case consisting chiefly of the sources and types of fluids involved. The transitions and possible overlaps are indicated by the arrows.

TABLE 32

Basic patterns of genetic interpretations, considering time, space, source directions and possible combinations thereof (Wolf, 1981, table XXV, p. 49)[1]

	Time	Space (of source)	Source direction
All transitions and combinations possible (↑↓)	*Syngenetic* = contemporaneous with enclosing rock	*Endogenous* = origin same as, or from within the rock with ± movement	*Stratifugic* = intraformational, ± from stratigraphic equivalents, ± horizontal
	Diagenetic = all physicochemical, biochemical and biological plus physical processes modifying deposits between accumulation and lithification near the surface of depositional environment	*Exogenous* = ore material from outside the locality of precipitation	*Supergene* = source from above *Hypogene* = source from below
	Epigenetic (catagenetic)[3] = formation later than hostrock		

Possible combination (time – space)[2]

syn-endo
syn-exo
dia-endo
dia-exo   → syn-, dia-, epi → stratifugic
epi[2]-endo   supergene
epi[2]-exo   hypogene

All transitions and combinations possible

---

[1] It is very important to distinguish between the sources of (a) the fluids, (b) the cations, e.g., Cu, Fe, U, Pb, Zn, etc., and (c) the anions, e.g., sulfur, all of which may or may not have the same or may have different sources and origins. Cations may be physicochemically mobilized, whereas sulfur biochemically. From a strict point-of-view, maybe many ores are diplogenetic.
The above scheme is mainly based on Amstutz (various publications) and Wolf (1967, in Chilingar et al., 1967).

[2] Those who prefer "catagenesis" to "epigenesis" (in the present context), can be use cata- as a prefix.

[3] Using any of the three terms that indicate "source direction", the prefix exo- is superfluous. The collective term exo- is only necessary in cases where the source direction is not known.

In this section the terms "exogenic" and "endogenic" (or their synonyms exogenous/exogenetic and endogenous/endogenetic) were employed in connection with diagenesis. On a grandeur scale they have been used to classify all rocks and ore deposits into two large groups, as shown in Table 35. The transitions and overlaps are again shown by the lines; note the approximated range of syngenesis – diagenesis – catagenesis. One more example of the application of certain nomenclatures in classifying ore deposits is provided in Table 36. The terms

TABLE 33

Divisions of sedimentary ores (and related terminology)[2] (Wolf, 1981, table XXI, p. 44)

Time[1]
1. Syngenetic   } genuine sedimentary
2. Diagenetic   }
3. Diplogenetic   } a. sedimentary
4. Epigenetic[3] } b. non-sedimentary

Location of source[1]
1. Endogene[4] – syngenetic }
2. Exogene – syngenetic   } "sedimentary"
3. Diplogenetic   }
4. Endogene – epigenetic   }
5. Exogene – epigenetic   } a. "sedimentary"
                             } b. non-sedimentary

Direction of fluid movement[1]
1. Hypogene – syngenetic   } a. sedimentary
2. Hypogene – diagenetic   } b. exhalative
3. Hypogene – epigenetic   } c. hydrothermal
4. Diplogenetic   }
5. Supergene – syngenetic } a. sedimentary
6. Supergene – diagenetic } b. indirectly exhalative
7. Supergene – epigenetic } c. indirectly hydrothermal

Source and mode of origin[1]
A. "Sedimentary"
1. Direct precipitation from surface water (e.g., lake or ocean)
2. Direct precipitation from connate water plus compaction fluids
3. Direct precipitation from circulating meteoric fluids plus compaction fluids
4. Direct precipitation from heated fluids (basinal)
5. Direct precipitation from descending groundwater
6. Weathering – residual
7. Placer

B. "Sedimentary – volcanic"
8. Exhalative – sedimentary
9. Hydrothermal, epithermal, telethermal

---

[1] Diplogenesis has been mentioned only under "time" in the original 1977 paper, but it can also refer to source types and locations thereof, direction of fluid movements, and mode of origin, as in each case two instead of one influence may be operative.

[2] The great variety of karst-hosted (including pseudokarst-hosted) ores can be of the varieties listed in this table, i.e., any of the types can fill the open spaces in carbonate rocks! What criteria does one have to distinguish them?
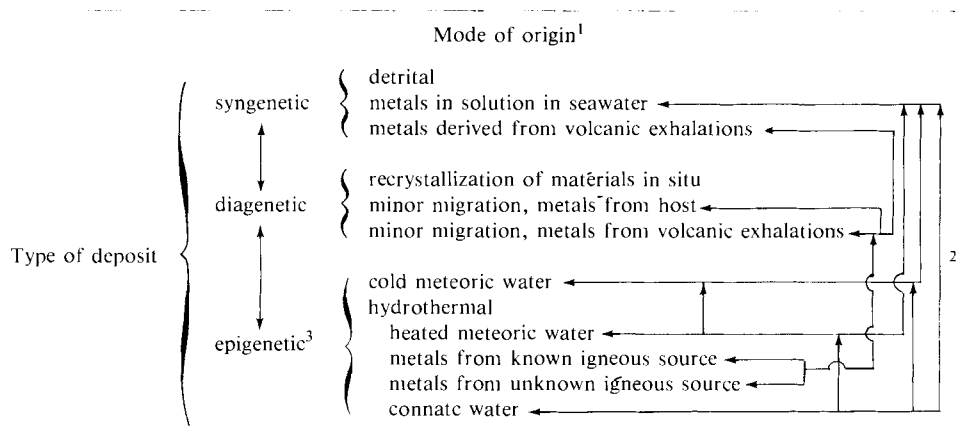
[3] Others prefer "catagenesis" instead of "epigenesis" – see the glossary for definitions.

[4] Cf. "Lithogene" of Lovering (1963), "stratafugic" of Beales and Jackson (1968).

synsedimentary and episedimentary are synonymous with syngenetic – diagenetic (a combination of both) and epigenetic – sedimentary (i.e., epigenetic ores within a sedimentary rock). The sedimentary and volcanic rock-hosted ores formed by con-temporaneous processes constitute the exogenic types, whereas the epigenetic and intrusive ores are the endogenic varieties. The diagenetic controls spread over the synsedimentary, episedimentary and volcanic types of ore deposits. Note the cor-relation between "modern process" and "ancient analogues" – only the former

TABLE 34

Syngenetic, diagenetic and epigenetic theories of origin (modified after Snyder, 1967, table 6, courtesy of Econ. Geol; see also Wolf, 1981, table XXVI, p. 50)

Mode of origin[1]

Type of deposit

syngenetic
- detrital
- metals in solution in seawater
- metals derived from volcanic exhalations

diagenetic
- recrystallization of materials in situ
- minor migration, metals from host
- minor migration, metals from volcanic exhalations

epigenetic[3]
- cold meteoric water
- hydrothermal
  - heated meteoric water
  - metals from known igneous source
  - metals from unknown igneous source
- connate water

[1] This "mode of origin" is based mainly on the *source* of the ore-forming constituents.

[2] The transitions or gradations due to fluid mixing, for example, that are possible have been added.

[3] Epigenetic is synonymous to catagenetic, in the present context.

TABLE 35

Exogenic and endogenic ore groups, with superimposed approximate influential range of syngenesis – diagenesis – catagenesis – metamorphism (Wolf, 1976, unpublished; cf. Söhnge, 1974, p. 160)

I. Exogenic ore deposits
    1. Formed in surface waters
    2. Formed in groundwater milieus

    syngenesis
    diagenesis

II. Endogenic ore deposits
    1. Related to volcanism
    2. Related to metamorphism
    3. Related to magmatism (intrusions)
    4. Related to tectonism

    catagenesis
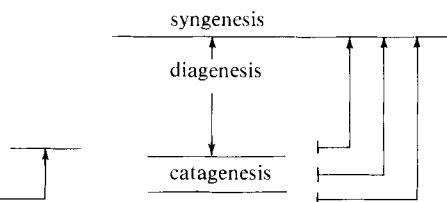
(III. Organic ore deposits, part of I)

TABLE 36

Summary of on-going modern processes of ore deposition and examples of ancient analogues (modified after Rickard, 1982, p. 672)

Classification		Modern process	Ancient analogue
Sedimentary	Synsedimentary	Mechanical concentration of Au, Pt, Sn and sulphides	Witwatersrand
		Chemical precipitation of metals in black muds	Swedish alum shale
	Episedimentary[1]	Pb – Zn concentrations in basinal brines	Mississippi Valley-type deposits
		Pb – Zn concentrations in karst	Les Malines, France
		Uranium precipitation from groundwaters	Sandstone U-V-Cu association
Igneous	Volcanic[2]	Precipitation of zinc-rich Fe – Mn oxides in association with submarine volcanism	Långban, Sweden; Franklin Furnace, U.S.A.
		Formation of Zn – Cu sulphide deposits at ocean ridges	Cyprus-type deposits
		Deposition of pyrite deposits in association with submarine volcanism	Massive pyrite deposits
	Intrusive[3]	Separation of immiscible sulphide globules from mafic volcanics	Ni – Cu deposits associated with basic and ultrabasic rocks
		Hydrothermal brines	Vein deposits associated with acid intrusives
		Porphyry copper deposits	Porphyry copper deposits

Vertical axis labels (left margin): Exogenic sedimentary — Endogenic sedimentary — Exogenic volcanic — Endogenic igneous; Diagenesis

[1] "Episedimentary" could be complemented by "epivolcanic", "epiplutonic" and "epimetamorphic" types(?). Each has several sub-types of epigenetic deposits. For example, the "episedimentary" types of mineralizations consist of many textural varieties, many of which are of early and late "epidiagenetic" origin.

[2] The volcanic types can also be divided into (a) synvolcanic, which would include the diagenetic types; and (b) epivolcanic varieties.

[3] Note that there are "syn-intrusive" and "epi-intrusive" types of ores.

can be *directly* investigated by inductive and deductive methods, so that much extrapolation is involved in using any concepts applied to fossil settings.

Table 37 presents a classification of ore deposits as related to stratigraphic unconformities – disconformities, subdivided into syngenetic and epigenetic types. As in most such "mega-classifications", finer specifics are not considered, so that diagenesis has been excluded. However, diagenesis does take place in both the syngenetic and epigenetic groups of mineralization. Important to realize is the fact that the various so-called epigenetic mechanisms (see the Glossary for definition) can become influential *very shortly* after a deposit has accumulated; consequently, one can refer to "diagenetic – epigenetic" processes and products (in contrast to numerous other varieties of epigenesis, e.g., "catagenic-epigenesis" and "metamorphic-epigenesis"). This approach has been employed in dividing the veins (Table 43). Of course, it may well be that some of the ore deposits in Table 37 are of the cata-epigenetic (below and above unconformities) variety, but others can be related to the diagenetic – epigenetic (= dia-epigenic, to provide an example of an abbreviation) stage. It all depends on the two time intervals (hiatuses) between the

TABLE 37

Classification of ore deposits related to stratigraphic discontinuities (after Button/Erikkson, 1981)
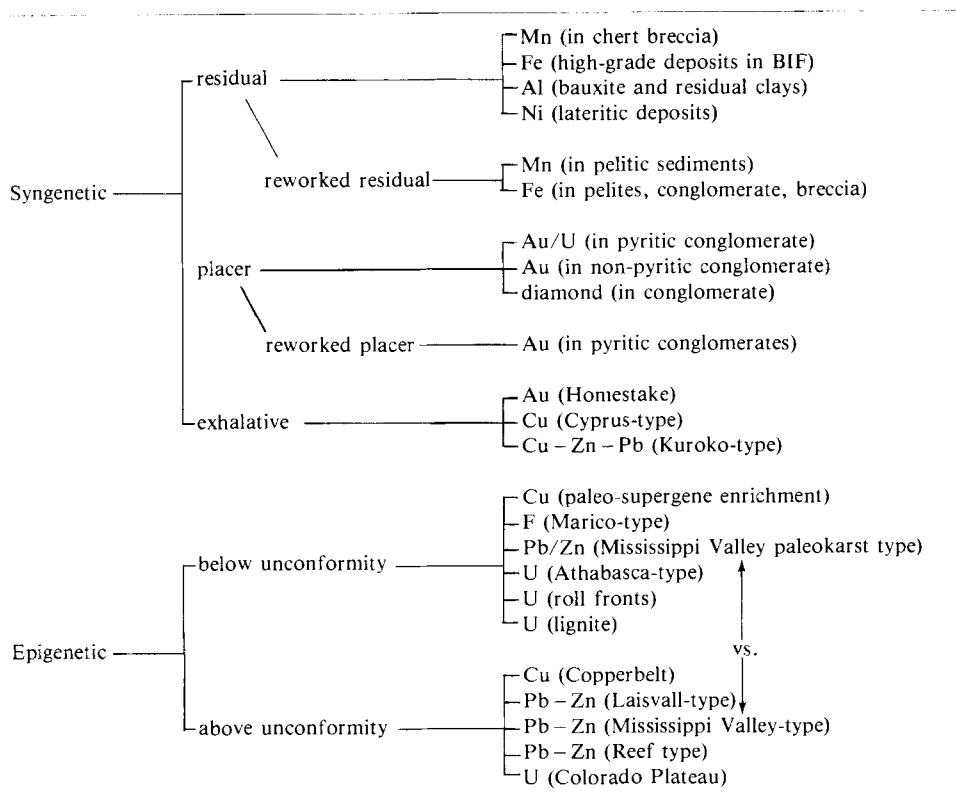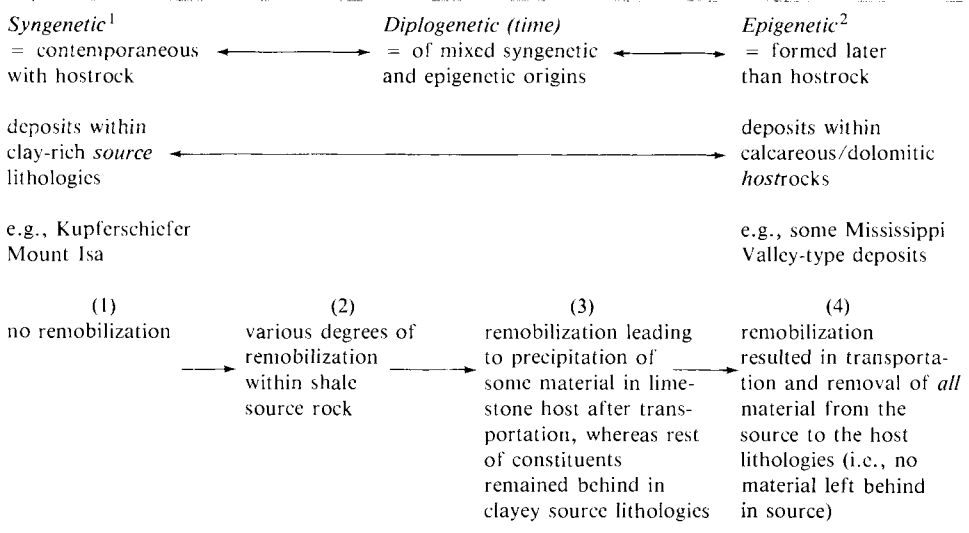
origin of the hostrock, the creation of the unconformity and when the ore-forming mechanisms were operative! If the hiatuses were relatively short, one can refer to "diastems" (rather than unconformities) and the epigenesis can then be related to early or late diagenesis.

Although the above systems do apply to natural occurrences, it must be made clear that they do so only when the situation is clear-cut and relatively uncomplicated in regard to (1) time of origin (three possibilities), (2) location of the source or sources (two possibilities), and (3) source or flow directions (three possibilities). In reality, however, there are numerous more complex geologic settings that have to be evaluated in various schemes, and this has led to the coining of additional terms. "Diplogenetic" or "diplogenesis", defined in Table 38, for example, has not been considered here as yet. There is an ever-increasing tendency to regard a two-fold (or multi-fold) (the Greek word "diplo-" means "two") origin of ore mineralizations as more realistic, because the various components that constitute deposits are believed to have been derived from more than one source, for example. The writers suggest that this has to be expanded in the future to "triogenesis", i.e., taking into account three sources. In Table 39, the diplogenesis can encompass time, location of source, and direction of fluid movement.

Table 39 depicts that the term diplogenesis, when used in both the *time* and *source* sense, can be transitional between syngenetic/diagenetic and epigenetic

TABLE 38

Scheme depicting syngenetic – diplogenetic – epigenetic transitions (an example based on clayey to calcareous hostrock types; Wolf, 1981, p. 51)

Syngenetic[1] = contemporaneous with hostrock	Diplogenetic (time) = of mixed syngenetic and epigenetic origins	Epigenetic[2] = formed later than hostrock
deposits within clay-rich *source* lithologies		deposits within calcareous/dolomitic *host*rocks
e.g., Kupferschiefer Mount Isa		e.g., some Mississippi Valley-type deposits

(1) no remobilization	(2) various degrees of remobilization within shale source rock	(3) remobilization leading to precipitation of some material in limestone host after transportation, whereas rest of constituents remained behind in clayey source lithologies	(4) remobilization resulted in transportation and removal of *all* material from the source to the host lithologies (i.e., no material left behind in source)

[1] Includes early diagenetic, in this context.
[2] Instead of epigenetic, others prefer catagenetic.

(catagenetic). A multiple diplogenetic system exists when (1) syngenetic and epigenetic or late diagenetic solutions mix to produce mineralizations; (2) cooler basinal stratafugic compaction fluids and hot hydrothermal hypogene solutions or cool supergene and warmer basinal stratafugic saline fluids mix to cause ore-precipitation; (3) the metals were derived by leaching of volcanic debris and/or

TABLE 39

Scheme indicating transitional/gradational genetic possibilities[1] (slightly modified after Wolf, 1981, p. 33)

SEDIMENTARY ◄——————— all transitions —————————► HYDROTHERMAL
(IGNEOUS)

Syngenetic[2] ◄——————————— many combinations —————————► Epigenetic[3]
(e.g., diplogenetic/triogenetic)

I	II	III	IV
(1) Type of deposit: syngenetic – sedimentary	ditto (as I)	combination of syngenetic and epigenetic (as I and II plus epigenetic)	epigenetic only
(2) Location: along water – sediment interface	as I	as I and II plus in underlying rocks	confined to subsurface rocks
(3) Metal source: from seawater and/or land source (i.e., no volcanic source)	from volcanic exhalations into surface waters with possible spreading out prior to precipitation	volcanic – exhalative and hypabyssal	hypabyssal, but volcanic – exhalative may be present at the surface
(4) Precipitation: purely physico-chemical and/or bacterial	as I	as I and II	mainly physicochemically but bacterial processes also possible
(5) Form: stratabound	as I	stratabound and cross-cutting, stratiform, plus possibly veins and disseminations	as III, with stratabound deposits as a result of open-space fillings and replacements by fluids and gases moving parallel to beds

General decrease in degree of volcanism involved, closer
◄——————— to Earth surface, and decrease in amount of volcanics in ——————————┤
hostrock assemblages

[1] This table uses "sedimentation – hydrothermalism" only as one example of transitions between syngenesis and epigenesis (catagenesis). There are many additional possibilities.
[2] Includes early diagenetic in the present context.
[3] Instead of epigenetic, some may prefer catagenetic.

arkosic units and the sulfur was supplied by basinal stratafugic fluids; and (4) early diagenetic pyrite is replaced by hypogene, stratafugic, or supergene (downward-moving exhalative solutions) Cu-carrying hydrothermal brines to form chalcopyrite. One can continue these examples to illustrate "triogenesis" . . . !

In Table 38, diplogenesis has been utilized to demonstrate transitional genetic possibilities within a shale (clayey) – carbonate continuum. On the other hand, Table 39 uses the sedimentology – hydrothermalism continuum, in combination with the syngenetic/diagenetic – epigenetic (catagenetic) spectrum, to illustrate various transitions to be expected, so that the type of deposit, the location, metal source (ignore the sulfur source for simplicity's sake), mode of precipitation, and the shape/form of the deposits may all be gradational.

TABLE 40

Transitional types of sedimentary and/or volcanic mineralization processes (Wolf, 1981, vol. 8, pp. 126 – 127, slightly modified and expanded)

1. syngenesis   ⟶   epigenesis[1]
   syngenesis   ⟶   diagenesis
   syngenesis   ⟶   supergenesis[2]
   syngenesis   ⟶   hydrothermal – exhalatism (see No. 2)
   diagenesis   ⟶   epigenesis[3]
   diagenesis   ⟶   supergenesis[2]
   diagenesis   ⟶   infiltration
   diagenesis   ⟶   hydrothermal – exhalatism (see No. 2)
   diagenesis   ⟶   metasomatism (surface)
   supergenesis[2]   ⟶   hydrothermal – exhalatism (see No. 2)
   infiltration   ⟶   epigenesis[3]
   epigenesis[3]   ⟶   low-grade metamorphism

2. "sedimentary"   ⟶   weathering-produced ores (supergenesis[2])
   "sedimentary"   ⟶   volcanic – exhalative ores
   volcanic – exhalative   ⟶   hypabyssal (subsurface) – hydrothermal ores

3. clastic   ⟶   physicochemical ores
   supergene[2] in situ   ⟶   clastic (reworked) ores
   physicochemical   ⟶   biochemical
   biochemical   ⟶   physicochemical

4. monogenetic   ⟶   diplogenetic[4]
   diplogenetic   ⟶   triogenetic
   triogenetic   ⟶   multigenetic

[1] See the Glossary and Table 45. Listed here with the understanding that "syngenesis" includes early diagenesis.

[2] Supergenesis has also been called hypergenesis, telogenesis and epidiagenesis (see text for details). The latter is especially misleading and not recommended, because it is a combination of epigenesis and diagenesis. Under certain conditions and when well defined, "epidiagenesis" might be useful.

[3] Or catagenesis according to numerous researchers (e.g., Vassoevich, 1969, 1974, and earlier; Tissot/Welte, 1978; Larsen/Chilingar, 1979, vol. A).

[4] One, two, three and more processes, factors, sources, etc., may be involved in ore genesis. Gradations are possible because a monogenetic deposit can be transitional into diplo-, trio-, and/or multigenetic mineralizations.

The above-discussed transitions are, of course, mere illustrations in a specific context defined by the terms syngenesis – epigenesis (catagenesis), for example. Gradations, however, can all range from relatively simple mono- and di-component to very complex multicomponent systems with innumerable combinations and gradations in regard to (1) time, (2) mode of origin, (3) source of cations and anions, (4) organic matter (type, source, mode of supply, etc.), (5) source, type and flow direction of solutions, and (6) mode of remobilization, concentration and precipitation. A full, especially quantitative, understanding is still meagre; the study of fluid mixing, for instance, is only in its infancy. Conceptual modeling, however, could be done prior to extensive laboratory testing (see, for example, Ripley et al., 1985).

As far as the transitional aspects are concerned, Table 40 provides the whole range of possibilities to be more closely investigated in the future.

Other schemes or classifications have been made available, as repeatedly mentioned, as for example Fairbridge's (1967). He divided diagenesis into three phases, prefixed by syn-, ana- and epi- (Fig. 11). This and similar simple approaches may be useful in *generalized* discussions, but once an attempt is made to apply these "generalizations", the terminology does not work properly. Especially "epidiagenesis" is inappropriate and confusing, because the combination of epigenesis with diagenesis can have another meaning, as explained elsewhere in this chapter. The earlier-mentioned schemes, and those that follow, are more "realistic". The next classification to be considered worthy of examination is likewise a three-fold division of secondary processes, rather similar to that by Fairbridge, but chooses to employ the less ambiguous "telogenesis" instead of the con-
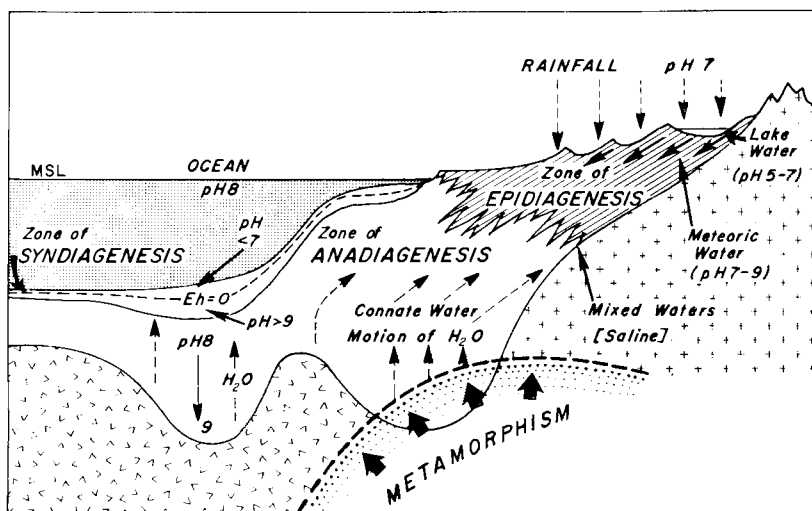
Fig. 11. Idealized profile through a continental margin, showing the sites of contemporary marine sedimentation and the three phases of diagenesis. Note the (1) diffusion potential during syndiagenesis; (2) upward liquid motion in anadiagenesis; and (3) downward motion in epidiagenesis. (After Fairbridge, 1967.)
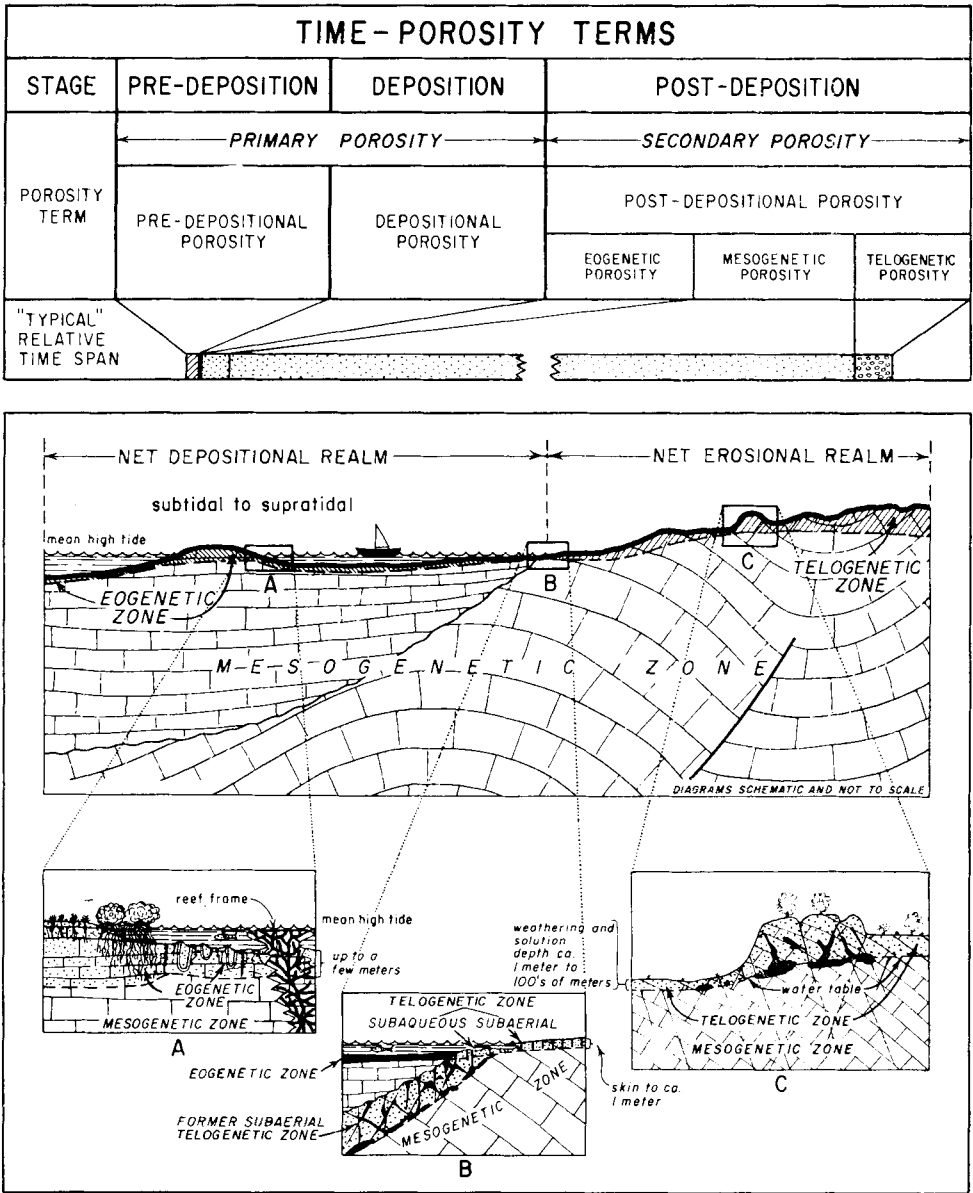
Fig. 12. Time – porosity terms and zones of creation and modification of porosity in sedimentary carbonates.

Upper diagram: Interrelation of major time – porosity terms. *Primary* porosity either originates at time of deposition (*depositional* porosity) or was present in particles before their final deposition (*predepositional* porosity). *Secondary* or *post-depositional* porosity originates after final deposition and is subdivided into *exogenetic, mesogenetic,* or *telogenetic* porosity depending on stage or burial zone in which it develops (see lower diagram). Bar diagram depicts concepts of "typical" relative duration of stages.

fusing epidiagenesis. These two schemes ought not to be equated with each other.

Choquette/Pray (1970) offered a useful scheme (Fig. 12), which was developed for the investigation of porosity. Inasmuch as this textural or fabric feature comprises many types that can originate in the predepositional stage (see Wolf, in Wolf/Conolly, 1965a), as well as during syngenesis and diagenesis – epigenesis (catagenesis), a neat parallel can be drawn between the system of Choquette/Pray and the other systems (as mentioned both above and in succeeding sections). As a first approximation, one might be inclined to equate the term "primary" in Fig. 12 with "syngenetic" (especially with "depositional"), and the "eogenetic" with "early diagenetic". "Mesogenetic" might be equivalent (more-or-less) with "late diagenetic" or epigenetic (catagenetic). As discussed below "telogenetic" refers to "supergenesis" when the rocks have been uplifted. The prefix "telo-" is less contradictory and confusing than Fairbridge's (1967) "epi-".

Although a scheme is offered near the end of this section, the classification by Choquette/Pray (1970) is utilized here also. The senior author (KHW) adopted their nomenclature to classify the open-space types of ore mineralizations (such as the karst and karst-like or pseudo-karst ores) and to divide the veins. Both schemes are merely preliminary attempts to sort-out and differentiate various potentially recognizable types that are customarily lumped together by their respective umbrella terms "karst" and "veins".

Using Choquette/Pray's (1970) ideas as a foundation (Fig. 12), one can attempt to substitute their "pores" by "open spaces" – that is by open spaces of any genetic type, shape and size. Among these "open spaces" are (1) the karst collapse structures, channels and cavities; (2) pseudo-karst features, including hydrothermally formed dissolution pseudo-karst structures; and (3) joints and faults of various sizes and origins (i.e., the soft-sediment, tectonic and unloading types of joints that form veins when filled by minerals). Choquette/Prays's eogenic, mesogenic and telogenic "pores" then become equal-named (or equal-prefixed) eo-, meso- and telo-type "open spaces". By one further extrapolation, one obtains "eogenic karst, pseudo-karst, joints, faults and veins", etc. (Table 41). The above terminological development was based purely on "logical arm-chair reasoning"! But is it factually representing natural processes (causes) and products (effects)? The answer seems to be affirmative in regard to most types of open spaces, especially the smaller-sized ones that can form under near-surface and deep basinal conditions. There may be one exception, however, in regards to karst features, represented in particular by the large cavernous variety.

Lower diagram: Schematic representation of major surface and burial zones in which porosity is created or modified. Two major surface realms are those of net deposition and net erosion. Upper cross-section and enlarged diagrams *A, B* and *C* depict major post-depositional zones. Eogenetic zone extends from surface of newly deposited carbonate to depths where processes genetically related to surface become ineffective. Telogenetic zone extends from erosion surface to depths at which major surface-related erosional processes become ineffective. Below a subaerial erosion surface, practical lower limit of telogenesis is at or near water table. Mesogenetic zone lies below major influences of processes operating at surface. The three terms also apply to time, processes, or features developed in respective zones. (After Choquette/Pray, 1970, fig. 1.)

It has often been assumed that karsts are formed by meteoric water by dissolution under *surface and near-surface* conditions. This would mean that they are formed only as eogenic and telogenic types. But to what depth in the subsurface can karstification take place? How low can the watertable sink, assuming that karstification is controlled by it? If karstification is confined to the upper parts of the Earth's surface, then no mesogenetic karsts per se exist in nature. However, pseudo-karsts can be created at any depth: maybe not the large-sized variety that forms mainly near the surface, but at least the smaller-sized karst-*like* structures which can form at great depth. These may have economic importance in providing open spaces for mineralization. Hot basinal (compaction) and hydrothermal solutions may dissolve carbonates to form "karstification" features in the deeper parts of a basin. If one accepts this argument, until further data is available to contradict or refute it, one can recognize four phases of karstification, designated as syndepositional – early diagenetic karstification, and eo-, meso-, and telogenetic epigenetic karstifications, independent of the precise origin/derivation/evolution of the fluids and hydrology. In regard to the just-debated, the question arises as to how much do the geomorphologists and paleogeomorphologists know at present about the maximum depth, the timing, relations to unconformities, etc., of karstification, which in turn the ore petrologists can utilize in differentiating the numerous cave-forming mechanisms? For that reason, the writers have stressed here the karst-*like* and *pseudo*-karst structures. Table 42 is self-explanatory, in particular to those who like to decipher, in this case minor, complexities. (It is strongly advised to read the numbered footnotes and explanations.)

Insofar as we have discussed here only one type of weathering product, i.e., the karst system, it may be the best place also to draw attention to a few other weathering-related mechanisms and problems. First, weathering is related to

TABLE 41

Open-space (including karst and karst-like[1]) features formed during various stages (Wolf, 1975, unpublished; after Choquette/Pray, 1970, porosity scheme)

Open-spaces formed during carbonate rock deposition
1. Syndepositional or depositional (or early diagenetic[2]) open-space structures, including karstification features

Post-carbonate rock depostion[3]
2. Eogenetic open spaces, including karstification
3. Mesogenetic open spaces, including pseudo-karstification[1,4]   } "epigenetic" open spaces
4. Telogenetic open spaces, including karstification

[1] "Karst-like" process and "pseudokarstification" are synonymous.
[2] See Bates/Jackson (1980) for "syngenetic karst".
[3] See Fig. 12 herein (from Choquette/Pray, 1970).
[4] If it is assumed that genuine karst features originated only under surface and near-surface conditions, then mesogenetic karst does not exist(?). However, open spaces that look similar to karsts can form in deeper subsurface parts of a basin (some the result of hot hydrothermal solutions?) – these can be called "pseudokarsts".

TABLE 42

Types of open-space infill (including in karst and pseudokarst systems) as related to ore genesis (Wolf, 1976, unpublished)[1,2]

Open-space types (including pseudokarst) in carbonate hostrock (according to stage)[3,4]	Ore-mineralization open-space infillings (type, source, origin)[3,4,6,9,10]
1. Syndepositional openings[5] Type No. 1 ± pene-contemporaneous[8] gradational	– residual (surface "supergenetic")[7] – syngenetic (marine ± hydrothermal – exhalative ± compactional – exhalative solutions) – diagenetic (infiltration)
2. Eogenetic openings[5] Early stage Hiatus = brief to long-time interval (from early to late eogenetic stage) Type No. 2 gradational Late stage	– residual and reworked surface residual (descending)[7] – syngenetic (infiltration: descending marine)[11] – diagenetic (infiltration: descending marine, stratafugic basinal; ascending hydrothermal)[11] – catagenetic (stratafugic basinal, ascending hydrothermal)[12]
3. Mesogenetic openings[5] Early stage (shallow sub-sidence) Type No. 3 ± penecontem-poraneous[5] gradational Type No. 4 much later[8] (deep sub-sidence) Late stage	– residual: (a) reworked surface residual (descending)[7], (b) stratafugic subsurface residual – diagenetic (infiltration: stratafugic basinal; ascending hydrothermal)[11] – catagenetic (stratafugic basinal, ascending hydrothermal)[12] – metamorphic fluids (stratafugic basinal, ascending hydrothermal)[12] – plutonic/hypabyssal hydrothermal solutions)[12]
4. Telogenetic openings[5] Early stage Type No. 5 After tectonism and uplift Late stage	– telogenetic (surface supergenetic after uplift)[13] – infiltrational (descending meteoric[14] descending hydrothermal) – syngenetic – diagenetic as in type No. 2 if exposed to *new* marine environment[14,15]

(Left vertical axis labels: Burial and maturation of rocks increases; Tectonism, uplift + erosion, "unroofing", peneplanation)

[1] This table ought to be read in conjunction with Fig. 12.

[2] Veins (Table 43), like pore and karst/pseudokarst systems, can be similarly classified. It should be remembered that "larger pores" and "small karst cavities" are transitional and may not be easy to distinguish from each other. Incipient (embryonic) karsts may be associated with diastems, whereas well-developed, widespread karst systems can be associated with unconformities. The hiatus is relatively brief in the former case, and long in the latter instance.

(Continued on the next page.)

TABLE 42 (*continued*)

[3] The numerous combinations of karstification and ore deposition ought to be modeled by using diagrams and flow-chart-like schemes. Once a few arm-chair-based models are developed, one can use them as guides to search for criteria to be tested and re-tested in subsequent studies. At present, most investigators seem to be haphazardly looking for features that remain unclassified – unstructured – unmodeled in most investigations (with a few exceptions).

[4] The outline in this table considers only *one* karstification period and *one* infilling stage, whereas in nature either one of the two or both can have undergone a multiphase development (each phase consisting of a cycle, possibly ranging from incipient to the mature stage?).

[5] See the "typical relative time span" in Fig. 12, as given by Choquette/Pray (1970, fig. 1).

[6] All the mineralizations are discordant (= "epigenetic", as used by some) and concordant (i.e., where karstification was parallel to the primary bedding) features.

[7] The process of "residual" accumulation in cavities is directly linked to the karstification during the syndepositional phase (i.e., the former is the result of the latter). But this "direct" link becomes increasingly "indirect" with a change to the eogenetic karst phase or with an increasing burial depth of the karst system. The link is only remote in the case of an early mesogenetic karst or pseudokarst system, when it may still be possible under rare conditions for surface-derived reworked supergene material to descend into the deeply situated cavities. In the late-mesogenetic stage, this is most likely impossible, and the cavities can be reached only by intraformational fluids.

[8] When infilling is more-or-less penecontemporaneous with karstification, there is a brief hiatus (= time interval) between them, physically marked possibly by a diastem. If much time has passed between karstification and ore precipitation, a well-marked unconformity is to be expected (see Types 1, 3, 4 and 5).

[9] The processes that deposit material in the karst system vary greatly according to (a) types of solution (e.g., marine surface water with/without exhalative hydrothermal fluids, vadose or phreatic waters, basinal compaction fluids, ascending hydrothermal solutions, burial metamorphic solutions, etc.), mode of transportation (particulate/granular, suspensates, colloids, complexes, ions, adsorbed material), and style of precipitation. Also, the parageneses and gangue – ore mineral relationships will vary.

[10] A researcher (a maverick thinker in this case) with neological inclinations, may wish to make distinctions between the several "syngenetic" and "diagenetic" stages and types by using prefixes (?). The present authors refrained from doing this up till now!

[11] "Infiltration" of small to minute particulate matter and colloidal and ionic material into open systems in the subsurface can occur to a depth of several hundred meters, depending on various geological factors. Consequently, either an earlier-formed, subsequently subsided karst system, or one that formed at a greater depth (especially pseudokarsts), can receive constituents from the surface that partly to completely fill the openings.

[12] The deeper the originally surface-formed karst system subsides (what is really the maximum depth to which a water table can be lowered and at which karstification through meteoric water − in contrast to hydrothermal-water-induced karstification − can occur?), the greater the possibility for catagenetic – metamorphic – plutonic fluids to reach the karst system. Especially fluid mixing can take place. Also, warm to hot basinal fluids of various derivation may produce karst-like dissolution (cavernous and labyrinthoid) systems that are similar to surface-formed systems. The latter, when they reach a greater depth during subsidence may be enlarged and reshaped by hot subsurface solutions. However, little concrete data are available to ore geneticists beyond the "arm-chair reasoning" approach.

[13] See No. 7 above, then compare the "residual surface supergenesis" of type No. 1 with the "telogenic-after-uplift" variety of supergenesis of type No. 5.

[14] The above-mentioned telogenetic-type of mineralization may be associated with the infiltration type.

[15] If the whole system is near a marine environment, for example, one might then speak of (15) as an "old carbonate landmass" undergoing karstification. Under the right conditions, it will be exposed to the *superimposed* syngenetic – diagenetic ore-mineralization (that is "syngenetic – diagenetic" in respect to the *new* marine milieu − totally unrelated to the originally carbonate-hostrock-forming syngenetic – diagenetic system). As explained above, there may be a short or a long hiatus between this telogenic karstification and ore precipitation!

diagenesis. The processes and products of both are interconnected because: (1) "submarine weathering" (= halmyrolysis) is part of diagenesis; (2) this halmyrolysis may be either transitional into or may be different from submarine volcanic – exhalative (metasomatic) diagenetic alterations; and (3) earlier-formed marine deposits, for example, with merely a slight change of sealevel, will be exposed to weathering, so that the syngenetic and early diagenetic materials are over-printed or obliterated by the "supergene" features. Certain diagenetic features formed under oxidizing conditions [i.e., if sedimentary constituents formed under a reducing milieu are later exposed to a new oxidizing environment, e.g., creating the following reactions: glauconite phase → leaching of K^+, Na^+, Ca^{2+} → chamosite phase → leaching of other components → hematite (maghemite phase); see Spoljaric/Crawford, in Ridge, 1980b] may be difficult to distinguish from those produced by "terrestrial" supergenesis.

There are at least two fundamentally different situations in regard to the time when a rock was formed compared to the time when the unit underwent weathering (supergenesis). These two extreme cases can be conveniently named "penecontem-poraneous" and "post-tectonic" (of course, with intermediate situations). The former takes place relatively shortly after the rock originated as a consequence of a relatively minor change in sealevel, whereas the latter occurs after millions of years, in the extreme case, when tectonism has lifted deeply buried rocks to the Earth's surface. The time interval between the origin of the rock and weathering, of course, varies greatly depending on the total geological history. A clear distinc-tion ought to be made in petrogenesis between these two possible types of supergenesis, and the senior author proposes to call the penecontemporaneous and post-tectonic supergeneses, respectively, "pene-supergenesis" and "telo-super-genesis" or, alternatively, "supergenesis" and "telogenesis".

There is an urgent demand for a classification of veins (just like there is one for breccias!) − that is, possibly several types of classification schemes are required to fulfill the variable needs of explorationists and researchers. Table 43 lists nine to ten types of veins, arranged according to the time when the original fissure/ fracture formed in relationship to the hostrock. Examination of the origin and definition of "veins" shows that veining is independent of the time and the degree of lithification of the hostrock (as well as independent of orientation, size, etc.). Thus, both unlithified (as long as the veining is not prevented by collapse of the sedimentary framework) and well-consolidated deposits (sediments and volcanics, or any other lithological variety) can be veined. The process of veining can operate either during syngenesis (? less common), or during diagenesis, catagenesis and metamorphism and, therefore, can be named accordingly. This scheme, consequently, is genetic − interpretive and thus subject to judgment, and its application to be founded on a well-reasoned argument and based on criteria or guides.

There are at least five or six groups of veins: sedimentary/volcanic diagenetic (in-cluding soft-sediment deformational type) veins; catagenetic and metamorphic (in-cluding lateral-secretion type) veins; telogenic (including unloading/decompres-sional type) veins; pedogenic (?) veins originating during soil formation and/or supergenesis; tectonic deformational type veins; and plutonic/hypabyssal type

veins. Some geologists may rearrange this division and, for example, add the decompressional vein types to those of tectonic deformational origin. Can any reader refer the writers to a publication summarizing the criteria to discriminate between these vein types (or to a paper that does the same for breccias)!? (The senior writer has been quite vocal lately about the need to solve certain *very fundamental* problems that ought to be tackled in addition to concentrating on a plethora of high-falutin research being undertaken. No computer will find the answer of how to discriminate between the dozens of breccia types — one has to know the criteria and types first to provide a "reasonable logical" input! Many field and laboratory descriptions are still in an unbelievable mess, and no electronic device can enhance non-sensical data. Garbage in, garbage out.)

In the classification of veins in Table 43, the prefixes proto-,meso-, and apo- have been adopted from Vassoevich et al.'s works (e.g., 1969, 1973) (see also Tissot/Welte, 1978, p. 71), who also used "hypergenetic" for supergenesis after tectonism and uplift. Thus, hypergenesis is equivalent to Choquette/Pray's (1970) "telogenesis" in Fig. 12.

TABLE 43

Types of vein and vein-like ores[1,2,3] (Wolf, 1974, unpublished)

Syndepositional-prediagenetic veins[3]
1.   Synepigenetic veins with material filling syndepositionally formed openings (but rare in occurrence?)

Diagenetic veins in sedimentary and/or volcanic rocks
2.   Proto-diagenetic[6] ⎫   ⎧ (= early diagenetic)
3.   Meso-diagenetic   ⎬   7   ⎨ (= intermediate diagenetic)
4.   Apo-diagenetic   ⎭   ⎩ (= late diagenetic)

Catagenetic veins
5.   Proto-catagenetic ⎫
6.   Meso-catagenetic   ⎬   "epigenetic"[1,4]
7.   Apo-catagenetic   ⎭

Metamorphic, etc. veins
8.   Metamorphic
9.   Telogenetic (= hypergenetic = supergenetic; some variety only)
[10. Pedogenetic (?)[5] (directly related to soil-forming processes)]

---

[1] Veins are usually lumped together as being of "epigenetic" origin, but a classification is required — if not the above, then some other scheme.

[2] Karstification and its features ought to be similarly classified; see Tables 41 and 42.

[3] The present scheme is based on the time when the opening or fracture was formed — infilling may occur soon afterwards, or much later.

[4] In this context, either catagenetic or epigenetic can be used (but the terms must be defined!), although the former is preferred.

[5] Telogenetic may be either synonymous or transitional, depending on the boundary drawn when defining the two terms.

[6] Proto-, meso-, apo- are from Vassoevich (1969, 1974) (see also Tissot/Welte, 1978, p. 71); cf. Figs. 13 and Table 45.

TABLE 44

General relationship of the process of compaction to diagenesis and veins (modified and expanded after Wolf, 1976, table 3-VI, p. 84)

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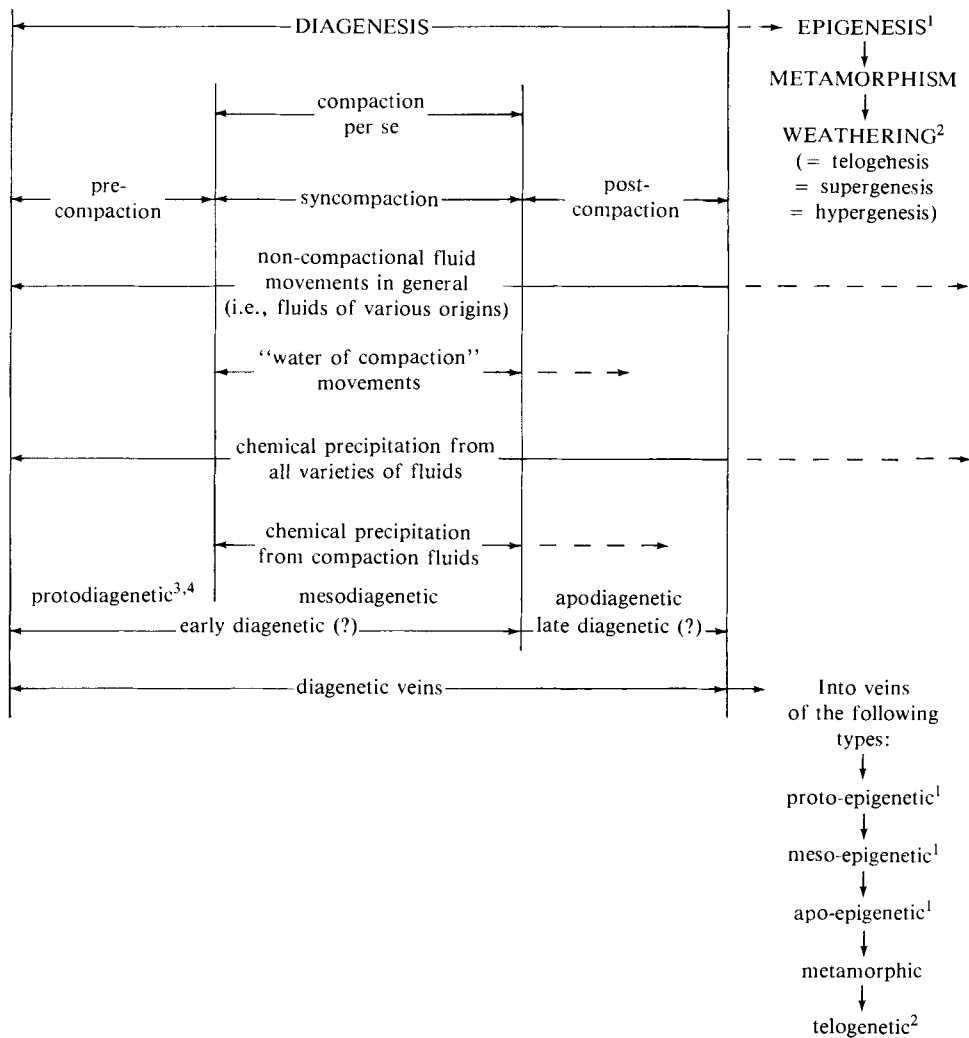
[1] Epigenetic can be replaced by the synonym catagenetic.

[2] Weathering, as used here, is equivalent to telo-, super- and hypergenesis — see the Glossary for definitions. In the present context, at least, they appear to be synonymous, although supergenesis comprises processes other than telo- and hypergenesis. Weathering can be either penecontemporaneous (more-or-less at the time when the rock is formed) or post-tectonism-uplift (i.e., after the rock subsided and was tectonized and uplifted).

[3] These three prefixes are from Vassoevich (1969, 1974) (see also Tissot/Welte, 1978).

[4] Although pre-, syn- and post-cementation is shown here as correlative to proto-, meso- and epo-diagenesis, other researchers may wish to rearrange this scheme to suit their particular requirements.

Table 44 is another example (expanded from Wolf, 1976, p. 84) of relating various genetic concepts and entities with each other, namely, pre-, syn- and post-compaction with diagenesis.

This leads us to the criteria or guides of dividing the petrologic/petrogenetic sequence, continuum or spectrum. It is easy to say, after a bit of arm-chair geology, that the continuum A to B will be divided into several stages, phases or episodes; but where exactly are the boundaries to be placed and based on what observable (hopefully, measurable, quantifiable) entities, criteria or guides? And are the stages to be equal in intensity, extent, size or length; and are each of the divisions to be founded on the same criteria or are different ones to be used? So far, these queries have not been answered in a plausible and satisfactory manner. The metamorphic petrologists have done an excellent job in dividing and classifying the low- to high-grade altered rock facies (although many problems remain); except perhaps at the upper end where a transition into *very low*-grade sedimentary-cum-burial metamorphically affected deposits by incipient or embryonic modifications (cf. the "greywacke problem") occurs. At this extreme incipient end of the spectrum of alteration, no definite boundary has been established as yet. For example, the classical greywackes' matrices range from depositional through diagenetic to burial metamorphic in origin, comprising a variety of clays, zeolites, chlorites, etc. — but it remained a "sedimentary" rock to the sedimentologists. Conversely, the bedded

Main stages of evolution			Vitrinite reflectance	LOM Hood & al. (1975)	Coal				
This book	Vassoevich (1969,1974)	Main HC generated			Rank USA	Int.hdbk coal petr. (1971)	Rank Germany	BTU ×10⁻³	% VM
	Diagenesis			0	Peat	Peat	Peat		
Diagenesis	Protocatagenesis	Methane		2 4 6	Lignite Sub bituminous C B	Brown coal	Braun-kohle	8 9 10	
Rₒ~0.5			0.5	8	A High C volatile B bituminous A			11 12 13 14	(45) (40)
Catagenesis	Mesocatagenesis	Oil	1.0 1.5	10 12	Med. vol. bit. Low vol. bit.		Stein-kohle	15	(35) 30 25 20
Rₒ~2		Wet gas	2.0			Hard coal			15
Metagenesis	Apocatagenesis	Methane	2.5 3.0 3.5 4.0	14 16 18	Semi-anthracite Anthracite		Anth.		10 5
Rₒ~4							Meto-Anth.		
Metamorphism				20	Meta-anth.				

Fig. 13. Main stages of evolution of organic matter. (See Tissot/Welte, 1978, p. 71, for original references.)

rocks in Precambrian terranes are "unmetamorphosed" to many geologists in spite of their low-grade to medium-grade metamorphic alterations[1]. A solution to this problem, however, is in the offing, at least to those who are doing more detailed studies. The data come from several "soft-rock" disciplines. The evolution of organic matter (coal and hydrocarbons) during the development of a basin may well be applicable to the study of sediment – volcanic rock-hosted ore deposits of Phanerozoic age. (Admittedly, some of this is outside the concern of the economic geologist's daily routine exploration work.)

Tissot/Welte (1978) provided a superb summary from the oil-exploration point-of-view. The main stages of evolution of methane – oil – wet gas – methane, the vitrinite reflectance, and the coal rank (peat – bituminous coal – anthracite – meta-anthracite – graphite) are an index to the lithologic changes. As Figs. 13 – 15 indicate, these compositional alterations allow a rough division into diagenesis (no
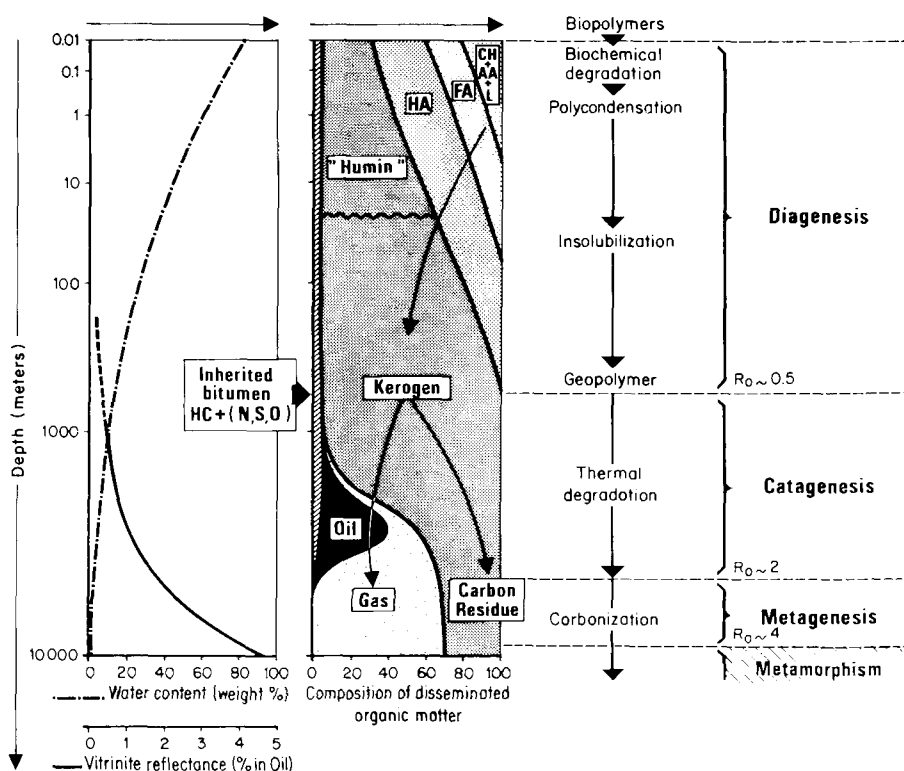
Fig. 14. General scheme of evolution of organic matter, from freshly deposited sediment to the metamorphic zone. CH = carbohydrates; AA = amino acids; FA = fulvic acids; HA = humic acids; L = lipids; HC = hydrocarbons; N,S,O = N,S,O compounds (non-hydrocarbons). (After Tissot/Welte, 1978, p. 70.)

[1] But this is merely a nomenclatural neglect, not a petrologic problem.
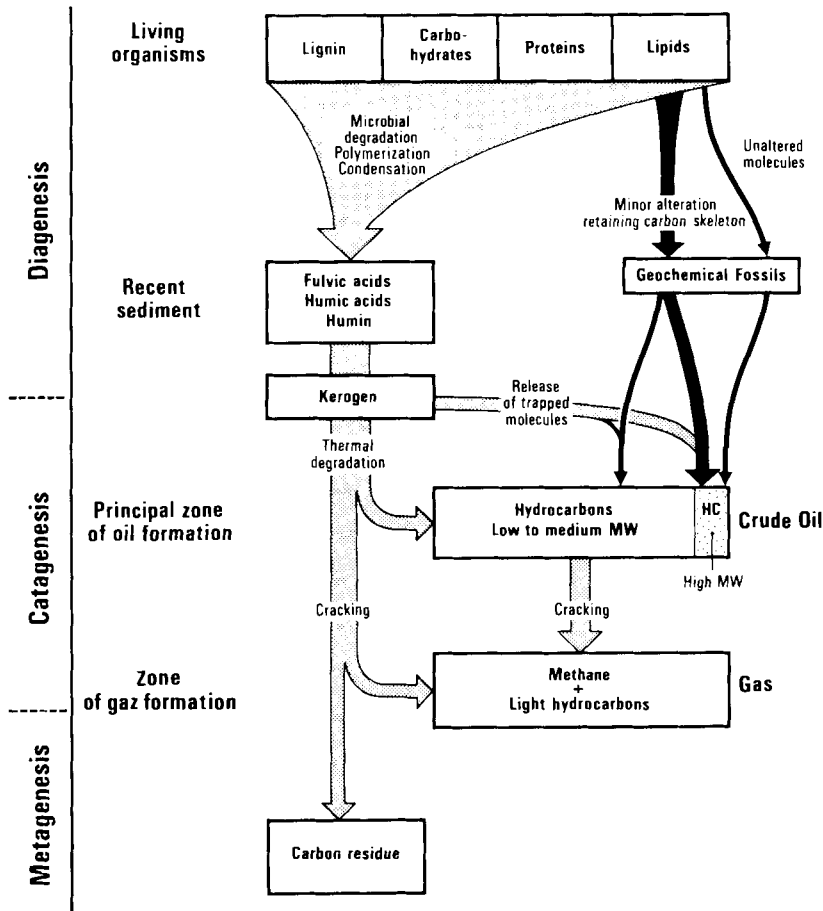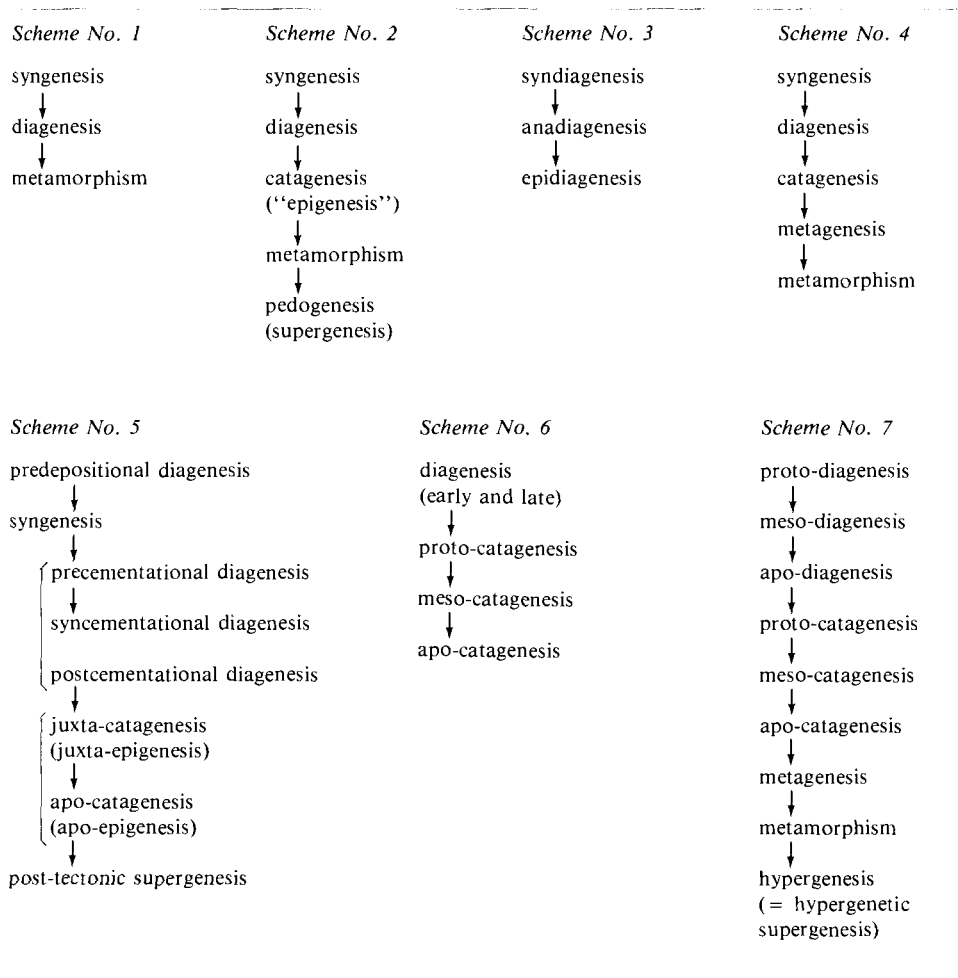
Fig. 15. Sources of hydrocarbons in geological situations, with regard to the evolution of organic matter. Geochemical fossils represent a first source of hydrocarbons in the subsurface (black solid arrows). Degradation of kerogen represents a second source of hydrocarbons (grey dotted arrows). (After Tissot/Welte, 1978, p. 93.)

doubt late diagenesis), catagenesis, metagenesis, and metamorphism. It is only a beginning, but eventually the criteria based on organic/carbonaceous matter will be supported and/or correlated with other guides, namely, by textural, mineralogical (clays using an X-ray index system, zeolites, chlorites, etc.), geochemical data (which is already being done to a certain degree). Here, too, comparative work on diagenetic, catagenetic, burial – metamorphic, and surface plus subsurface hydrothermal alterations are to be undertaken in the search for discriminatory guides.

Having deliberated on many aspects of the continuum syngenesis-to-metamorphism, Table 45 offers finally nine schemes from which the reader can choose the one or several that suit his purposes. All begin with either syngenesis or

TABLE 45

Variations of petrologic/petrogenetic sequential schemes (Wolf, 1982, unpublished)[1]

Scheme No. 1	Scheme No. 2	Scheme No. 3	Scheme No. 4
syngenesis	syngenesis	syndiagenesis	syngenesis
↓	↓	↓	↓
diagenesis	diagenesis	anadiagenesis	diagenesis
↓	↓	↓	↓
metamorphism	catagenesis ("epigenesis")	epidiagenesis	catagenesis
	↓		↓
	metamorphism		metagenesis
	↓		↓
	pedogenesis (supergenesis)		metamorphism

Scheme No. 5	Scheme No. 6	Scheme No. 7
predepositional diagenesis	diagenesis (early and late)	proto-diagenesis
↓	↓	↓
syngenesis	proto-catagenesis	meso-diagenesis
↓	↓	↓
⌠precementational diagenesis	meso-catagenesis	apo-diagenesis
↓	↓	↓
syncementational diagenesis	apo-catagenesis	proto-catagenesis
		↓
postcementational diagenesis		meso-catagenesis
↓		↓
⌠juxta-catagenesis (juxta-epigenesis)		apo-catagenesis
↓		↓
apo-catagenesis (apo-epigenesis)		metagenesis
↓		↓
post-tectonic supergenesis		metamorphism
		↓
		hypergenesis (= hypergenetic supergenesis)

Explanation (the numbers correspond to the Scheme numbers above:
(1) Many publications use this simplistic division which still serves its purpose during generalized, less precise discussions.
(2) This scheme is also to be found in numerous studies. It is similar to No. 1, except that catagenesis (synonymous with "epigenesis", but only in the present context) and pedogenesis have been added. Insofar as ore petrologists have used "epigenesis" in another sense, it is advisable to *redefine* the definitions-cum-explanations in this section. The same applies to pedogenesis/supergenesis and related terms.
(3) This scheme is from Fairbridge (1967), which is not recommended for detailed studies, although it is quite useful for generalized deliberations (and then the terms must be unequivocally defined). The prefix "epi-" is reminiscent of "epigenesis" or "epigenetic", so that the question arises as to the meaning and applicability of combining it with diagenesis to form "epidiagenesis" in the *narrow sense* employed by Fairbridge. "Epidiagenesis" is better used in context of a broader scheme of "epigenesis". Fairbridge's epidiagenesis may be covered by hypergenesis/telogenesis in Schemes 7–9.

TABLE 45 (continued)

Scheme No. 8		Scheme No. 9

Scheme No. 8

pre-depositional diagenesis
↓
syngenetic   "fully open system"
↓
early diagenetic
↓
late diagenetic   "partially open system"
↓
early catagenetic   "slightly open system"
↓
late catagenetic
↓
metamorphism   "closed system"
↓
hypergenesis (= telogenetic supergenesis)   "reopened system"

Scheme No. 9

pre-depositional diagenesis
↓
syngenesis (including hydrothermal exhalative processes, alterations, etc.)
↓
pre-cementation diagenesis
↓
syn-cementation diagenesis
↓
post-cementation diagenesis
↓
proto-catagenesis
↓
meso-catagenesis
↓
apo-catagenesis
↓
metamorphism
↓
hypergenesis (= telogenetic supergenesis)

(4) This sequence is from Tissot/Welte (1978, p. 71) who have adopted the terminology of Vassoevich in an abbreviated form − see Schemes 7 − 9. Note the *two* stages in-between diagenesis and metamorphism, in contrast to *one* in Scheme 2.

(5) Scheme 5 is from Wolf's (1963, 1965, 1981) works (see also Wolf/Conolly, 1965, and Chilingar et al., 1967, 1979), commencing with sedimentary petrology and expanding into ore genesis. This sequential scheme is only an example or "model" which can be modified to suit one's purposes, because it was applied to open-textured rocks (i.e., to those with numerous types of open spaces that were filled by several generations of internal-mechanical and chemical precipitates). Diagenesis was divisible into predepositional (see Wolf's various publications; this term was later adopted by Choquette/Pray, 1970), and pre-, syn- and post-cementational diagenetic phases, processes and products. (For predepositional, see Scheme 9.)

(6) Vassoevich (1969, 1974) presented the four-fold division in Scheme 6 that might be acceptable to some investigators by adding syngenesis and metamorphism at both extremities.

(7) Earlier, Vassoevich (1962; see table 11 in Dunoyer de Segonzac, 1968) employed the same prefixes to both diagenesis and catagenesis, thus obtaining seven divisions between syngenesis and metamorphism. If this number of stages can be identified during an investigation, this terminology is recommended; however, see Schemes 8 and 9 as alternatives.

(8) In contrast to Scheme 7, this one is somewhat simpler.

(9) This scheme offers an alternative to Schemes 7 and 8. Any of the divisions or terms in the last three sequences can be combined or intermixed to serve specific purposes and preferences. Certain researchers may especially like to replace the "-cementation diagenesis" by either "early" and "late" or by "proto-", "meso-" and "apo-diagenesis". Note that "predepositional diagenesis", as used by Wolf (1963, and in numerous publications thereafter) and by Choquette/Pray (1970), is applied to that diagenesis that can be deduced from features in lithic fragments, i.e., diagenetic features in larger rock fragments eroded from an older terrigenous or carbonate source.

the predepositional phase. From then on, each scheme is different — some are simple, others very detailed. Having read the text, this table ought to be self-explanatory.

To conclude this section, two examples representing the petrologic sequence as outlined above are examined here (Tables 46 and 47). The first one is a hypothetical situation where syngenetically accumulated clays with adsorbed metals are being desorbed with a consequent release or diagenetic (re)mobilization of the metals to first form disseminations as they become precipitated as part of a primary disseminated organic matter. Subsequent diagenesis may again (re)mobilize chemical elements (both metals and non-metals) to be precipitated as cements, nodules and thin lenses or laminae along bedding planes that offered high permeability. Late-stage diagenesis, catagenesis and/or burial metamorphism may give rise to a further remobilization of the metals, resulting in their concentration in veins. During high-grade metamorphism, all these features can be recrystallized. Table 47 again is self-explanatory.

A final word: always keep in mind that the choice of a descriptive (e.g., petrographic) and a genetic/interpretive (e.g., petrologic, petrogenetic, environmental-reconstructive) classification may determine the methodology and general philosophical approach one chooses and, thus, this selectivity controls the success of every study right from the beginning. The type of classification scheme adopted, for example, influences the *initial basic questions* being asked that, in turn, may direct the course of investigation. The converse is likewise true.

Like the descriptive information obtained from different natural systems, for example, so also should the genetic/interpretive data and concepts be compared and contrasted. This means that certain methodological aspects commonly "conveniently" ignored must be high-lighted, e.g., assumptions made, limitations involved,

TABLE 46

Syngenetic, diagenetic, and metamorphic processes in sedimentary ore genesis (the results can range from disseminations and intergranular cements to nodules, beds, veins, and coarsely recrystallized ore-mineral products) (Wolf, 1976, table 5-VII, p. 568)
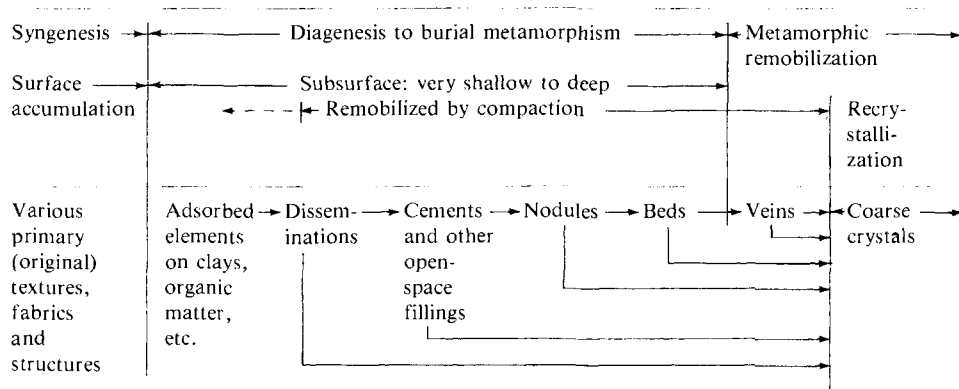
TABLE 47

Example of applying the petrologic/petrogenetic sequential scheme to the study of a stratiform ore deposit (Wolf, 1982, unpublished)

1. *Syngenesis:* Accumulation of (a) epiclastic, (b) pyroclastic, and (c) chemical precipitation of exhalative – sedimentary rocks (e.g., silica gel and microscopic Fe-oxide)

2. *Pre-cementation diagenesis:* (a) Hydrothermal – exhalative fluids descend into epiclastic and pyroclastic deposits and alter the least stable mineral and rock fragments to a chlorite – sericite – etc. assemblage; (b) some mechanical reworking by periodic turbulence and by organisms (burrowers – where normal marine conditions prevail); (c) establishment of local reducing conditions within specific layers due to the presence of organic matter and bacteria, whereas oxidization milieu is maintained elsewhere; (d) crystallization/recrystallization of silica and Fe-oxide

3. *Syn-cementation diagenesis:* (a) Cementation by non-ore mineral (e.g., aragonite and calcite) occurring in certain epiclastic rocks, especially in nearshore environment where evaporation of interstitial fluids is possible; (b) leaching – dissolution – mobilization of metals from volcanic clasts (especially during divitrification) into saline solutions, which move (during compaction!) into reducing porous epi- and pyroclastic rocks where Cu-sulfide minerals are bacterially precipitated

4. *Post-cementation diagenesis:* (a) The aragonitic needle-like cement and some of the gangue minerals of the ore assemblage in open spaces are recrystallized. (b) A second-generation cementation fills the last pores. (c) Mechanical reworking of a fairly thick stratigraphic section of a pyroclastic rock-hosted sulfide deposit produced an intra-environmental breccia; the fragments were transported to produce a penecontemporaneous ore-rich breccia due to reworking

5. *Proto-catagenesis:* (a) The above-described intra-environmental breccia, comprising Cu-sulfide cementing pyroclastic fragments (the fragments' outer fracture boundaries neatly cut across the sulfide open-space-filling cement), have undergone cementation by a new generation of Cu-sulfide minerals due to the ascending passage of hydrothermal solutions. This is a second-stage sulfide cementation of the intra-breccia fragments by ascending fluids, in contrast to the earlier syn-cementation – diagenetic sulfide cement of the syngenetically accumulated pyroclastic grains by descending solutions (A complex description for a complex natural setting!)

6. *Meso-catagenesis and apo-catagenesis:* (a) No record is left in the hydrothermally affected organic-matter-poor pyroclastics, but evidence is present in those time-equivalent epiclastic and pyroclastic rocks that are very "carbonaceous" (see Tissot/Welte, 1978, for various procedures to determine degree of maturity produced during burial). (b) Some tectonic features, e.g., fracturing and healing of ore and gangue minerals

7. *Metamorphism:* (a) Pervasive low-grade metamorphic mineral assemblage(s) in both epi- and pyroclastic rocks. A vertical alteration sequence from the shallow to the deeper parts of the basin is recognizable in detailed investigations. (b) Remobilization – reprecipitation of ore minerals into dilation zones is decipherable

8. *Telogenetic supergenesis (= hypergenesis):* (a) Those parts of the ore-bearing tectonized, uplifted and exposed units that have undergone weathering are marked by a gossan, underlain by Cu-oxide minerals

contradictions and counter-criteria recognized, advantages and disadvantages established, range of applicability (e.g., as controlled by scale), and the power-of-resolution or interpretability or recognizability, all determining the grade of reliability, plausibility and objectivity of the final results. The senior author's preferred methodological nostrum is to present "the full picture".

Part II – Parameters of diagenesis (i.e. that must be considered)

"Human endeavours are fragmentary, consequently, the sciences are segmented."
K.H. Wolf, Sydney, N.S.W., February 8, 1983

"An 'Informational Geological Cosmos' is our ultimate aim, but at present it does not exist inasmuch as human studies, including our scientific disciplines with their separate concepts and methodologies, are still unstructured."
K.H. Wolf, January 1/February 8, 1983

("Cosmos" refers to the world or universe as an ordered system; order, harmony or a harmonious system.)

In this section a plethora of variables are discussed as based on recent references that serve as exemplars[1]. Here lies a real challenge to our "computer playmates": store parameter-by-parameter (many more than used below, of course) and any other significant information (including pertinent diagrams and tables) that can all be retrieved "by the push of a button"! (Note that the old-fashioned hand-written, human-mind-produced data still constitute the first phase prior to computerizing the material.)

To provide a quick overview, the following is a list of the preferentially selected variables involved in ore diagenesis:

(1)	Adsorption (sorption, desorption)	(18)	Color
(2)	Advection	(19)	Compaction
(3)	Age (dating)	(20)	Complexing – complexation – complexes
(4)	Aging	(21)	Concentration
(5)	Algae, algal mats	(22)	Concretions – nodules
(6)	Association – assemblages (minerals)	(23)	Copper
(7)	Bacteria	(24)	Coprecipitation
(8)	Barriers	(25)	Crystallography
(9)	Biological factors	(26)	Cycles
(10)	Carbonates	(27)	Dating (ages)
(11)	Cementation	(28)	Depth
(12)	Chromium	(29)	Differentiation – fractionation – partitioning
(13)	Clay minerals	(30)	Diffusion – dispersion
(14)	Climate	(31)	Distribution (elemental, etc.)
(15)	Coagulation	(32)	Dolomitization – dolomite – dedolomitization
(16)	Coated grains		
(17)	Colloids		

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[1] The "encyclopedic" format chosen for Part II may appear monotonous, but the adherence to the selected sequence of "author(s) – year(s) of publication – paraphrased data – evaluative comments ± suggestions" seems preferable for the present scientific compilation in contrast to a prosaic style that varies occasionally merely for literary and aesthetic appeal.

(33) Eh-controls (oxidation, reduction)
(34) Electrodiagenesis
(35) Energy
(36) Entropy
(37) Environments (depositional)
(38) Epigenesis
(39) Estuary environments
(40) Evaporites – evaporation
(41) Evolution – trends
(42) Facies
(43) Fjord environments
(44) Fluids (solutions)
(45) Fluid inclusions
(46) Fluorite
(47) Fracturing
(48) Gases
(49) General aspects
(50) Glauconite
(51) Gold
(52) Heat
(53) Historical development
(54) Hydrology (fluid dynamics)
(55) Hydrothermal
(56) Interstitial fluids
(57) Ion-exchange
(58) Ion potential
(59) Iron
(60) Isotopes
(61) Karst – karstification
(62) Kupferschiefer-type deposits
(63) Kuroko-type deposits
(64) Lake/lacustrine environments
(65) Leaching
(66) Magnesite
(67) Magnetism
(68) Manganese
(69) Mass balance
(70) Maturation (of sedimentary basins)
(71) Metamorphism (e.g. burial, catagenesis)
(72) Mississippi Valley-type deposits
(73) Mixing (of fluids)
(74) Mobility (elemental)
(75) Multi-factorial
(76) Multi-stage
(77) Nucleation – nuclei
(78) Oil – ore relationships
(79) Organic matter

(80) Osmosis
(81) Paragenesis
(82) pH
(83) Phosphates – phosphorites
(84) Photochemistry
(85) Pollution
(86) Porosity – permeability
(87) Precipitation
(88) Pressure
(89) Pyrite
(90) Rare earth elements (REE)
(91) Recrystallization
(92) Red-beds
(93) Reducing (anoxic, euxinic, stagnant, black shales)
(94) Remobilization – mobilization
(95) Replacement
(96) Reworking (chemical, mechanical)
(97) River environments
(98) Salinity
(99) Sandstones
(100) Silicification – silica – chert
(101) Silver
(102) Solubility
(103) Solutions
(104) Sources
(105) Specialization (e.g. chemical)
(106) Structures
(107) Suspensate (-type diagenesis)
(108) Tectonism
(109) Temperature
(110) Textures – microstructures – fabrics
(111) Thermodynamics
(112) Thixotropy
(113) Time – rate – residence time (related to processes, etc.)
(114) Transportation (e.g. elemental)
(115) Traps (natural, man-made experimental)
(116) Unconformities
(117) Uniformitarianism
(118) Upwelling
(119) Uranium
(120) Volcanic – exhalative processes (hydrothermal – diagenesis)
(121) Water (including ocean seawater)
(122) Weathering – supergenesis
(123) Zoning

ADSORPTION (SORPTION, DESORPTION)

Heydemann (1959) demonstrated the adsorption of Cu by various clay minerals, quartz and calcite at different pH-values and concentrations. The clays and quartz adsorb Cu according to the Freundlich adsorption isotherm – but a chemical reac-

tion takes place with calcite. The influence of pH and concentration is most pronounced with kaolinite, and only small with montmorillonite. The adsorption capacity, however, of the clays is in the order of (from low to high): kaolinite, illite, montmorillonite. The significance of such adsorption is discussed in terms of geochemical processes. For example, considering the low Cu-content of seawater, lakes, etc. $(1-15 \gamma$ Cu $1^{-1})$, the question is how one can explain the vast amount of Cu in the Kupferschiefer deposits? The clays of shallow seas contain 45 g Cu t^{-1}, deep-sea clays of the Atlantic 120 g Cu t^{-1}, and those of the Pacific 320 g Cu t^{-1}. Adsorption can explain this concentration. Insofar as it has often been suggested that the Cu in the Permian Kupferschiefer (average 3% Cu) was precipitated by H_2S from seawater, the experiments by Heydemann indicate that adsorption may have played a role as well. The Kupferschiefer consists of illite, kaolinite, calcite and quartz, among others, so that its 3% Cu average value cannot be explained by mere adsorption of Cu on these minerals. However, the syngenetically adsorbed Cu (and other metals, see Jung/Knitzschke, 1976) was affected by the bacterial (?) decomposition of the sediment-associated organic matter. The produced H_2S reacted with the remobilized Cu during early diagenesis to form the sulfide minerals. (See also Correns, 1924, for Cu – Pb adsorption experiments applied to ore genesis interpretations.)

Note: (a) What are the p: :.se mechanisms that caused the upgrading or concentrating of the syngenetic lower-grade copper during the diagenetic stage? (b) To what extent is the *chemical* reaction of Cu with calcite significant in the source rock question, in contrast to the adsorption of Cu on clays and quartz? It has been found during some experiments that biological, not physicochemical, processes are particularly effective in concentrating (coprecipitating?) metals with carbonates. Are *both* organic and chemically formed limestones equally capable of concentrating and releasing metals during diagenesis – catagenesis? Are adsorbed metals on clays greater in volume and easier to desorb into interstitial fluids in contrast to carbonates, for example? (c) The application of laboratory metal-adsorption data to ancient environments is difficult to impossible insofar as clays, etc., are diagenetically and metamorphically altered and, consequently, the *original* composition cannot be determined.

Temple/LeRoux (1964): Clays and ferric hydroxide in "freshwater" with adsorbed Fe^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} were exposed to a saline system containing active sulfate-reducing bacteria. The metals were desorbed and precipitated as sulfides. The adsorbed metals were displaced presumably by Na^+ in amounts which are characteristic of the metal ion and adsorbent. The percentage recovery of adsorbed metal as sulfide was greatest for Cu and Zn, and least for Pb. Adsorption followed by desorption near a zone of sulfide ions can act as a concentrating and separating mechanism during diagenesis.

Note: (a) Weiss/Amstutz (1966) carried such experiments further in that they used not a static hydrologic system but a dynamic one. Solutions moved through the system and the precipitated sulfides exhibited microstructures that, when fully understood, will serve as indicators of flow directions, rate, force, etc. (b) It is also necessary to determine in the laboratory and by natural observations the influences

of salinity, temperature, pressure, rate of flow (time variable), etc. — en toto all factors related to maturation (late diagenetic, catagenetic, and burial metamorphic) in sedimentary basins.

Chester (1965) demonstrated an increase of adsorbed Zn and Co on illite with an increase of the metals in solution and an increase in temperature of seawater. O'Connor/Kester (1975) studied the Cu – Co adsorption under freshwater and marine conditions. What are the similarities and differences?

Muto et al. (1965), Langmuir (1978), Giblin (1980), and Eupene (1980) provided data on the adsorption and desorption of U on clays and organic matter, and on the U-content and U-concentration of solutions in contact with it (Fig. 16). It is proposed that the U can be released later into fluids (diagenetic, compactional, and metamorphic) for reconcentration into economic ore deposits.

Bourg/Filby (1974), Bittell/Miller (1974), Farrah et al. (1980), Wold/Pickering (1981), and Borovec (1981), plus many others discussed metal sorption (adsorption and desorption) on clays. What are the differences under oxidizing and reducing environments?

Weiss/Amstutz (1966) and Love (1967) discussed desorption of metals from their host into interstitial fluids to be reconcentrated elsewhere as sulfide minerals under reducing conditions. Much more experimental data, however, is needed on desorption during early and late diagenetic milieus as well as during low-grade (catagenesis, burial metamorphism) and high-grade metamorphic processes.

Millot (1970) described the results of numerous research jobs done on the adsorption-absorption of metal ions on/into clay minerals: Mg, Ni, Fe^{2+}, Fe^{3+}, Zn, Co, and Mn^{2+}, among others, can enter the octahedral sheet of clays at low
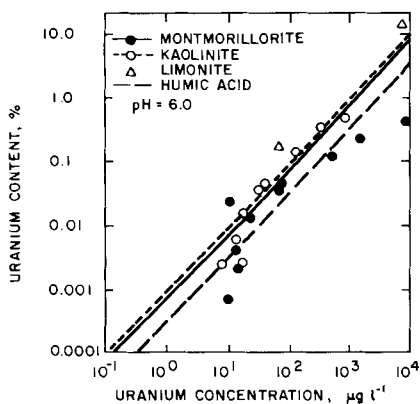
Fig. 16. Relation between adsorbed uranium content and uranium concentration of solution in contact with it. (After Eupene, 1980.)

temperatures. In particular the pH (from 6 to > 9) and the Al/Zn ratio is important in determining the types of minerals as depicted in Fig. 17 (after Esquevin, in Millot, 1970, table XIV, p. 339). In the sedimentology of clay-rich deposits, such data are valuable in determining the provenance (source area). In the study of diagenetic ores, the information makes a contribution to the understanding of metal sources – the metals being remobilized during diagenesis or metamorphism, for example.

Jenne (1968, 1977) treated trace-elemental sorption and concentration controls of soils. This is important for the understanding of the supply of metal on clays, organic matter, etc., to sedimentary milieus where diagenesis then takes over. Ehrlich et al. (1973) experimented on the bacteriology of Mn-nodules, demonstrating that Cu, Ni and Mn are adsorbed onto manganese nodules (Fig. 18).

Ludwig/Hare (1973) concluded that the relationship between Ca^{2+}- and Mg^{2+}-sorption depended on diagenesis and depth of burial. Similar studies, however, are needed on other elements.
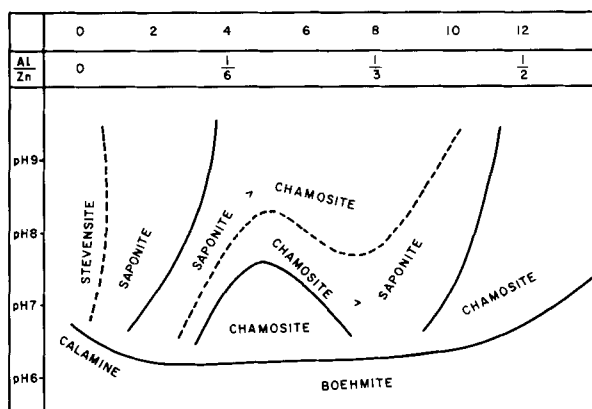
Fig. 17. Conditions of formation of zinciferous clay minerals. (After Esquevin, in Millot, 1970, p. 339.)
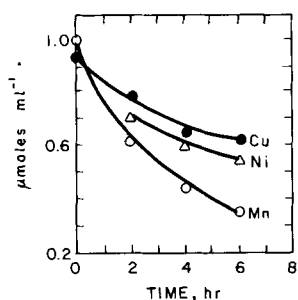
Fig. 18. Simultaneous adsorption of copper, nickel and manganese by a 1.43 g ferromanganese nodule fragment. (After Ehrlich et al., 1973.)

Appelo (1977) proposed that the chemistry of expelled compaction fluids was changed by "negative adsorption" due to preferential release of ions (see also Ion-exchange).

Altschuler (1980) offered a list (Table 48) of the trace elements concentrated in marine phosphorites relative to shale (the latter usually exhibits a higher enrichment factor of concentrated elements in contrast to other sediments, except organic matter).

TABLE 48

Concentrations of trace elements in marine phosphorites relative to shale (data in ppm) (after Altschuler, 1980)

	Average shale[1]	Average phosphorite	Enrichment factor[2]	Normal abundance	Depletion factor
Ag	0.07	2	Ag 30		
As	13	23		As	
B	100	16			B 6
Ba	580	350		Ba	
Be	3	2.6		Be	
Cd	0.3	18	Cd 60		
Co	19	7			Co 3
Cr	90	125		Cr	
Cu	45	75		Cu	
Ga	19	4			Ga 5
Hg (ppb)	400	55			Hg 7
La	40	147	La 4		
Li	66	5			Li 13
Mn	850	1230		Mn	
Mo	2.6	9	Mo 4		
Ni	68	53		Ni	
Pb	20	50	Pb 2		
Sc	13	11		Sc	
Se	0.6	4.6	Se 8		
Sn	6	3			Sn 2
Sr	300	750	Sr 2		
Ti	4600	640			Ti 7
U	3.7	120	U 30		
V	130	100		V	
Y	26	260	Y 10		
Yb	2.6	14	Yb 5		
Zn	95	195	Zn 2		
Zr	160	70			Zr 2

[1] From Turekian and Wedepohl (1961).

[2] An element is considered "enriched" if its abundance is at least twice that of shales, and "depleted" if its abundance is half or less. Abundances between these limits are classed as "normal", following Tooms et al. (1969).

Note: The precise processes and modes of occurrences (adsorbed – absorbed, crystallographic substitution, coprecipitated material, etc.) are not known in many cases. Some of the elements enriched or fractionated, such as Cd (60 times enriched; 18 ppm) and U (30 times enriched; 120 ppm), may be economically recovered eventually, possibly as a byproduct.

Nash et al. (1981) investigated the importance of organic matter serving as adsorbant – reductant agent in the origin of sandstone-hosted uranium deposits (see also Organic matter). Rashid (1974), Kernsdorff/Schnitzer (1980), and Freeman/Cheung (1981) reported on sorption of uranium on organic matter.

Baturin (1982) showed that the U-content gradually increases from unconsolidated to dense phoshatic concretions. The original phosphate gels sorb U-organic complexes from the interstitial waters. Subsequently, when the organic matter decays, the U enters into Ca-phosphate both in the form of an isomorphous substitution and sorptionally (Fig. 19). It has also been shown that there is a direct $P - Fe$ correlation (Table 49), in the absence of a $P - Ca$ correlation, due to the chemical sorption on the surfaces of iron hydroxide particles which either formed when the volcanic Fe^{2+} was oxidized, or by the formation of iron phosphate.

Yariv/Cross (1979), Van Olphen (1963a, b), Eitel (1975), among others, provided introductory and advanced concepts on the various sorption mechanisms, including those related to metallic ions.

Hildebrand/Blum (1974), James/McNaughton (1977), Tipping (1981), Balistrieri/Murray (1982b), Tipping/Cooke (1982), Putilina/Varentsov (1983), Chelishchev/
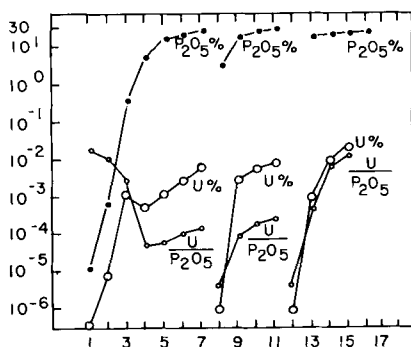
Fig. 19. Uranium in the course of Recent phosphorite formation (after Baturin, 1982). *1* = sea waters; *2* = interstitial waters; *3* = diatomaceous sediments in which phosphorite concretions are forming; *4* = phosphatized diatomaceous ooze; *5 – 7* = phosphorite concretions (*5* = unconsolidated; *6* = compacted; *7* = dense); *8 – 11* = coprolites (*8* = living marine organisms; *9* = unconsolidated, from the bottom; *10* and *11* = compacted and dense, from sediments); *12 – 15* = bones of fish and marine mammals (*12* = fresh; *13* = unfossilized, from sediments; *14* = slightly fossilized; *15* = fossilized).

Gribonova (1983), and Laxen (1984/5) have studied adsorption of metals on the following respective substances: clays, iron oxide, humic acids; inorganic minerals, iron oxides, goethite, manganese oxide, $Fe-Mn$ nodules, and Fe^{2+} oxide. Comparative-type adsorption/desorption experiments are required. (See also Kuaner et al., 1982, for additional references.)

Lyle et al. (1984) modeled the transport and release of transition elements during early diagenesis (Fig. 20).

TABLE 49

Deposition of phosphorus with volcanogenic iron in the East Pacific Rise (Berner, 1973; Fe, after Boström, 1970, in Baturin, 1982)

Rate of deposition of Fe (kg km^2 yr^{-1})	Area of zone (10^6 km^2)	Rate of deposition of P (10^4 t yr^{-1})
50 − 100	4	3 − 6
100 − 150	1.5	2 − 3
150 − 300	0.5	1 − 2
300 − 4000	1.5	10
total	7.5	16

Weight ratio P: Fe = 0.15 ± 0.05.
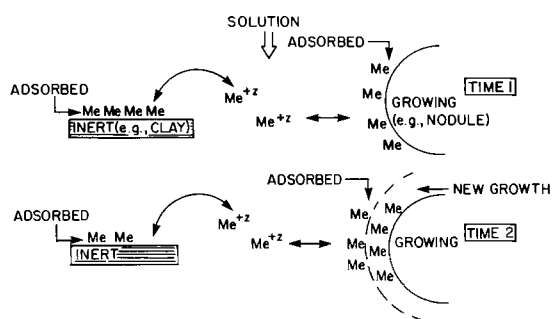
Fig. 20. Cartoon of the proposed model for transition metal transport to ferromanganese nodules by means of adsorption onto sediment grains. Metal concentration in porewaters are in equilibrium with metals sorbed onto sedimentary grains. The growth of a nodule depletes the sorbed pool of metals on its surface, resulting in transfer of metals out of porewater, and ultimately from inert or dissolving material. Bioturbation moves freshly sorbed material to the reaction sphere around the nodule. (After Lyle et al., 1984.)

ADVECTION

Sayles/Jenkins (1982), Burdige/Gieskes (1983), and Maris et al. (1984) investigated advection and related or associated processes and products, e.g., fluxing, element cycling, water – sediment interface mechanisms, redox reactions, pore-water profiles, micro-zoning, including diagenetic "hydrothermal upwelling" through sediments.

– See also Interstitial fluids.

AGE (DATING)

Van Moort (1973) discussed Ca-, Mg-, Fe^{2+}-contents and carbonate contents (dolomite, siderite, calcite) of Precambrian to Cainozoic shales, as a function of age and metamorphism. Such studies ought to be expanded to include ore hostrocks and source rocks in determining the syngenetic – diagenetic to metamorphic evolution through geologic time.

Sangster (1980) discussed the problem of correlating chronologically and by absolute-age concepts the syngenetic, exhalative, volcanic rock-hosted massive ores and the epigenetic, disseminated, carbonate-hosted deposits. Basically, there are two problems: (a) the correlation of the hostrocks; and (b) the correlation of the ore mineralization within and between ore types and ore districts. Similar problems exist in the correlation of syngenetic and diagenetic ores.

Page (1981) gave the depositional ages of base-metal concentrations by using the age of associated tuffs. How can late diagenesis and metamorphism change the *true* age to *apparent* age?

Bonhomme (1982) used dating methods as a stratigraphic tool by analyzing sedimentary rocks and their minerals. How effective are these methods in the study of paragenetic sequences of diagenesis, catagenesis, and low-grade to high-grade metamorphism?

Haszeldine et al. (1984) employed fluid-inclusion techniques to date diagenesis in a basin.

Kohler/Köster (1982) commented on the influence of depositional environments on radiometric ages. How did diagenesis affect these dates? Morton/Long (1980) demonstrated that the Rb – Sr ages of glauconites are short by 17% due to diagenetic/burial metamorphic recrystallization. How many other systems have been "mis-dated"? Halliday/Mitchell (1983) deliberated on the ages of clays which are associated with mineralization. What are the sampling and analytical procedures useful in discriminating between "primary" and "secondary" (e.g., diagenetically produced) ages?

Darby (1984) used trace elements in ilmenite to determine both the provenance and age of sandstones.

— See also Dating, and Isotopes.

AGING

Elderfield/Hem (1973) described crystallization of polymorphs on aging. Does diagenesis and catagenesis cause crystallization and recrystallization due to increase in pressure and temperature that resembles the changes purely based on aging? Studies of the aging of contemporary Mn-nodules may provide the answer (see, for example, Nedjatpoor et al., 1985).

Yariv/Cross (1979) made some general and specific comments on aging of minerals, which has some application in studying ore mineral textural evolution. For example, they provide data on aging of aqueous solutions of Al and precipitation of hydroxides in the origin of bauxites (pp. 167 – 168); and on aging and diagenesis of clay minerals and recrystallization of amorphous gels, which may control the uptake or release of metallic ions (pp. 325, 408 – 413). Eitel (1975, p. 553) also offers some comments -- but in general the concept of aging of minerals is a neglected petrologic phenomenon.

ALGAE, ALGAL MATS

Disnar (1981) and Disnar/Trichet (1981) studied the fixation of numerous metals on algal matter, whereas Dissanayake (1984/5) undertook a geochemical investigation of algal mats. Disnar/Trichet (1984) then examined the influence of divalent metal ions on the thermally induced evolution of algal mat-type organic matter. Note that during the past few years numerous researchers have suggested that algal mats were important collectors (traps?) of gold, for example, and upon its release contributed to the origin of the Witwatersrand-type deposits. Mann/Fyfe (1984) studied the selective uptake of Ba and U by algae.

Jones/Goodbody (1982) remarked on the geological significance of algae.

Gillan/Johns (1982) described diagenetic products indicative of past oceanic algal populations and diversity.

Estep (1984), among others, have reported on algae and bacteria from hydrothermal environments. These organisms/plants are present in volcanic – exhalative milieus on land as well as in the sea. What is their temperature/pressure range? Are those organisms or plants involved in low-T/P diagenesis different from the processes under higher-T/P environments (i.e., shallow versus deep-water conditions)? What are their sedimentary products? (An enormous amount of literature, especially on

bacterial processes, is now available. The above will merely wet the novice's appetite.)

— See also Bacteria, and Biological factors.

ASSOCIATION – ASSEMBLAGES OF MINERALS

Lydon et al. (1979) suggested that the textures, structures, mineral association and diagenetic features of barite and calcite were primary in sediments (part of a stratiform barite – sphalerite – galena deposit), precipitated from hydrothermal – exhalative solutions.

Shcherbakov (1979) investigated the distribution and association of chemical elements in geochemical provinces and ore deposits: e.g., he offered a geochemical classification of elements as to their "radial distribution" in the Earth's crust and surface/near-surface environments (see his models). Which associations are the result of primary versus secondary (including diagenetic) processes?
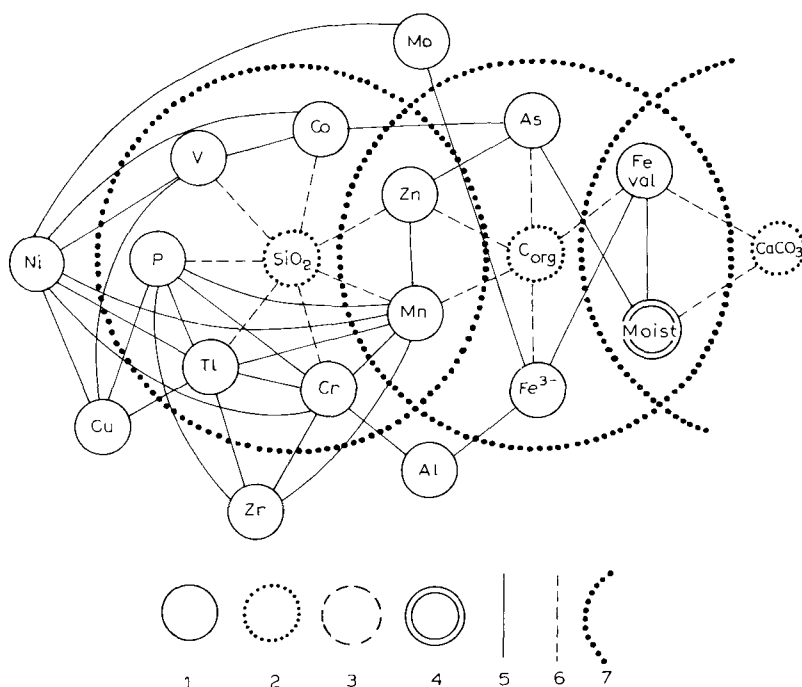
Fig. 21. Graph of correlations between chemical components for the entire profile. Components: 1 = terrigenous; 2 = biogenic; 3 = diagenetic; 4 = hydrous. Relationships: 5 = positive; 6 = negative; 7 = concentric boundaries. (After Devdariani/Volkov, 1980.)
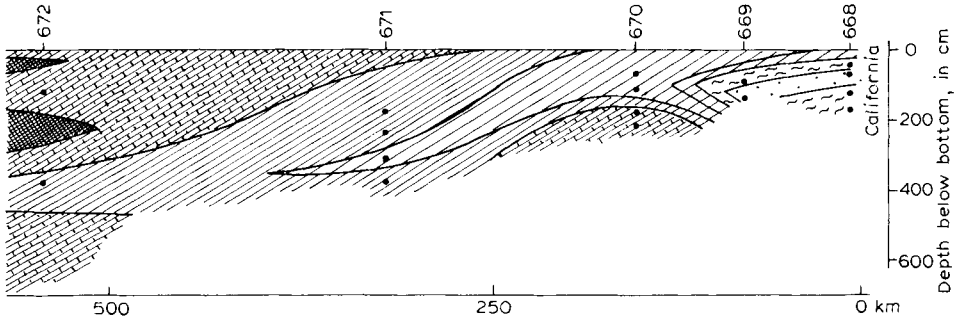
Fig. 22. Accumulation intensity relationship of terrigenous and authigenic material in the Californian section of the profile. Denser shading indicates a relative increase in intensity of accumulation of terrigenous material, whereas lighter shading indicates greater authigenic accumulation. (After Devdariani/Volkov, 1980.)
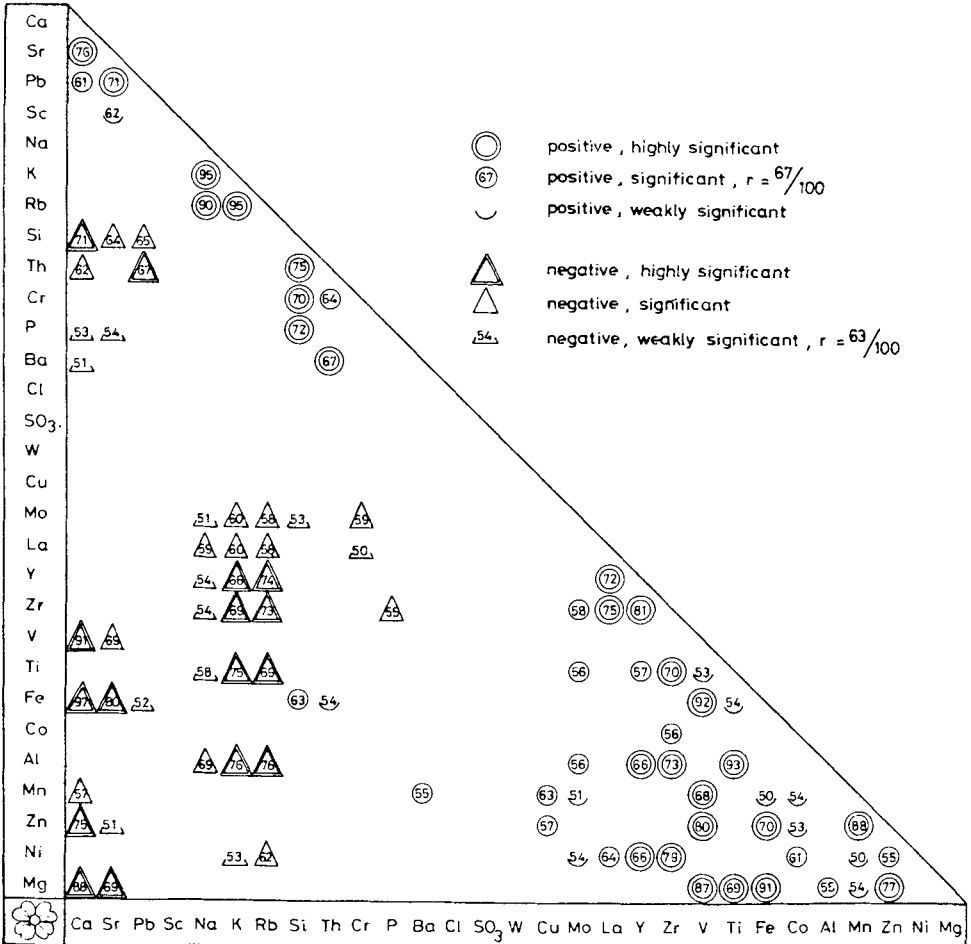
Fig. 23. Correlation matrix calculated from X-ray analyses of the sediment fraction < 63 μm from five sediment cores (20 samples). (After Marchig/Gundlach, 1982.)

Devdariani/Volkov (1980) produced correlation graphs of chemical components comprising terrigenous, biogenic, diagenetic and hydrous contributions (Fig. 21). They also outlined the "accumulation intensity relation" of terrigenous and authigenic material (Fig. 22), thus identifying the proportions of components from different sources, their degree of accumulation (= association) and, therefore, the regional distribution. This is a fine study of a multi-component, multi-factorial system.
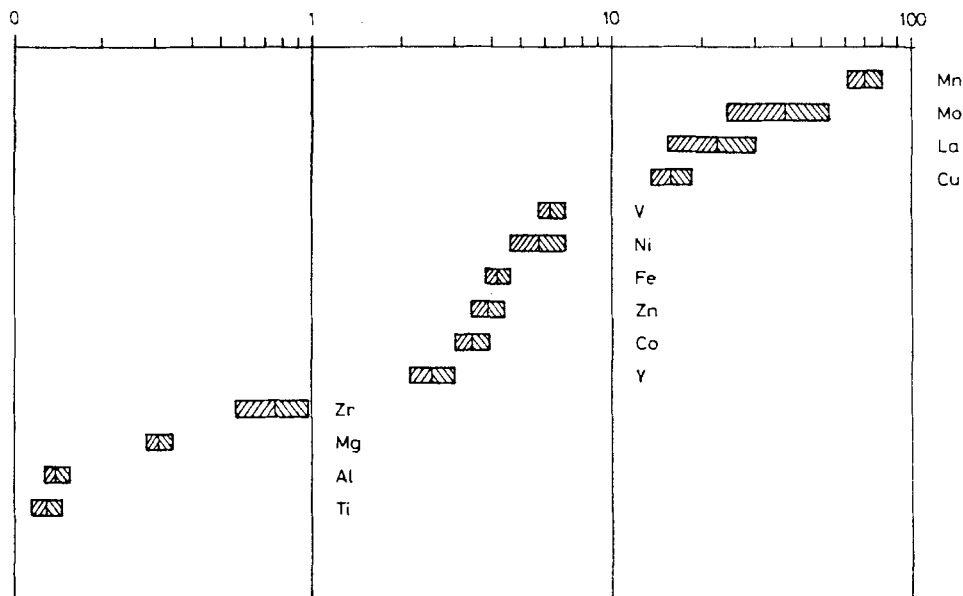
Fig. 24. Ratios of elements in hydrothermal precipitates to the content of the element in tholeiitic basalt. The vertical line in the middle of the hatched area shows the arithmetic average for the ratio, the hatched area shows the standard deviation. (After Marchig/Gundlach, 1982.)
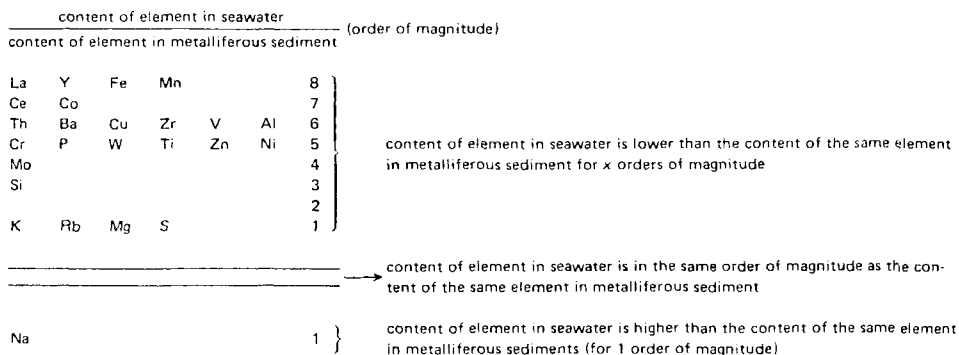
Fig. 25. Ratios of contents of elements in seawater to the content of the same elements in the hydrothermal precipitate. Only the order of magnitude of ratio is given. (After Marchig/Gundlach, 1982.)

Bloch (1981) demonstrated an antipathetic Mg – Mn relation in metalliferous sediments.

Marchig/Gundlach (1982) modeled and tabulated comparatively the trace-element associations of Fe-rich metalliferous oceanic rise sediments as a prototype of undifferentiated metal deposit on divergent plate boundaries (Figs. 23 – 26). Thus, both hydrothermal – exhalative and sedimentary systems were considered.

Millero (1985) studied the oxidation and ion interaction/association of metals in natural waters.

– See also Parageneses, and Textures.

BACTERIA

Ehrlich (1962, 1964, 1966) and Ehrlich et al. (1973): These are merely a few earlier studies of bacteria, e.g., on (1) mobilization/dissolution and precipitation/concentration of sulfur by sulfur-oxidizing and sulfate-reducing bacteria, respectively; (2) bacteriologically catalyzed reactions involving Cu_2S (chalcocite), for example; (3) oxidation of numerous minerals (e.g., arsenopyrite) and Fe-solubilization from arsenopyrite, solubilization of Cu and As, etc.; (4) bacterial processes involved in Mn-accretion to and Mn-release from oceanic nodules during enzymatic action; and (5) Fe-solubilization from limonite, goethite and hematite.

Rickard (1969): Five iron sulfide minerals were formed experimentally by a bacterium, namely, greigite, mackinawite, marcasite, pyrite and pyrrhotite (Fig. 27).
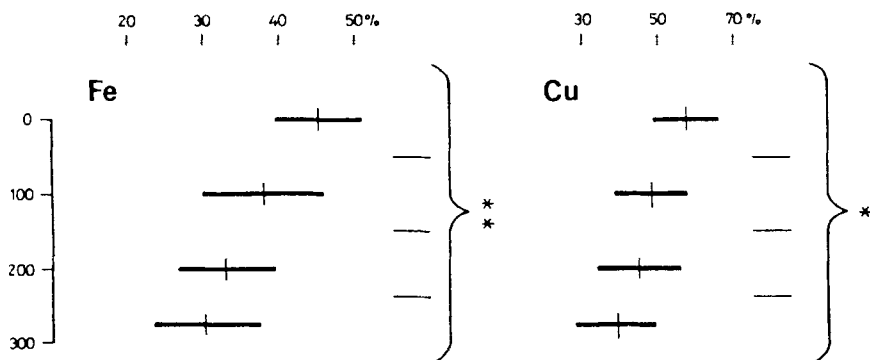
Fig. 26. Proportions of iron and copper which can be dissolved by reductive leaching. Averages for different depths in the sediment (in m). Average values (vertical lines) and standard deviations (horizontal lines) are shown. Dashes = the difference between neighboring average values is not significant; ⁺* = the difference between first and last average value is significant; * = the difference between first and last average value is weakly significant. (After Marchig/Gundlach, 1982.)

Fe^{2+}_{aq} (S^{2-}_n) PYRITE

(S^{2-}) (S^{2-}_n)

MACKINAWITE S^0 MARCASITE

(S^{2-}) equilibration

equilibration

GREIGITE

equilibration

PYRRHOTITE

(S^{2-})

$FeCO_3$ SMYTHITE   equilibration

———— abiogenic (S^{2-}) sulphide (S^{2-}_n) polysulphide
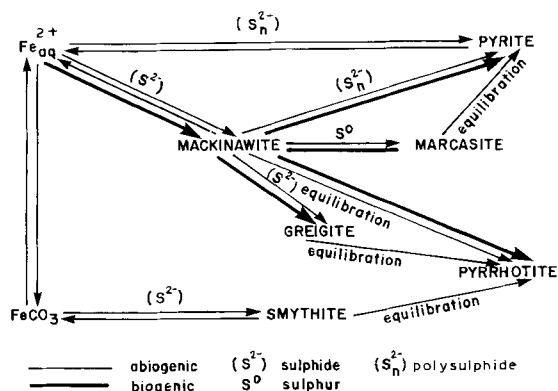———— biogenic S^0 sulphur

Fig. 27. Summary of the major iron sulphide interrelationships in aqueous solutions and their biogenic counterparts observed in this investigation (reactions involving ferric iron not included). (After Rickard, 1969).

TABLE 50

Categories of energy metabolism utilized by bacteria (after Rittenberg, 1969, table 5.3, p. 219)

Type of energy metabolism	Energy source	Source of reducing power	Example
A. Phototrophy			
1. Photolithotrophy	Light	H_2S	*Chromatium*
2. Photoorganotrophy	Light	Organic substrate	*Rhodospirillum*
B. Chemotrophy			
1. Chemolithotrophy	Inorganic substrate	Same as energy substrate	*Nitrosomonas*
2. Chemoorganotrophy	Organic substrate	Same as energy substrate	*Pseudomonas*
3. Mixotrophy	Both inorganic and organic	Same as energy substrate	*Hydrogenomonas*

TABLE 51

Carbon and energy sources for bacteria (after Rittenberg, 1969, table 5.2, p. 217)

Condition	Energy source	Carbon source	Example
1	Inorganic	CO_2	*Nitrosomonas*
2	Inorganic	Organic	*Desulfovibrio*
3	Inorganic	CO_2 + organic	*Thiobacillus*
4	Organic	CO_2	*P. oxalaticus*
5	Organic	Organic	*Pseudomonas*
6	Organic	CO_2 + organic	*Neisseria*
7	Mixotrophic	CO_2	?
8	Mixotrophic	Organic	*Hydrogenomonas*
9	Mixotrophic	CO_2 + organic	*Hydrogenomonas*

TABLE 52

Energy-yielding reactions employed by chemolithotrophic bacteria (after Rittenberg, 1969, table 5.7)

Inorganic energy substrate	Formal equation for reaction		Bacterium
NH_3	$NH_4^+ + \frac{3}{2}O_2$	$\rightarrow NO_2^- + H_2O + 2H^+$ $\Delta G^0 = -66$ kcal	*Nitrosomonas*
NO_2^-	$NO_2^- + \frac{1}{2}O_2$	$\rightarrow NO_3^-$ $\Delta G^0 = -17.5$ kcal	*Nitrobacter*
H_2	$H_2 + \frac{1}{2}O_2$	$\rightarrow H_2O$ $\Delta G^0 = -57$ kcal	*Hydrogenomonas*
S^0	$S^0 + \frac{3}{2}O_2 + H_2O$	$\rightarrow H_2SO_4$ $\Delta G^0 = -118$ kcal	*Thiobacillus*
Fe^{2+}	Fe^{2+}	$\rightarrow Fe^{3+} + e^-$ $\Delta G^0 = -11$ kcal	*Ferrobacillus*
CO	$CO + \frac{1}{2}O_2$	$\rightarrow CO_2$ $\Delta G^0 = -66$ kcal	*Carboxydomonas*

TABLE 53

Inorganic compounds and ions as final electron acceptors for bacteria (after Rittenberg, 1969, table 5.8)

Terminal electron acceptor	End product(s)	Bacterium
NO_3^-	NH_4^+, NO_2^-	*Escherichia coli*
NO_3^-	N_2	*Pseudomonas denitrificans*
NO_3^-	$N_2 + N_2O$	*Pseudomonas aeruginosa*
NO_3^- or NO	N_2O	*Corynebacterium nephridii*
SO_4^{2-}	H_2S	*Desulfovibrio desulfuricans*
CO_2	CH_4	*Methanosarcina barkeri*
CO	CH_4	*Methanosarcina barkeri*
$HTeO_3^-$	Te^0	*Staphylococcus aureus*
$HSeO_3^-$	Se^0	*Salmonella typhosa*
$S_4O_6^{2-}$	$S_2O_3^{2-}$	*Salmonella typhosa*
H_2VO_4	$VO(OH)_2$	*Veillonella alcalescens* *(Micrococcus lactilyticus)*
$UO_2(OH)_2$	$U(OH)_4$	*Veillonella alcalescens*
Se^0	Se^{2-}	*Veillonella alcalescens*
S^0	S^{2-}	*Veillonella alcalescens*
Au^{3+}	Au^0	*Veillonella alcalescens*

Doetsch/Cook (1973) summarized in an excellent book the multifarious complex bacterial processes, all of which influence syngenetic and early to late diagenetic mechanisms (even in the sub-surface) under a wide range of temperature, pressure, pH – Eh, etc., conditions. Tables 50 – 54 and Figs. 28 – 34 merely exemplify this.

Orr (1974), Degens and Mopper (1975), among many others, discussed the factors controlling the diagenesis of organic matter, the bacterial processes involved, and the cycles of sulfur (e.g., see Fig. 35).

McLerran/Holmes (1974) reported on the precipitation of Zn – Cd by marine bacteria in estuarine sediments. Can such deposition also occur in freshwater and supersaline sediments?

Trudinger (1976, 1981) provided a modern review of the bacterial origin of sulfide and other ore minerals in sediments.

TABLE 54

Fractionation of sulfur isotopes in biological reactions (data from Kaplan/Rittenberg, in Rittenberg, 1969, table 6.2)

Reaction	Typical organism	Observed $\delta\,^{34}S$ in product*
$SO_4^{2-} \rightarrow H_2S$	*Desulfovibrio*	-10 to -46
$SO_3^{2-} \rightarrow H_2S$	*Saccharomyces*	-34 to -40
$H_2S \rightarrow SO_4^{2-}$	*Thiobacillus* sp.	-10 to -18
$H_2S \rightarrow S^0$	*Chromatium* sp.	-3 to -10
$H_2S \rightarrow S_4O_6^{2-}$	*Thiobacillus* sp.	$+3.2$ to $+19$
$S^0 \rightarrow SO_4^{2-}$	*Thiobacillus* sp.	-0.1 to $+1.4$
Cysteine $\rightarrow H_2S$	*Proteus* sp.	-4 to -5
Sulfate assimilation	*E. coli*	-1 to -2.8

$$*\delta\,^{34}S\,\text{‰} = \frac{(^{34}S/^{32}S)\ \text{sample} - (^{34}S/^{32}S)\ \text{starting material}}{(^{34}S/^{32}S)\ \text{starting material}} \times 1000.$$
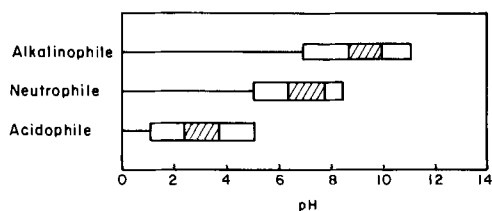
Fig. 28. pH ranges for multiplication of acidophilic, neutrophilic, and alkalinophilic bacteria. Hatched portions indicate approximate optima. (After Doetsch/Cook, 1973.)

112

Tissot/Welte (1978) summarized the early transformation of organic matter – the diagenetic pathway from organisms to geochemical fossils and kerogen, including the genesis of H_2S, for example (Fig. 35).

Ehrlich (1981) offered a neat summary of geomicrobiology useful for diagenetic interpretations. Krumbein (1983a), on the other hand, reviewed microbial geochemistry. Kandler (1981) discussed phylogeny of organisms, including the evolution of bacteria and the correlation of paleochemical data.

Muir (1981) described the microfossils of a Proterozoic shale at Mt. Isa and their
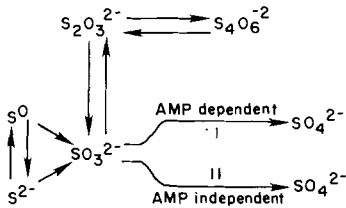
Fig. 29. Oxidation of sulfur compounds by *thiobacilli*. Sulfide (S^{2-}), elemental sulfur (S^0) and thiosulfate ($S_2O_3^{2-}$) are oxidized via sulfite (SO_3^{2-}) as a common intermediate. Possibly another reaction pathway (*II*) exists for sulfite oxidation in addition to the AMP-dependent APS-reductive pathway (*I*). (After Doetsch/Cook, 1973.)
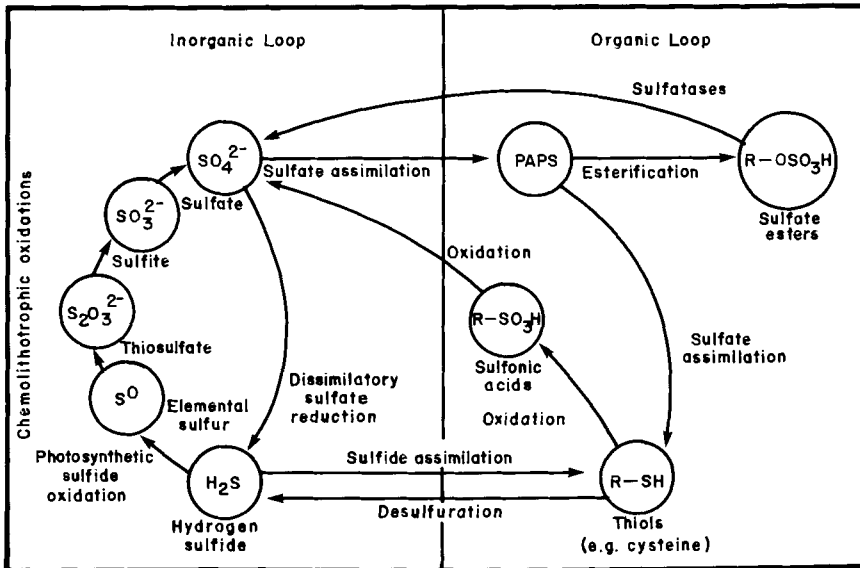
Fig. 30. The biological sulfur cycle. (After Doetsch/Cook, 1973.)
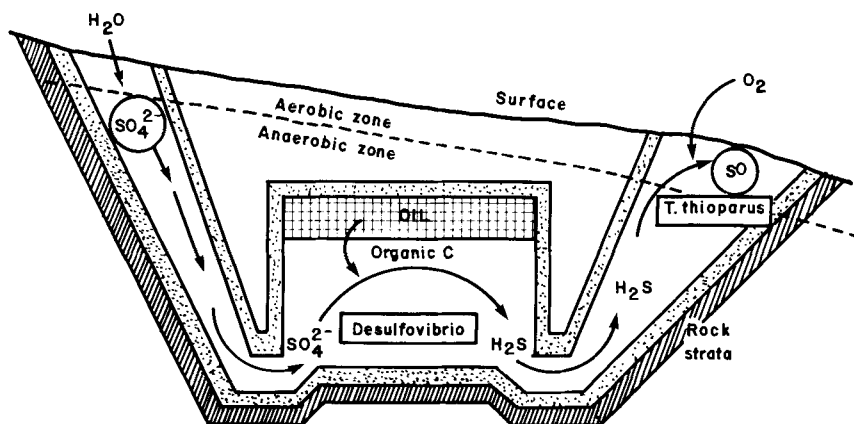
Fig. 31. Possible mode of formation of epigenetic sulfur deposits by bacteria. Infiltrating groundwaters dissolve sulfates which are reduced to hydrogen sulfide by *Desulfovibrio* in region of oil pocket, and finally sulfide is oxidized to elemental sulfur by *Thiobacillus thioparus* near surface. (After Doetsch/Cook, 1973, from Kuznetsov et al., 1963.)
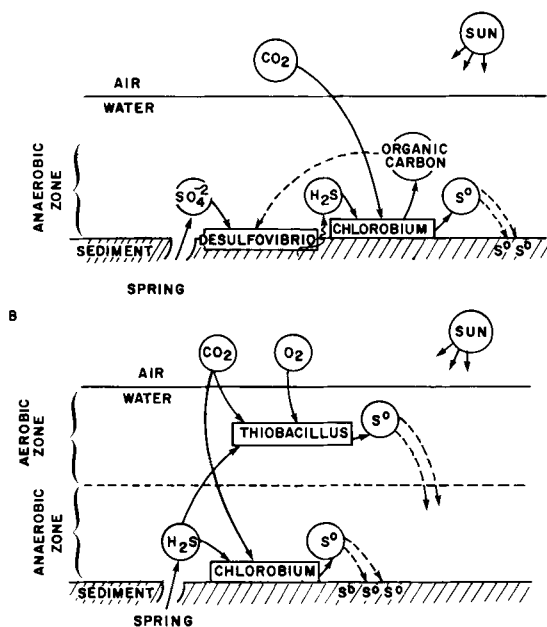
Fig. 32. Bacterial mechanisms in deposition of elemental sulfur in lakes. (A) Fully anaerobic system, with bacterial generation of H_2S from sulfate and photosynthetic oxidation of sulfide to elemental sulfur as in Lake Ain-ez-Zauni, Lybia. (B) Mixed system, with anaerobic photosynthetic and aerobic non-photosynthetic oxidation of sulfide from mineral springs, as in Lake Sernow, USSR. (After Doetsch/Cook, 1973.)
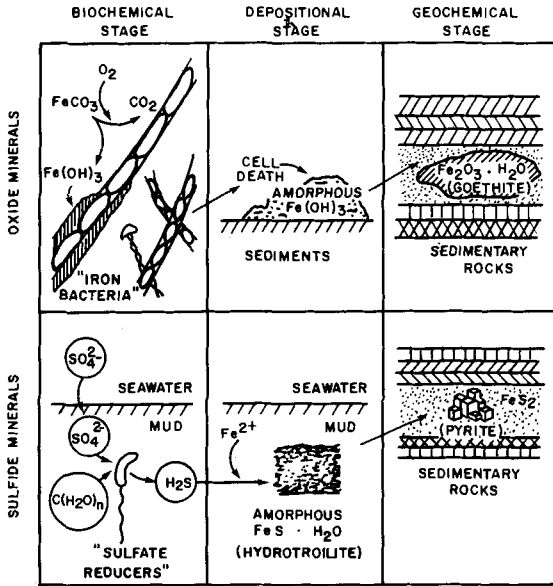
Fig. 33. Bacterial processes postulated as leading to formation of iron mineral deposits. Iron oxide minerals may arise from alteration of the ferric hydroxide precipitated by *Leptothrix, Gallionella,* and other iron-oxidizing bacteria. Sulfide minerals may result from reaction of iron with H_2S generated by *Desulfovibrio* in marine sediments. (After Doetsch/Cook, 1973.)
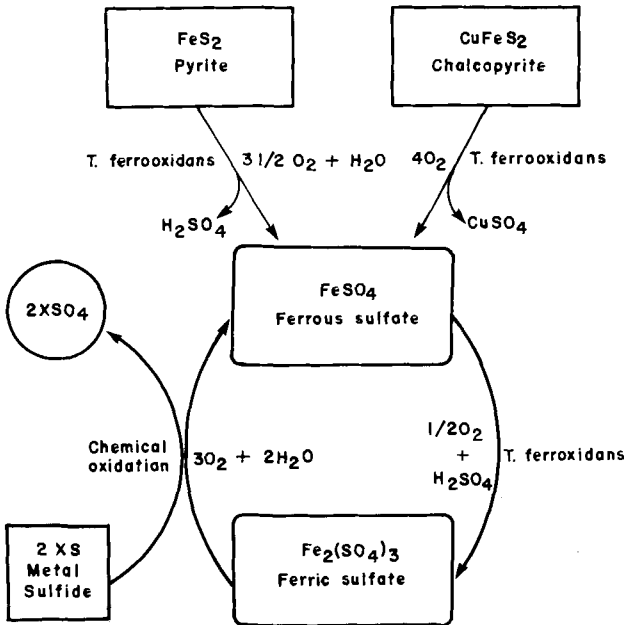
Fig. 34. Bacterial and chemical reactions in the leaching of sulfide minerals. Oxidation of sulfide ores by *Thiobacillus ferrooxidans* produces ferric sulfate, which acts as a chemical oxidant for oxidizing and solubilizing metallic sulfides not amenable to direct bacterial oxidation. (After Doetsch/Cook, 1973.)

significance related to the depositional milieu, diagenesis and mineralization. Ripley/Nicol (1981) provided S-isotope evidence of sulfate-reducing bacteria in Archean times and modeled the process. Dexter-Dyer-Grosovsky et al. (1984) offered one of many papers that discuss the microbial pathways in Precambrian ore genesis.

Mustoe (1981) and Dorn/Oberlander (1981) described bacterial oxidation of Mn – Fe in a cold spring and the bacterial Mn-coating of desert varnish, respectively.

Pooley (1982) remarked on bacterial accumulation of Ag during sulfide ore leaching. To what degree can the data of bacterial leaching be applied to interpret fossil diagenetic settings?

Peryt (1983, pp. 344 – 357) described pelagic phosphate-rich oncoids and stromatolites and their diagenesis. Both bacterial and algal processes were operative in the primary and secondary (diagenetic) origin of the macro- and microstructures and textures. Beveridge et al. (1983) described the diagenetic complexing of metals to bacteria.

Boyce et al. (1983b) illustrated bacterial S-fractionation in a fossil hydrothermal chimney/mound ore body. See their fig. 5 on exhalations, interstitial seawater, brine pool, bacterial processes, etc. Jannasch (1985) and Jannasch/Mottle (1985) investigated organisms, including bacteria, in the deep oceans, in particular of hydrothermal vents/smokers.
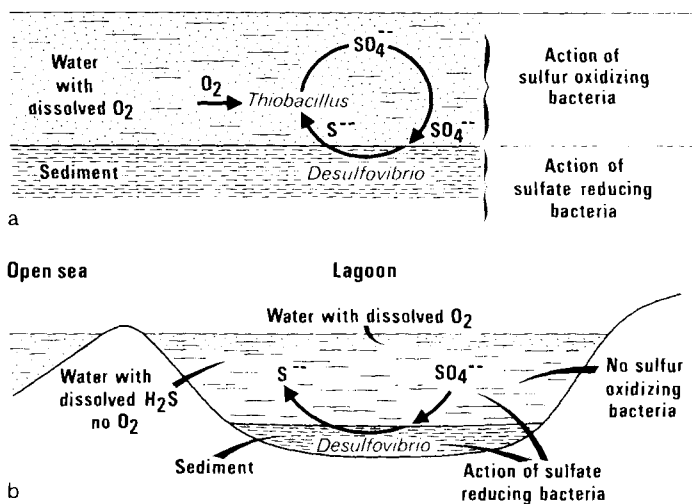

Fig. 35. Formation and destruction of H_2S in sediments and bottom waters. (a) Open sea conditions: there is an equilibrium between formation and destruction of hydrogen sulfide. (b) Restricted water circulation: no dissolved oxygen in bottom waters. This results in the absence of aerobic sulfur-oxidizing bacteria. Thus, there is no destruction of hydrogen sulfide in bottom waters, which are anoxic and contain H_2S. (After Tissot/Welte, 1978.)

Lewin (1984b) studied the transport of Fe by microorganisms (see his model in fig. on p. 402).

Lazaroff (1983) and Birnbaum/Wireman (1984), among others, offered very specific, selectively chosen data on bacterial sulfate reduction and pH controls on diagenesis and on bacterial exclusion of D_2O from the hydration of Fe-minerals.

Bargar et al. (1985) discovered particles in fluid inclusions that are possible bacteria(?).

– See also Algae, and Biological factors.

BARRIERS

Perel'man (1967) (see also Beus/Grigorian, 1977, table 15, p. 46; and Levinson, 1980, table 2A-1, p. 630) discussed the numerous geochemical and physical "barriers" that result in the precipitation of chemical elements (see Table 6).

Makarov/Morozov (1980) described hydrodynamic barriers in a petroliferous basin. Similar barriers must be considered in relation to diagenesis, in the origin of compaction/formation/meteoric and hydrothermal fluids, and in the study of mixing of various types of solutions.

BIOLOGICAL FACTORS

Lowenstam (1981) discussed the minerals formed by organisms, and Carlson/Forrest (1982) the uptake of dissolved sulfide. Ernst (1974) summarized the heavy metals in vegetation; Bowen (1966) and Goldberg (1954, 1957) offered data on trace elements in biochemistry and chemical scavenging; whereas Noddack/Noddack (1940), Stiles (1946), and Lange-de la Camp/Steinmann (1953), among many others, have reported trace elements in animals and/or plants – these publications indicate the status about 40 years ago. Berger (1950) studied the geochemical role of organisms, and Vahrenkamp (1973) the metals' functions in biological processes.

Lee/Hoadley (1967) investigated the relation between biological activity and chemical equilibria of natural waters, and Williams (1971) the solution chemistry of metals in biological systems, whereas Ridout et al. (1984) analyzed the biological flux of minor elements affecting the composition of Fe – Mn nodules.

Wood (1975) and Bolin/Cook (1983) treated biological/biogeochemical cycles; Krumbein (1978) the environmental biogeochemistry and geomicrobiology; whereas Gates (1979) summarized biophysical ecology.

Morris (1971), Codispoti et al. (1982), and Hallam (1984), for instance, described

some indirect, yet important, organism – environment – sediment relationships, such as trace metals controlling organic bloom, which in turn changes the organic/inorganic C system of seawater and eventually of sediments. Hallam also discussed the causes of mass extinction of organisms.

Swart (1981) and Graham (1982), among literally hundreds of others, studied the Sr, Ca, Mg and Na composition of corals and foraminifera and the mechanisms related to seawater and hydrothermal flux of elements. Why do researchers confine their analyses so often to the non-metallic elements? What are the differences in the processes of uptake and release of various types of elements? Which elements represent the hydrothermal component?

McCall/Tavesz (1982) offered a good cross-section of the animal – sediment relationships, including biological and chemical alterations and diagenesis of sediments. Many journal articles treated specific aspects, such as Petr (1977), bioturbation and chemical exchange and Hutson (1980), bioturbation influencing O-isotope composition and stratigraphic interpretations; Flegal/Martin (1977) dealt with the contamination of biological samples by ingested sediment (faecal pellet-type); Ausich/Bottjer (1982), described tiering in suspension-feeding communities throughout the Paleozoic; Degens/Ittekkot (1982), the metal-staining of biological membranes in sediments; Wefer et al. (1982), the fluxes of biogenic material from sediment traps; Aller (1984), the influence of burrow structures and irrigation on sedimentary solute distributions; and Andrews et al. (1984), the metabolic activity and bioluminescence of faecal pellets and sedimentary particles.

Edmunds et al. (1982, in Holland/Schidlowski, 1982) modeled the known and postulated roles of microbes in the sea (Fig. 36), most of which control diagenesis in a direct and/or indirect manner (e.g., precipitation and adsorption of elements versus alteration of Eh/pH).

Westbroek (1983) modeled a few important biochemical reactions that comprise also diagenesis, cycles of elements, zonation, pH/Eh controls, etc. (see Cycles, Bacteria, etc., sections; and Fig. 37).

Walter (1984) offered an ecological classification of the Earth. What is the correlation between diagenetic systems and ecological environments?

– See also Algae, and Bacteria.

CARBONATES

Chilingar et al. (1967) and Larsen/Chilingar (1967a,b, 1979, 1983), among numerous others, offered fundamental concepts of diagenesis, many of which ought to be applied to the study of ore hostrocks. Macqueen (1983) summarized carbonate sedimentology in the context of mineral exploration. See also James/Choquette
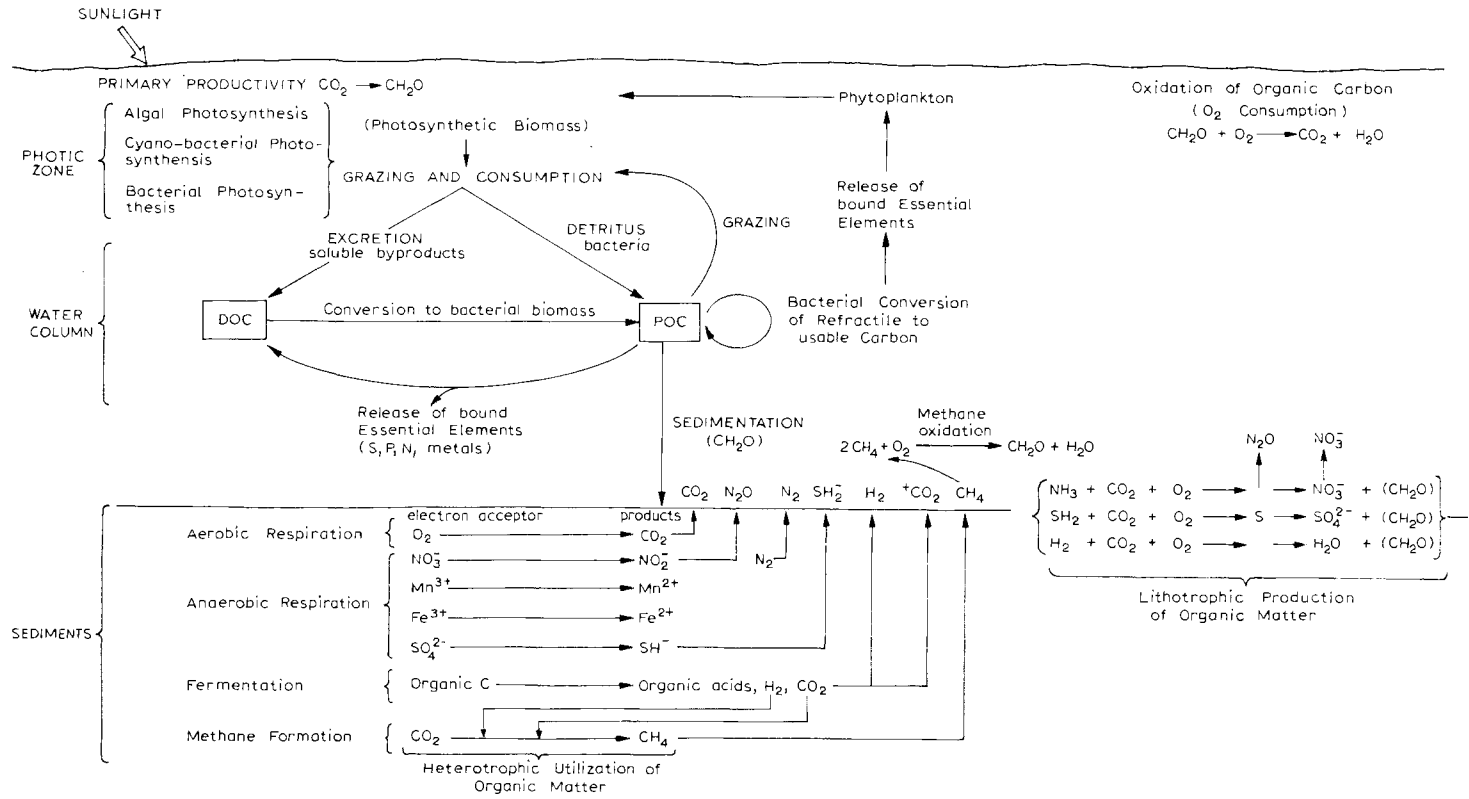
SUNLIGHT

PRIMARY PRODUCTIVITY $CO_2 \rightarrow CH_2O$

PHOTIC ZONE
- Algal Photosynthesis
- Cyano-bacterial Photosynthensis
- Bacterial Photosynthesis

(Photosynthetic Biomass)

GRAZING AND CONSUMPTION

Phytoplankton

Oxidation of Organic Carbon
(O_2 Consumption)
$CH_2O + O_2 \longrightarrow CO_2 + H_2O$

Release of bound Essential Elements

GRAZING

EXCRETION soluble byproducts

DETRITUS bacteria

WATER COLUMN

DOC

Conversion to bacterial biomass

POC

Bacterial Conversion of Refractile to usable Carbon

Release of bound Essential Elements (S, P, N, metals)

SEDIMENTATION (CH_2O)

Methane oxidation
$2CH_4 + O_2 \longrightarrow CH_2O + H_2O$

N_2O NO_3^-

CO_2 N_2O N_2 SH_2^- H_2 $^+CO_2$ CH_4

SEDIMENTS

	electron acceptor	products
Aerobic Respiration	O_2	CO_2
Anaerobic Respiration	NO_3^-	NO_2^-
	Mn^{3+}	Mn^{2+}
	Fe^{3+}	Fe^{2+}
	SO_4^{2-}	SH^-
Fermentation	Organic C	Organic acids, H_2, CO_2
Methane Formation	CO_2	CH_4

N_2^-

$NH_3 + CO_2 + O_2 \longrightarrow NO_3^- + (CH_2O)$
$SH_2 + CO_2 + O_2 \longrightarrow S \longrightarrow SO_4^{2-} + (CH_2O)$
$H_2 + CO_2 + O_2 \longrightarrow H_2O + (CH_2O)$

Lithotrophic Production of Organic Matter

Heterotrophic Utilization of Organic Matter

Fig. 36. Known and postulated roles of microbes in the sea. (After Edmunds et al., 1982, in Holland/Schidlowski, 1982.) *POC* = particulate organic carbon; *DOC* = dissolved organic carbon. Eh ranges: aerobic respiration = +500 to +800 mV; nitrate reduction = +300 to −500 mV; metal reduction = +100 to +400 mV; sulfate reduction = −100 to −400 mV; methanogenesis = −800 mV.
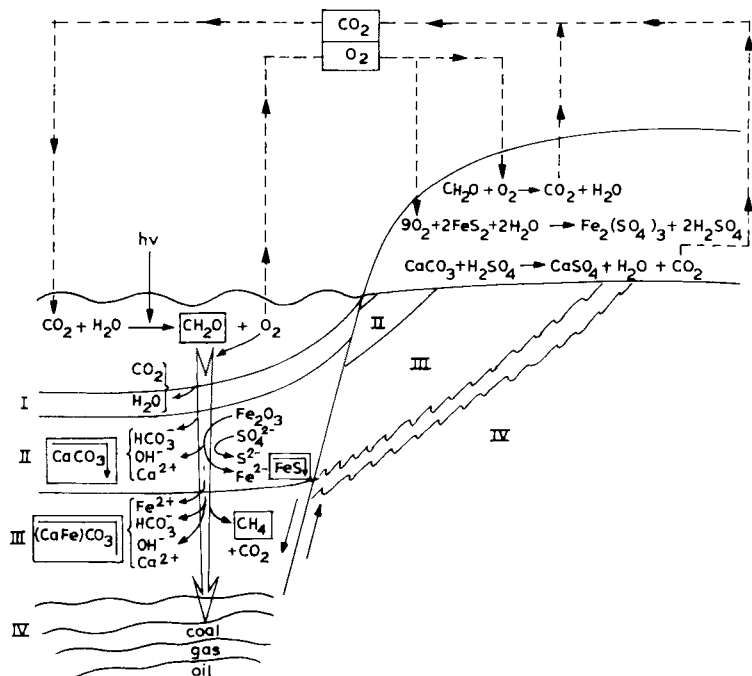
Fig. 37. Very simplified survey of a few important biogeochemical reactions.

Left: a subsiding sedimentary basin where a fine mud is deposited. Organic carbon formed by photosynthesis is partly taken up in the sediment and causes a chemocline with increasingly reducing conditions downward. I = Aerobic zone; part of the organic matter is oxidized by O_2-dependent respiration. II = Zone of sulphate reduction and deposition of FeS_2; the oxygen is consumed (anaerobic conditions) and instead sulphate is used as a terminal electron acceptor by sulphate-reducing bacteria, so that sulphide is produced. Also, the reduction of ferric to ferrous iron may be catalyzed by bacteria. Black FeS is formed; later, this may be slightly oxidized to FeS_2. III = Zone of methanogenesis; sulphate is consumed and methanogenic bacteria use CO_2 or acetic acid as a terminal electron acceptor for the respiration of "CH_2O". Methane is produced. IV = Zone with nonbiological diagenesis and further metamorphism. Finely distributed kerogen is the main form in which "CH_2O" occurs; coal, gas, and oil are only available in relatively small amounts. Note that in the chemocline the pH tends to be between 6 and 8, and that carbonates can easily form.

Right: the chemocline is uplifted and oxidized. Organic matter is mineralized and bacterial oxidation of pyrite gives rise to an acid and strongly oxidizing solution of H_2SO_4 and $Fe_2(SO_4)_3$. This mechanism is used in the mining of sulphide and uranium ores by bacterial leaching. Carbonates are dissolved and crusts of ferric oxides and diagenetic gypsum may be formed. (After Westbroek, 1983.)

(1983a,b) who have briefly reviewed limestone diagenesis — but dozens of additional reviews are available.

Wolf et al. (1967) summarized the elemental composition of carbonates. Much contradictory data exists as to the possibility of carbonates acting as the source of metals for ore deposits (see M.V.-type ores), so that extensive experiments are still required, combined with studies of natural occurrences to determine whether diagenetic processes are involved.

Pingitore (1978) and Morrow et al. (1980) examined the behaviour of Zn – Mn during carbonate diagenesis; Brand/Veizer (1980) studied trace elements of multicomponent carbonate systems; Yudovich (1980) treated the distribution coefficients of elements in carbonates; Lorens (1981) the Sr, Cd, Mn, Co distribution coefficients in calcite as a function of precipitation rate; and Morse et al. (1984) provided data on the interaction of uranyl ions in a carbonate media. Timofeev et al. (1984) deliberated on the factors controlling the elements of the iron family and their distribution in carbonate rocks, whereas Mirsal/Zankl (1985) tested the phenomenological aspects of carbonate geochemistry and the effect on transitional metals. The latter pointed out the dualism in geochemistry in regard to organic or inorganic processes, which is replaced by a chemical mechanism based on transition-metal and organic matter controls. Five metals (Ni, Co, Fe, Mn, Zn) form chelates/complexes. What are the implications for the source of metals? Fouillac/Criand (1984) evaluated critically the stability constants of carbonate/bicarbonate trace-metal complexes.

Longman (1980) studied near-surface carbonate diagenetic textures. Can they eventually be used to discriminate surface from deeper basinal textures in association with ores to establish the time/depth relations of the hostrock – ore parageneses? (See M.V.-type deposits section.) Irwin (1980) related early diagenetic carbonates to pore fluid-migration (see his models), and Marshall (1981) studied zoned calcites, their trace elements and isotopes, revealing pore-fluid chemical changes. Similar investigations are needed of the gangue minerals of ore deposits.
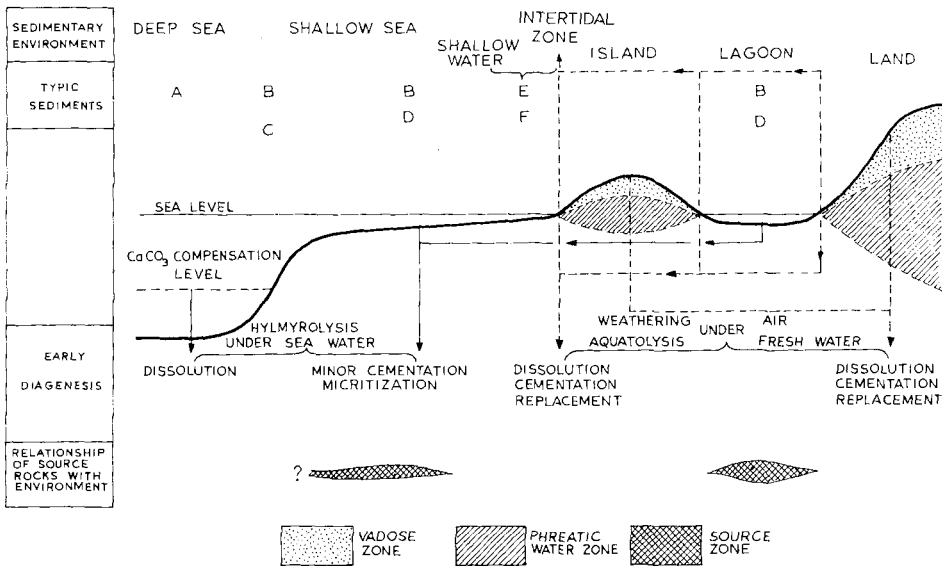
Fig. 38. Sedimentary facies and diagenetic facies of limestones and their bearing on the source rocks. (A) Deep-sea ooze; (B) micritic sediments; (C) turbidity sediments; (D) biomicritic sediments; (E) biosparitic sediments; (F) oolitic sediments. (After Jiamo, 1980.)

Jiamo (1980) modeled the sedimentary and diagenetic facies of limestones (Fig. 38) to put the characteristics of the evolution of organic matter within the carbonates into proper overall context. The importance of this to ore genesis: What features indicate conditions that permitted diagenetic ore genesis in contrast to those that precluded them; e.g., vadose/meteoric versus marine diagenesis, oxidation versus reduction processes, internal versus external metal sources; cementation/open-space ore filling versus replacement mechanisms, etc.? The development of organic matter in basin evolution is merely one aspect.

Schmoker et al. (1985) outlined some characteristics of carbonate "reservoirs"; a similar study must be undertaken on carbonate "hostrocks" and the features of the hydrocarbon-containing rocks ought to be compared with ore-bearing reservoir-cum-hostrock lithologies.

Matsumoto/Iijima (1981) investigated the diagenetic (burial) stages of authigenic Ca – Mg – Fe carbonates in various facies (e.g., freshwater, brackish water to marine, and marine sediments) and thus unravelled calcitization, dolomitization, ankeritization, sideritization, etc., in both space and time. Numerous processes were invoked: reduction, fermentation, dissolution, bacterial influences, dehydration, recrystallization, syneresis, mixing of fluids, thermal alterations, oxidation, porosity reduction, and increase in pressure or depth. Many sediment-hosted ore deposits need such detailed investigation.

Takano et al. (1980) dealt with sulfate ions in travertine. Can such travertine also be associated with ore deposits or can travertine-associated sulfur be made available to form sulfides? Hutton/Dixon (1981) studied calcretes and their dolomitization. How can they be recognized in ancient deposits? How does this type of dolomitization differ from diagenetic/epigenetic dolomite associated with ores?

Netterberg (1980), Watts (1980) and Wilson (1983), among others, reviewed the calcretes as well as other residual accumulations and discussed the diagnostic features, classification, mineralogy and diagenesis, including those associated with uranium concentrations. Diagenetic and supergene types must be differentiated.

Klappa (in Wilson, 1983) modeled the non-pedogenic U-bearing calcrete (Fig. 39); whereas Watts (1980) offered a flow-chart-like model of the major pedogenic (pedodiagenic?) and diagenetic mechanisms in the origin of a calcrete complex (Fig. 40). Their origin must be clearly understood in testing them for potential economic deposits, and when calcrete samples are utilized in geochemical exploration. Calcrete, silcrete, and related concentrations also serve as paleoenvironmental guides.

Matsumoto/Iijima (1981) determined the diagenetic evolution of Ca – Mg – Fe carbonates in coalfields. Apply this method to ore hostrocks (see other references in the above publication).

Kropacheva/Ponomarev (1983) described S-bearing carbonates and gave a classification of genetic types, whereas Germanov et al. (1982) studied the transformation of carbonates during biogenic sulfate reduction and methane formation – all these concepts could be related to ore genesis in some systems.

Borodenkov/Rusinov (1982) deliberated on the physicochemical conditions of carbonates in some ore deposits (compare eventually the high-T versus the lower-T carbonates); Hattori/Sakai (1980b) provided O- and C-isotope data of meteoric hydrothermal calcite types; McNaughton/Wilson (1983) used ^{13}C-isotopes to distinguish various genetic types of marbles (i.e., their pre-metamorphic precursors
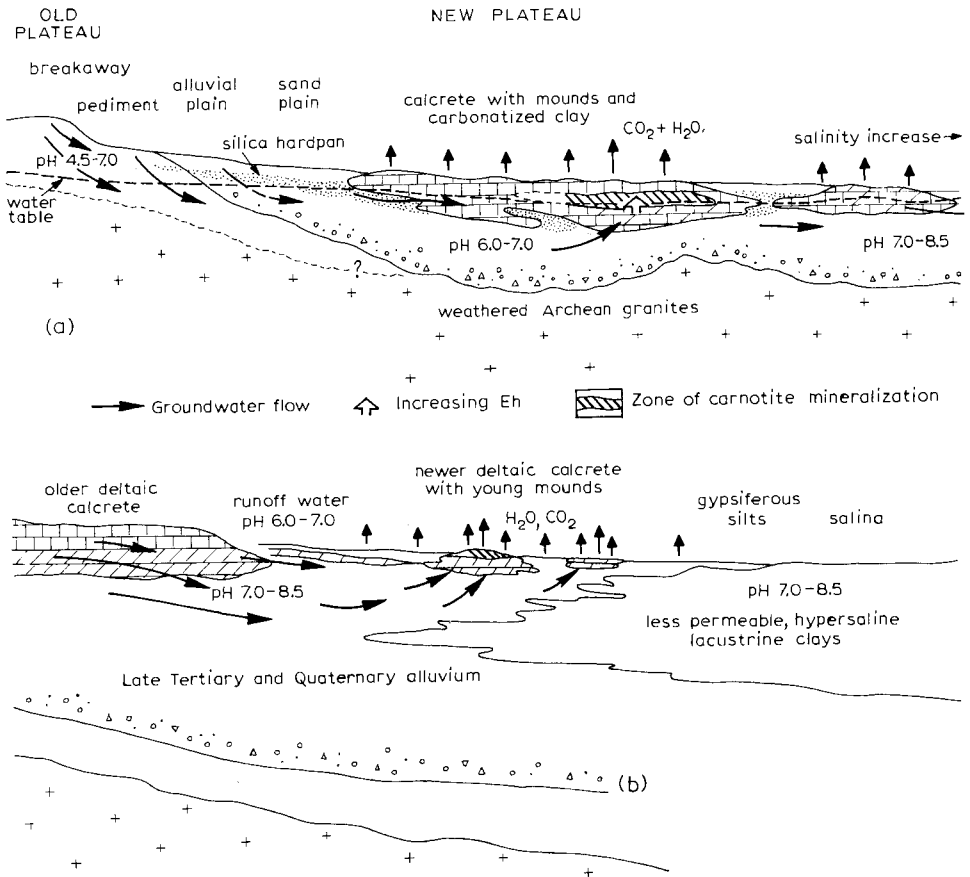
Fig. 39. Schematic models for non-pedogenic, uranium-bearing calcrete, Western Australia. (a) Valley calcrete with bedrock constriction. (b) Newer deltaic calcrete – salt lake model. Breakaways and pediments are largely within the mottled and pallid (kaolinitic) zones of the lateritic profile and in weathered Archean granitic rocks. Older valley and deltaic calcretes and included carnotite are subject to dissolution. (After Klappa, 1983.)

by contrasting hypersaline depositional and diagenetic varieties with other types); Möller et al. (1984) discriminated types of calcites from Pb – Zn veins (see their model); Pomârleanu/Pomârleanu (1982) used fluid inclusions in calcite from some ore deposits to distinguish hydrothermal, porphyry-Cu and skarn types, the method which ought to be applied to diagenetic, catagenic, etc., carbonates; Ruiz et al. (1984) dated ore deposits by using calcite and other minerals; Dietrich et al. (1983) determined the origin of calcite in syntectonic veins by employing C-isotope ratios (syndiagenetic veins could be similarly analysed); and Larson/Tullborg (1984) recognized three calcite veins based on stable isotopes (each also had a different texture and was of either low-T or high-T origin, including hydrothermal origin) (diagenetic carbonates can, therefore, be discriminated from other types).

Pingitore (1982) modeled the role of diffusion during carbonate diagenesis, including that of Zn, Mn, for example (Fig. 41). If carbonates are suggested as potential metal sources in the origin of M.V.-type ores, we must understand the styles of earlier metal concentrations.

Given/Wilkinson (1985) outlined the kinetic control of various parameters affecting carbonate genesis, including limestone diagenesis. The data can be applied in the study of carbonate gangue minerals and host rocks.

– See also Dolomites, Karsts, and M.V.-type ores.
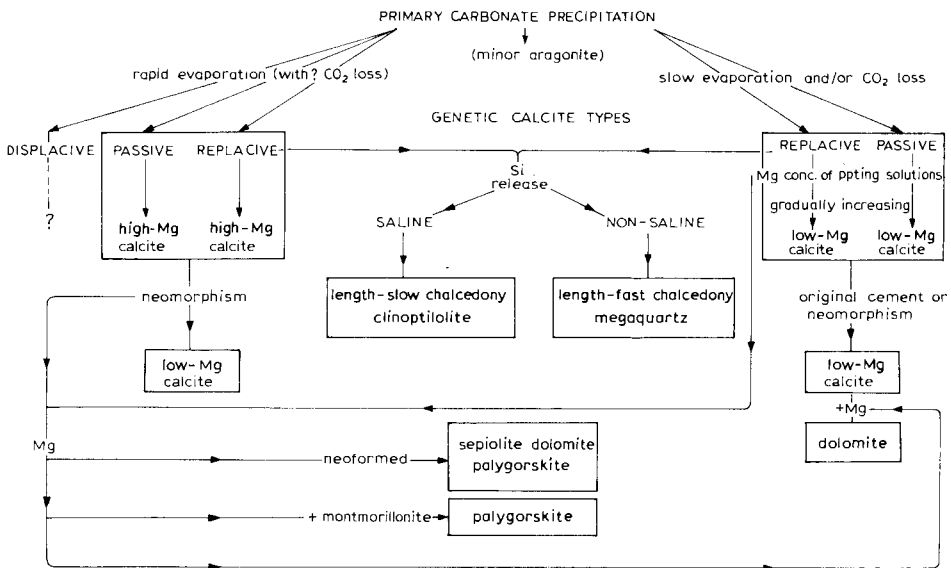
Fig. 40. Schematic flow diagram summarizing the major pedogenic and diagenetic processes within the Kalahari calcretes. Note that aragonite is not shown in detail. (After Watts, 1980.)
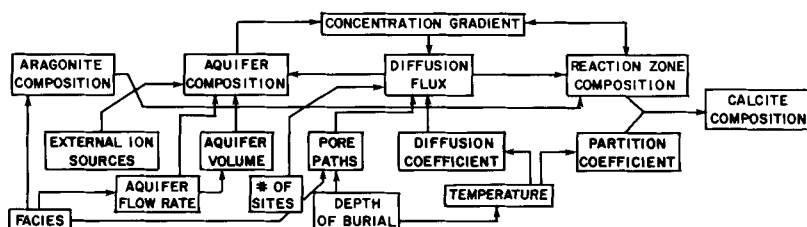
Fig. 41. Many parameters and relations determine this incorporation of trace elements during aragonite/calcite transformation in a diagenetic setting controlled by diffusion. An important feature of the system is the degree of chemical autonomy maintained between the reaction zone and the aquifer solution. This determines whether the diagenetic calcite encodes the chemistry of its aragonite or a modification thereof. (After Pingitore, 1982.)

CEMENTATION

Meyers (1978) concluded that four types of calcite cements with varying Fe^{2+}- and Mn^{2+}-contents provide "time stratigraphic" zoning, correlatable over 30,000 km^2, and are of meteoric – phreatic origin, divisible into meteoric – marine mixing-zone, phreatic, marine subtidal, and beach-rock cements. This concept and technique could be applicable to Mississippi Valley-type ore deposits.

Knoll/Simonson (1981) examined Proterozoic quartz cementation in iron formation (see also Dimroth, 1968, 1976, 1979; and Dimroth/Chauvel, 1973).

Pye (1982) studied humate-cemented sands (= humicretes), a type that must be given consideration in future geochemical facies analyses. Can this type of humate sand adsorb metals, for example?

Pye (1981, 1984) described Fe-sulfide and siderite cementation in intertidal salt-marsh sediments.

Grover/Read (1983) considered deep-burial cementation related to a paleoaquifer, including cementation of M.V.-type mineralization, as defined by cathodoluminescence. Many researchers treated cementation of all lithologies, but many ignore the ore hostrocks. Why?

Krajewski (1984) modeled early diagenetic phosphate cements in condensed glauconitic limestones.

CHROMIUM

Coipel/Dimanche (1981) reviewed the diagenesis of Fe-chromium and Ti-oxides.
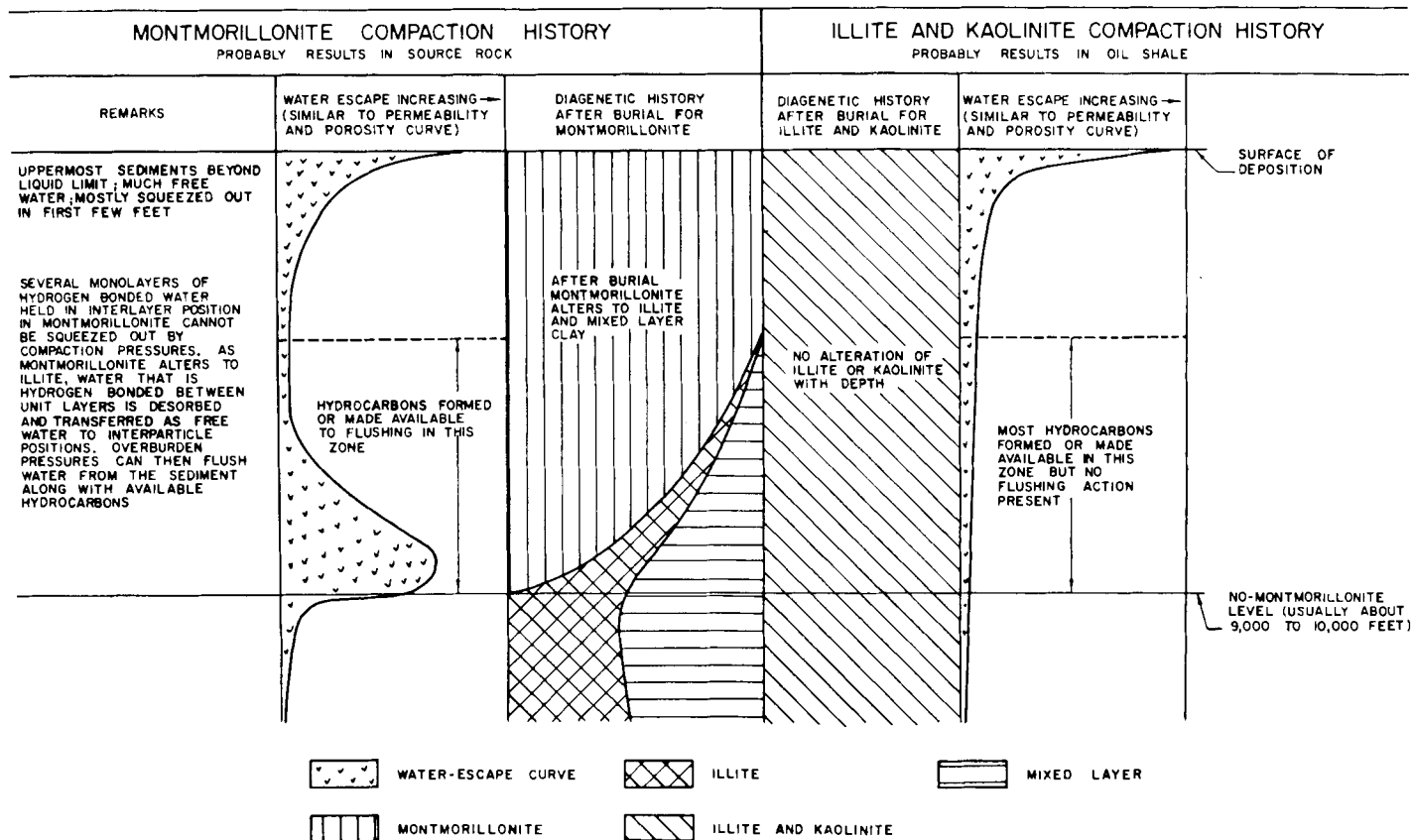
Fig. 42. Compaction history of various clays when deposited in marine environments and its probable relation to release to hydrocarbons from mudrocks. (From Powers, 1967, in Rieke/Chilingarian, 1974, fig. 58.)

CLAY MINERALS (metal adsorbants, transformations, fluid release, burial metamorphism, etc.)

Yariv/Cross (1979), Van Olphen (1963a,b), Eitel (1964, 1975), and many others provided basic data on clays, including ion-exchange of metals important in the study of source rocks, remobilization, and related topics. Goudie/Pye (1983) summarized the clay minerals in laterites and bauxites. Hanshaw/Coplen (1973) described ion-exchange and ultrafiltration in the origin of brines and concentration of metals.

Schmidt (1973) provided data on (a) the contrasts in composition and concentration of interstitial waters from shales and sandstones; (b) fluid-pressure variations; (c) conversion from expandable to non-expandable clays (e.g., montmorillonite to illite); (d) major temperature gradient changes; and (e) changes in shale porosity, shale lithologies, salinity, etc. Observations were made in drillholes up to 14,000 ft in depth. The release of mineral-bound water is also related to the late diagenetic conversion of montmorillonite to illite, as shown in Fig. 43, for example. Cation-exchange and, thus, the adsorption – desorption of both metal and non-metal ions from and into intrastratal solutions is likewise controlled by the clays. As depicted in Fig. 44, this changes with depth and with the conversion of montmorillonite to illite.

Rieke/Chilingarian (1974) reviewed the compaction history of fine-grained sediments during basin evolution. Figure 42 (Powers, 1967) shows the changes of three groups of minerals. The following questions arise: Are desorbed metals in
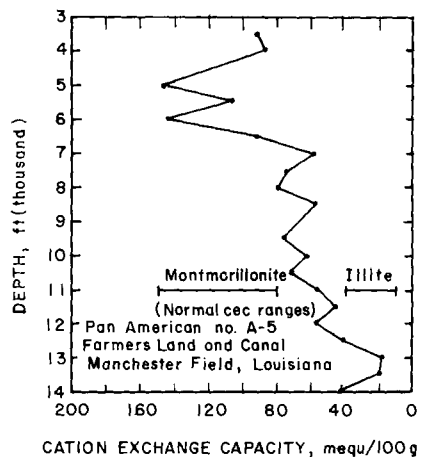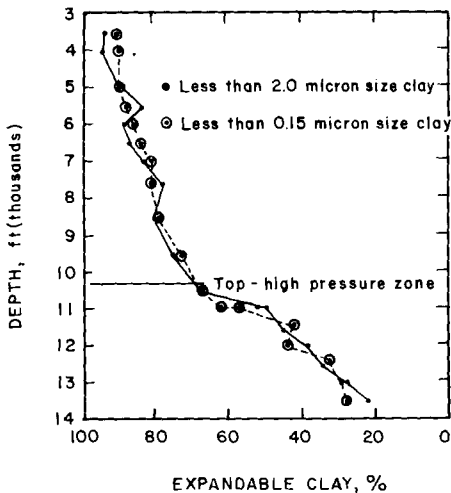
Fig. 43. Plot of percent expandable clay versus depth showing accelerated increase in diagenesis of montmorillonite to mixed-layer montmorillonite – illite at top high-pressure zone. (After Schmidt, 1973.)

Fig. 44. Plot of variations of cation-exchange capacity (CEC) of shale with depth. (After Schmidt, 1973.)

compaction fluids derived from clays and organic matter? If so, what is the evolution of desorption of cations and anions, and the formation and destruction of organic matter (including oil and gas), as related to the release of the fluids? Is there a metal-desorption sequence with depth of burial or maturation of the basinal sediments and volcanics? Several factors must coincide to permit the origin of metalliferous deposits from compacting basins.

Reimer (1975) studied the origin of the matrix in one Precambrian turbidite – greywacke sequence: it was of diagenetic derivation from decomposed, unstable clastic fragments and the Ca and Mg were released to form dolomite. In the present context, it is of interest that the Ni-content in the greywacke correlates positively with the matrix content (Fig. 45).
   Note: Inasmuch as there is a conspicuous lack of data on the trace-element contents of greywackes and turbidite basin sediments in general, it is difficult to judge their potential as sources for economic ore deposits. Two exceptions to this rule are the publications by Sehm (1976) and Grunewald (1976).

Brooks/Campbell (1976) described the secondary, diagenetic introduction of organic matter into sandstone that hosts U and V mineralization. These metals are enriched in the clay matrix.

Kharaka/Smalley (1976) studied the flow of solutes through clays that acted as membranes and retarded selectively numerous cations, thus changing the composition of solutions.

Schultz (1978) studied the change of clays of shales and bentonites during "depth diagenesis". No data, however, was supplied on the amount of the fluid released.
   Note: This is a good example of analyzing clay transformations during basin evolution. However, the approach is somewhat limited.

Potter et al. (1980) provided an excellent introduction and reference source on claystone – mudstone – shale sedimentology in general, including petrology (com-
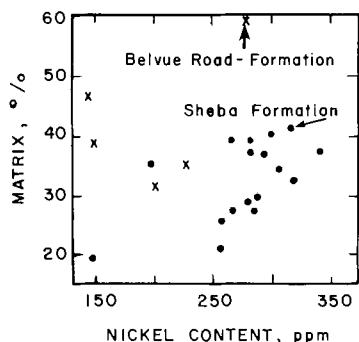

Fig. 45. Nickel content of greywackes depending on the amount of matrix. (After Reimer, 1975.)

128

prising sources, syngenesis, diagenesis, and burial metamorphism), environments, and geochemistry.

Cameron/Garrels (1980) studied geochemically Precambrian shales: the elements were controlled by rapid deposition of weathering products. The results are compared to younger shales when other processes (e.g., biochemical) came into effect. See also McLennan et al. (1983) for a geochemical investigation of Archean shales.

Aoyagi/Kazama (1980) and Singer (1979), for example, described neoformation and transformation of clays during diagenesis; whereas McMurty et al. (1983) examined geochemically/isotopically the clays of a hydrothermal mound field, and Sterne et al. (1984) the clays of a Zn – Pb – Ag deposit. A *comparison* of all genetic clay-sized minerals must eventually be undertaken: including the supergene, detrital/clastic, diagenetic, burial to higher-grade metamorphic, volcanic, hydrothermal, exhalative, etc. varieties.

Takeno et al. (1981), among many others, offered data on the metal concentration on clays as controlled by pH and other variables.

Bergaya/Van Damme (1982) studied stability and demetallization processes of metalloporphyrins adsorbed on clays. (See also Adsorption, and Organic matter.)

Mikhailov (1982), Keller (1982), and Gorbachev (1983), for instance, reviewed specific aspects, e.g., terminology of aluminous rocks, offering a compositional – genetic scheme of clays and others; textures revealing genesis, for example; and kaolin-bearing geologic associations. ALL such aspects will be useful in diagenetic/catagenetic investigations of ore hostrocks.

Pye/Krinsley (1983) described inter-layered clay stacks in shales, e.g., with chamosite, glauconite, and others. The clay-rich shaly hostrocks of ores deserve more attention in unravelling their history in contrast to the metalliferous concentration.

Debrabant et al. (1985) microanalysed clay minerals from the Atlantic to determine the source and environment of formation of detrital/clastic/terrigenous, authigenic, diagenetically affected, and hydrothermal clays.

CLIMATE

Strakhov (1967, 1969, 1971), Bernard/Samama (1976), Bjørlykke/Sangster (1981), and Gustafson/Williams (1981) have considered the potential influence of climatic factors on the origin of ore deposits − either indirectly (via soil formation) or directly. Much less is known about the climatic controls on diagenesis. For example, Gustafson/Williams (1981, Table 55, p. 151) gave the "Stratigraphic Setting of Selected Sediment-Hosted Stratiform Deposits", correlating twenty-seven deposits

with red-beds, among other variables (see also Bjørlykke/Sangster, 1981). Numerous questions can be posed, as for example: did the climate control the origin of the hostrocks, the ore precipitation, and the diagenetic mechanisms in general (e.g. in the pre-ore preparation of source, aquifer, host- and caprocks, and in the transportation and precipitation of the metals)?

Seibold (1970) described the characteristics of land-locked seas (= "adjacent seas", in contrast to open seas) in humid and arid climates. Many differences exist that control the body of water, the sediments, and the diagenesis, therefore. The climatic setting influences (1) the amount and distribution of the saline fluids; (2) the O_2-, PO_4- and SiO_2-content in the water; (3) the types of sediments, such as carbonate

TABLE 55

Stratigraphic setting of selectected sediment-hosted stratiform deposits (after Gustafson/Williams, 1981, p. 151)

Name	"Marine" transgression over terrestrial red-beds	Within "marine" succession with red-beds	Terrestrial red-bed succession	Within "marine" succession without red-beds
Mufulira	X			
Rokana	X			
Chibuluma	X			
Shaba	X			
Udokan		X		
Redstone River		X		
White Pine	X			
Spar Lake		X		
Creta		X		
Boleo	X			
Corocoro			X	
Nacimiento			X	
Dzhezkazgan		X		
Mansfeld	X			
Lubin	X			
Mt. Isa		X(D)		
McArthur River		X		
Tynagh		X		
Silvermines		X		
Rammelsberg				X
Meggen				X
Lady Loretta		X		
Sullivan				X
Broken Hill				
Howards Pass		X(D)		
Laisvall				?
Largentière			X(FW red)	

"Marine" includes restricted marine and lacustrine sediments. D = only distant association with red beds in section.

and organic matter; and (4) the metal contents. The presence of peat may characterize the humid and that of evaporite the arid conditions.

Wopfner/Schwarzach (1976) summarized the numerous direct and indirect influences of climate on ore genesis, such as on the origin of (1) Fe- and Mn-rich deposits, (2) laterites and bauxites, (3) supergene/infiltration-type uranium, (4) arid-concentration deposits, (5) metals in evaporitic (red-bed) basins, (6) ores in reef complexes and carbonate shelves, and (7) ores of glacial and cool-temperature climates.

  Note: (a) Although the climatic controls on diagenesis were not specifically treated, there is no doubt about such an influence – one often has to read "between the lines" of genetic discussions to deduce that diagenesis was operative.

  (b) There are several indirect influences of climate on ore genesis (and diagenesis). For example, a hot tropical climate is required for the formation of reefs and associated limestones, which in turn can become the hostrocks for the Mississippi Valley-type ores. The reasoning is: in the absence of hot climate, there are no reef or platform limestones, no dolomitization, etc., and consequently also no M.V.-type mineralization. This does not mean that no ores can form; only the *carbonate* hostrocks are absent. In this case, all other factors being equal, mineralization could be present in *clastic* rocks. This may be the danger of basing the classification of ores on their host lithologies mainly. Thus, all other variables must be given full credit.

Crick et al. (1980) suggested that major climatic changes can rejuvenate or expand the groundwater regime, followed by an increase in leaching of U (and other metals) from volcanic rocks, which formed uranium ore deposits upon transportation and precipitation of the metal(s).

  Note: Such major climatic changes must have a general widespread and intense effect on syngenesis – diagenesis (see Strakhov's three volumes on lithogenesis, 1967, 1969 and 1971).

Giresse (1980) discussed upwelling, climate, depositional environment, iron, organic matter, Eh, and pH, all of which control the origin of glauconite and other minerals (Fig. 46).

Turner (1980) compiled a superb review of continental red-beds, discussing most aspects of their origin – including diagenesis. However, only occasional reference is made to the association of red-beds with Cu and U – Mo concentrations, and to the genetic relations between this facies and ore deposits.

Grandstaff (1980), among many before and after him, dealt with characteristics of uraniferous, conglomerate-type deposits and the implications of the Precambrian atmosphere (e.g., oxygen level).

Mörner (1981), Barron (1982), Hay et al. (1982), and Walker (1982a,b), for example, supplied data and concepts on eustasy – paleoglaciation – paleoclimatology,

paleogeography – climate, tectonism – climate, and atmosphere – climatic relations from the Precambrian to Recent environments.

Cooke (1981) studied salt-weathering in deserts, including in sabkha environments. To what extent in this process identifiable in ancient sediments or rocks?

Kemper/Schmitz (1981) and Kazakov (1983) interpreted glendonite as polar-marine environmental indicator, and glauconite as climatic and geochemical sedimentary criteria, respectively.

Williams et al. (1982) outlined seasonality and average sea-surface temperatures from isotope records.

Danin et al. (1982) utilized patterns by lichens and algae in carbonate rocks as paleoclimatic indicators. How useful are these features in the interpretation of ancient milieus?

Rippey (1982) examined the rainfall variation-record in the sediments of a sub-humid lake. The evidence suggests seasonal changes.

Berger et al. (1983) described Mn-spike as an indicator of glacial – Holocene transition in deep-water sediments. Can this approach be used in ancient deposits?

Kent (1982) correlated the paleomagnetic intensity and the climatic record.

Goudie/Pye (1983) offered an excellent review of the chemical sediments/precipitates and residua of the near-surface environment, demonstrating the control of
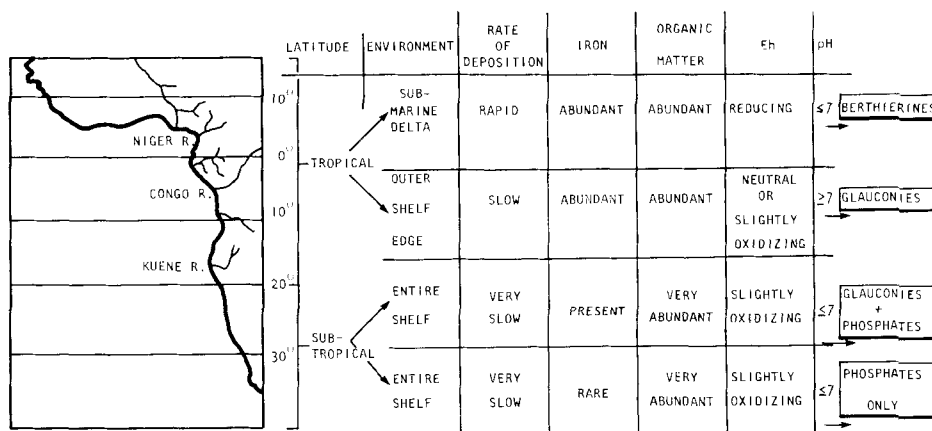
Fig. 46. Distribution of present-day minerogenesis off Africa as function of geographic zones and physicochemical environmental conditions. (The scheme assumes the relative stability of the shelf.) (After Giresse, 1980.)

geomorphology and climate/paleoclimate in the origin of laterites/bauxites, silcretes, calcretes (some bearing uranium), gypsum crusts, evaporites in lakes, nitrates, red-beds, cave deposits, phosphates, etc.

Owen/Rea (1985) linked seafloor hydrothermal activity to climate plus tectonics. If climate controls rainfall that in turn influences subsurface hydrologic systems, and because meteoric water is part of certain hydrothermal models, then climate controls both indirectly and directly certain hydrothermal – exhalative – diagenetic systems.

Sigleo/Helz (1981), Rao (1981), Nesbitt/Young (1982), and Statham et al. (1985) proffered ideas on elements in sediments that are controlled by climate or seasonal variations, on tropical vs. subpolar carbonates, on the influence of both climate and tectonism on elemental chemistry of lutites, and on specific elements (e.g., Cd and Mn) controlled by climate among many other variables, such as river supply, mobilization of sediments from shelves, pollution, atmospheric input, etc. But the complicated systems are still not well understood. In an earlier contribution Veizer/Demovič (1973) determined the possible environment, including, climate, that controlled fractionation of elements in carbonate sequences; they also contrasted the influence of primary (syngenetic) depositional and secondary (diagenetic) repartition.

Chumakov (1984) provided an example of climatic influence on geological environments and processes as exemplified by the principal glacial events. Such severe worldwide periods control the atmosphere (reciprocally, no doubt: what came first, the atmospheric change or the glaciation?) as well as the hydro- and litho-/asthenospheres, which in turn must be reflected in local to regional and worldwide diagenetic modifications. Little data is available on such mega-systems.

Barron (1985) modeled numerically (paleo-)climates in predicting petroleum source rocks and, among others, considered upwelling. The latter (in conjunction with climate) has been invoked as an important factor in the origin of phosphorites and iron ores as well as black shales. If euxinic/anoxic environments are requisites for shale-hosted ores and/or the shales originally acted as metal sources, then it seems logical to assume that upwelling was necessary for the origin of the ores.

— See also Multi-factorial, and Weathering – supergenesis.

COAGULATION

Hahn/Stumm (1970) described the role of coagulation in natural waters. All processes related to coagulation should be reviewed in the context of syngenesis, diagenesis and catagenesis.

Edzwald et al. (1974) examined coagulation in estuaries. What are the environmental factors that control coagulation?

Eckert/Sholkovitz (1976) described flocculation of Fe, Al and humates in river waters. How does this affect the supply of metals to the lakes and oceans?

Sholkovitz/Copland (1981) provided data on coagulation solubility and adsorption of Fe, Mn, Cu, Ni, Cd, Co, and humic acids.

COATED GRAINS (oolites, pisolites, sphaeroids, etc.)

Different types of coated grains have been described in the literature (e.g., Peryt, 1983; Augustithis, 1982). These grains are of both primary (e.g., physicochemical and calcareous algal oolitic and oncolitic/pisolitic kinds, and volcanic accretionary lapilli varieties) and secondary (e.g., lateritic/bauxitic pisolitic) origins and are present in nearly all lithologic rocks of sedimentary, volcanic, plutonic, low- and high-grade metamorphic associations. Note that in the present context of ore-related diagenesis a number of syngenetic, diagenetic and exhalative – hydrothermal types of ores are charaterized by coated constituents. The best-known exemplars are oolitic iron, manganese, and phosphate ores. The gangue material of ore deposits, e.g., dolomite of Pb – Zn Pine Point and other M.V.-type ores, exhibit "colloidal"-type features that are part of the group of the collectively called coated textures/fabrics/structures. To fully reconstruct the environment of formation of the ore, the gangue minerals must be investigated with equal vigour.

As in so many other sub-disciplines in geology, here too comparative studies of the multifarious coated grains are needed in order to establish the similarities and differences of their petrographic features and petrology/petrogenesis; we also must recognize the transitional/gradational and overlapping cases. The power of contrastive-type approaches is well-illustrated in the following case: one of the authors (KHW) worked in bauxite exploration (Queensland, 1957) and thus became familiar with pisolitic bauxite accretions which formed from the precipitation of components delivered by up-and-down moving groundwater within a clay-rich greywacke precursor. Wolf (1961, 1962, 1965b) then proposed that a similar weathering-residual type process operative on carbonate rocks could possibly form in-situ pisolitic calcrete-like limestones. This was later reconfirmed by Dunham (1965) and Thomas (1965) in their investigations of vadose caliche.

COLLOIDS

Van Olphen (1963), Mason (1965), Berner (1971), Rösler/Lange (1972), and Krauskopf (1979) should be consulted for a general introduction to colloids.

Morgan/Stumm (1964), among many others, discussed the colloid-chemical properties of Mn-oxides.

Yariv/Cross (1979) treated some aspects of colloid systems that control compaction of sediments. Many aspects of the geochemistry of colloids have as yet not been fully applied to diagenesis in general and to ore genesis in particular.

COLOR

Blatt et al. (1980) and most other sedimentological, environmental and stratigraphic (e.g., Weller, 1960) books deal with color in sediments, and some in ore deposits.

Morad (1983) investigated the diagenesis and geochemistry of a Proterozoic sedimentary deposit and obtained evidence for the origin of color differentiation.

Southam et al. (1982) in their study of the dynamics of anoxia discussed also the color of sediments, black muds and Eh.

COMPACTION

The literature on petroleum origin offers numerous papers on compaction that do not treat metal transportation, however. The general principles developed by the hydrologists in the oil industry ought to be applied in the future to ore genesis.

Anikouchine (1967) modeled mathematically the distribution of dissolved chemical species in interstitial water of compacting clayey marine sediments (e.g., steady-state distribution of dissolved silica and diffuse flux of Mn across sediment – water interfaces).

Powers (1967) studied the fluid-release mechanisms in compacting marine mudstones/shales (Fig. 42). Mookherjee (1976) reviewed such data in the light of
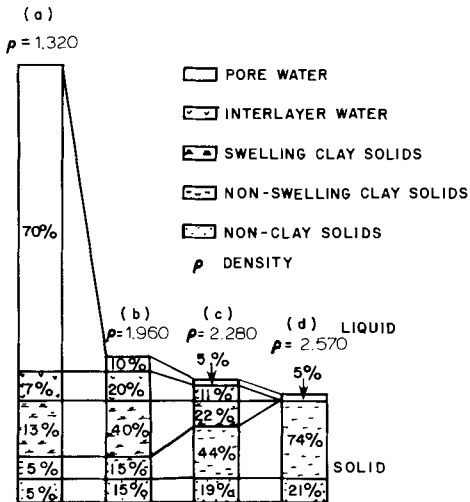
Fig. 47. The changing aspect of marine mud bulk composition during burial and compaction. (*a*) Recent muds, (*b*) after first dehydration, (*c*) after second dehydration, (*d*) after third dehydration. (After Leeder, 1981.)

basin evolution and origin of potential metal-bearing fluids in the formation of both stratabound/stratiform and, for example, late diagenetic/catagenetic vein-type ores.

Dickey et al. (1968) studied high fluid pressures (overpressured condition) associated with slump-type faults that originated contemporaneously with sedimentation. Compaction fluids were prevented from escaping by adjacent shales and faults which acted as barriers.

Burst (1969) illustrated in Fig. 47 the changing of marine mud bulk-composition during compaction/burial from its initial syngenetic (depositional) stage through the first and second stages to the third dehydration stage. The change in pore water is: $70 \rightarrow 10 \rightarrow 5\%$. More data is required as to the concomitant release of metals during dehydration.

Trendall/Blockley (1970) and McGeary/Damuth (1973): Both groups of investigators proposed mobilization of iron and silicates, or merely iron, by early diagenetic compaction. The solution passed upwards through the unconsolidated sediments and reprecipitation of the iron occurred (Figs. 48 and 49). Separation of the chemical phases took place as a consequence of diagenetic differentiation (Fig. 50).

Rieke/Chilingarian (1974) reviewed the many aspects of compaction of fine-grained sediments, and the numerous mechanisms, phases and stages thereof (e.g. Fig. 51).
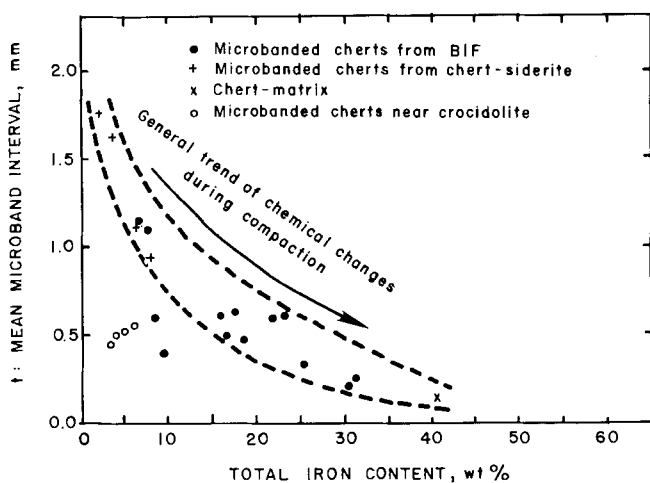
Fig. 48. Graph showing the relationship between total iron content and microband interval in some microbanded chert mesobands of the Dales Gorge Member, Western Australia. (After Trendall/ Blockley, 1970, in Wolf, 1976.)

Roll (1974) offered a detailed semi-quantitative study of the long-time compaction processes of sediments and provided data on both the amounts of fluids released and the remaining bounded water. Is the latter an estimate of potential metamorphic water available?

Note: To determine the maximum possible amounts of metals (and oil) that can be released from sediments, such calculations are indispensable.

Seibert (1976) proved the early diagenetic authigenic origin of glauconite by ascending pore fluids (i.e., by diagenetic hypogene fluids?). The genesis of greensands is divisible into three phases: sedimentary, early diagenetic (mechanical compaction, weathering, glauconitization), and late diagenetic (chemical compaction, partial replacement of glauconite by calcite).
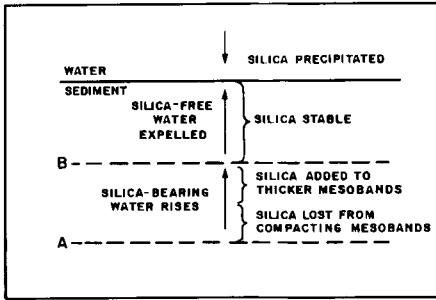
Fig. 49. Diagram illustrating the suggested movement of silica during the diagenesis of iron formations. (After Trendall/Blockley, 1970, in Wolf, 1976.)
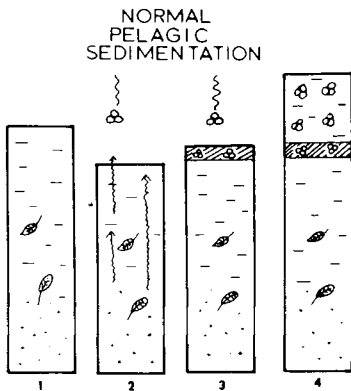
Fig. 50. Mechanism of crust formation. *1* = Plant-bearing turbidite is deposited; *2* = decaying plants reduce iron, which dissolves; compaction fluids carry reduced iron upward in solution; *3* = reduced iron comes in contact with sea water, oxidizes, and precipitates, cementing pelagic ooze; *4* = compaction is over; normal pelagic sedimentation buries crust. (After McGeary/Damuth, 1973, in Wolf, 1976.)

Sharp/Domenico (1976) studied the energy transport and gravitational compaction of sediment which generate pore-fluid pressure and determine porosity and temperature distribution in a basin.

Wolf (1976) reviewed the numerous processes, phases, etc., of compacting coarse-grained sediments, including the control of compaction on ore genesis.

Einsele (1977) discussed the range, velocity, and material flux of compaction-fluid flow as controlled by sedimentation rate, underconsolidation, diagenetic reduction of pore space, etc.

Tweedie (1979) described a multi-metallic hydrocarbon-containing mineralization which may have been formed from metal- and hydrocarbon-rich compaction fluids that migrated from buried Devonian sediments up through fractures into the granite. The latter was hot enough to cause intense hydrothermal alteration (Fig. 52).

Bishop (1979) discussed the compaction history of shales as shown by density/depth and pore pressure/depth profiles. The controls are the rate of sedimentation, thickness of the overburden, and the density of sediments.

				Expulsion Of Free Water	Liquid
				Expulsion Of Adsorbed Water	Phase
				Loss Of Water Through Chemical Combination	
				Mechanical Rearrangement Of Particles	Solid
				Mechanical Deformation Of Particles	Phase
				Solution And Recrystallization	
				Elasticity In The Presence Of Water	
0 - 10	10 - 35	35 - 75	75 - 90	Per Cent Porosity	
Recrystal-lization	Mechanical Deformation	Dewatering	Mechanical Rearrangement	Stages	

Fig. 51. Hedberg's compaction model (processes of consolidation and lithification of clay). (After Hedberg, 1936, in Rieke/Chilingarian, 1974, fig. 56.)
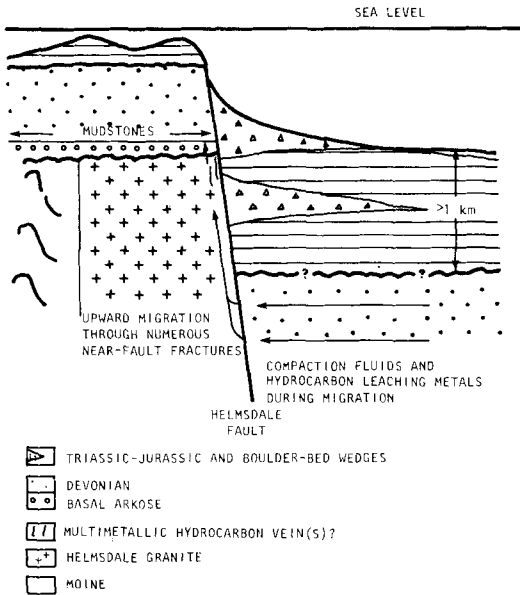
Fig. 52. Possible mechanism for migration and emplacement of metals and hydrocarbons found in Helmsdale Granite and overlying Outdale arkose. (After Tweedie, 1979, p. 151.)

Palciauskas/Domenico (1980) described a certain microfracture development in compacting sediments during burial that raises the question as to whether these fractures could act as conduits to fluids, and upon in-filling could form veins. They also discussed fluid flow as a pressure-dissipating mechanism, and water expansion and gravitational loading as a pressure-producing process.

Henderson et al. (1979) proposed a brine-leaching mechanism of phosphorite genesis. The Australian Georgina deposits are "typically underlain by an interval of what was black organic-rich shale prior to weathering. This in turn passes down to a leached collapsed horizon formerly occupied by an evaporite of uncertain original thickness, now represented entirely by chert pseudomorphs". The nature of "collapse-related" deformation structures suggests that evaporite dissolution was an early diagenetic event which took place before the accretion of a substantial overburden and lithification of the overlying shale. The black shales represent a disseminated phosphate source and the brines, derived from dissolution of the evaporite, leached phosphate during their upward migration toward the seafloor. Concentrated brines, largely as a result of Mg-ion pairing, show a dramatic increase in phosphate solubility relative to normal seawater. As seawater concentrated to a tenth of its volume, its phosphate solubility potential increased by two orders of magnitude. The phosphate concentrated and transported in this way was precipitated near the sediment/seawater interface where the brines must have experienced dilution and eventual oversaturation in phosphate. Mechanisms involving calcium carbonate replacement, probably under kinetic control, appear to have been

important in nucleating apatite precipitation. Petrographic data suggest that most clasts of pelletal phosphorite varieties are replacements of calcium carbonate precursors. The final concentrating process appears to have been mechanical. Submarine reworking of the sediment column is thought to have occurred, leaving clean well-sorted pelletal phosphorite, typical of the Georgina deposits, essentially as a "lag accumulation" that may be economically viable in the future. This model may have general application for black shale – dolomite – chert – phosphorite associations, with the formerly present evaporites removed by dissolution.

Bonham (1980), Magara (1980, and many other articles by him), Borst (1982), and Bond et al. (1983) provided general data on aspects directly or indirectly related to compaction as well as associated subsidence, eustasy, hydrocarbon migration, porosity – depth relations, lithification, delithification, etc. – all to be considered eventually in general basin analysis in the study of ores.

Pavlov/Postel'nikov (1980), Garlick (1981), Badham (1981), N.G. Smith et al. (1983), Mostaghel (1983), Goryainova (1983), and Sawkins (1984) applied the compaction hypotheses to ore and/or hostrock genesis in reconstructing, for example, the source of iron, slumping features, "exhalations" of meteoric (non-volcanic) formation fluids; in geophysical log documentation of fluid migration from compaction shales to form Pb – Zn M.V.-type ores; and in evaluating tectonic-decompression effects in ore genesis, and episodic dewatering of basins to form Proterozoic Pb – Zn deposits.

Guidish et al. (1985) provided an overview of using burial history calculations in evaluating basins. (See also Metamorphism.)

Goryainov/Goryainov (1984) explained the "unsinkability" of Fe – Mn nodules as the consequence of fluid movements to the surface due to the "plastic pressure" in association with compaction of pelagic oozes.

Sawkins/Russell (1985) related dewatering of sedimentary basins, and thus hydrology and compaction, for example, to ore genesis (e.g., Pb – Zn deposits).

– See also Remobilization for several papers on U supplied by compaction fluids; see also Hydrology, Fluids, and M.V.-type ores.

COMPLEXING

Irving/Williams (1948, 1953) offered data on the order of stability of metal and transition metal complexes; Mortensen (1963) described complexing of metals by soil organic matter; Mortland (1970) and Bayer (1964) studied clay-organic complexes and their interactions; whereas Saxby (1973) and Gardner (1974) examined complexing as related to sulfides in sediments.

Seward (1973) and Nicholson (1980) suggested that the transport of Au in solution can occur in a number of ways: e.g., as Au – thio complex species and Au-chloride complex species, and Au in colloidal state are the important modes. Can warm to hot compaction fluids provide Au and other metals?

Granier et al. (1979), Křibek/Podlaha (1980), Wilson (1980), Ruppert (1980), and Sohn/Hughes (1981) provided data on U – Pb in acidic and chelating environments, and discussed stability of UO_3 – humic acid and other complexes, complexing effects on rate of Mn-oxidation, chemical speciation and fixation of metals on hydrous Mn and Fe-oxides during nodule formation, and Zn – Cu – Cd complexing and elemental enrichment.

Balakishiyeva/Rashidova (1980) modeled chemically the process of complexing, considering also river input, pH, Eh, and dissociation versus temperature, among others.
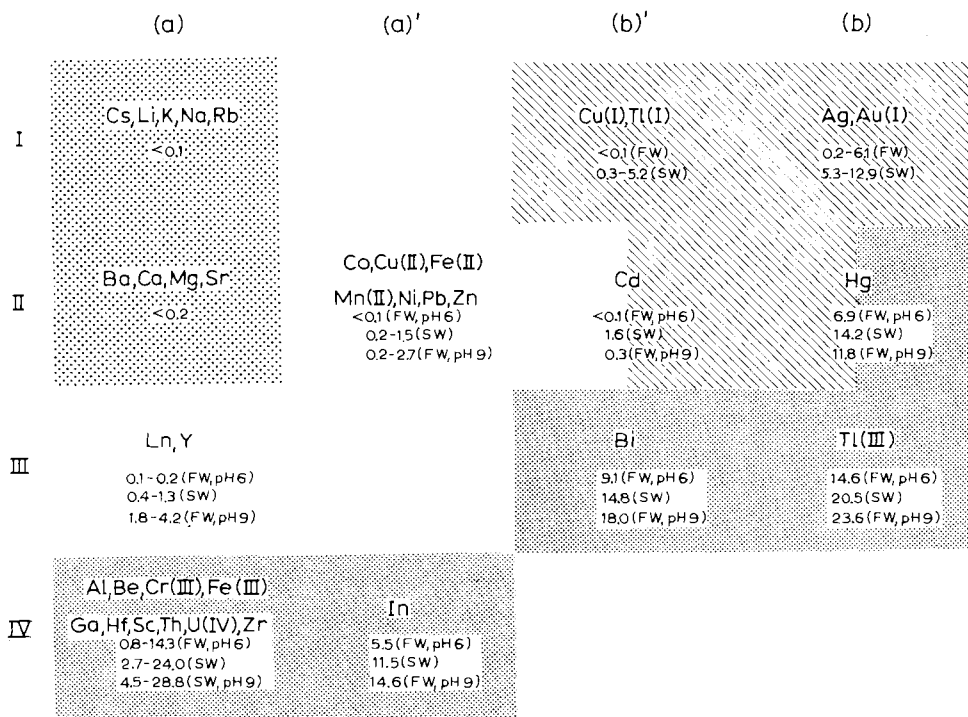
Fig. 53. Complexation field diagram for the cationic elements. The symbol Ln^{3+} represents the lanthanide series. The cations are divided into four groups both on the horizontal axis ($\Delta\beta$, see fig. 6 in Turner et al., 1981) and on the vertical axis (z^2/r, see fig. 3 in Turner et al., 1981). The figures given below each group of elements show the range of $\log\bar{\alpha}_m$ values calculated for model seawater and freshwater (see tables 1 – 4 in Turner et al., 1981). Darker shaded area = very weakly complexed cations; cross-hatched area = chloro-dominated cations; lighter shaded area = hydrolysis-dominated cations. (After Turner et al., 1981.)

Rashid (1971, and other articles), Patchineelam/Förstner (1977), Hallberg et al. (1979), and Dramer/Duinker (1984) offered general information on complexation of metals in natural waters and sedimentary systems.

Giordano/Barnes (1981) concluded that bisulfide and chloride complexes as well as complexes involving ligands are capable of supplying Pb for the formation of Mississippi Valley-type ores; that is, organometallic complexes are important metal-carriers in contrast to inorganic complexes which are inadequate in this respect.

Turner et al. (1981) studied, among numerous other aspects (see pH and Thermodynamics), the complexation of the elements in the periodic table. Figure 53, for example, outlines the complexation field for the cations, divided into four groups: e.g., very weakly complexed, chloro-dominated, and hydrolysis-dominated cations.

— See also Adsorption, Clays, Organic matter, and pH (e.g., Goleva, 1980).

CONCENTRATION (of solutions, rocks, etc.)

Kinsman (1966) discussed the relations between brine concentration and sedimentary environment (lagoon − algal flat − sabkha), molar concentration of ions, and molar $Mg^{2+}:Ca^{2+}$ ratio, on one hand, and the origin of aragonite, gypsum, anhydrite, magnesite, and dolomite, on the other (Fig. 54). Such data must be considered in the origin of hostrocks and gangue minerals, and compared/contrasted with the geochemical constraints on the ore-forming minerals. The total paragenetic history of an ore deposit must be reconstructed, not merely that of the ore minerals.

Rieke/Chilingarian (1974) reviewed part of the literature on the evolution of the composition of fluids during compaction (see Figs. 55 − 62).
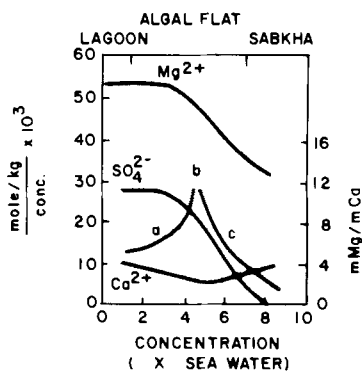
Fig. 54. Relations between molar concentration of ions, the molar ratio $Mg^{2+}:Ca^{2+}$ and brine concentration in the Abu Dhabi sabkha. (After Kinsman, 1966, in Leeder, 1981.) a = aragonite, gypsum; b = magnesite; and c = anhydrite, dolomitization.
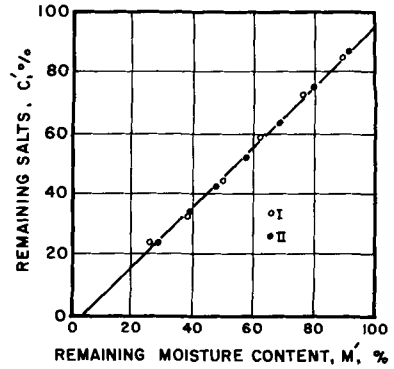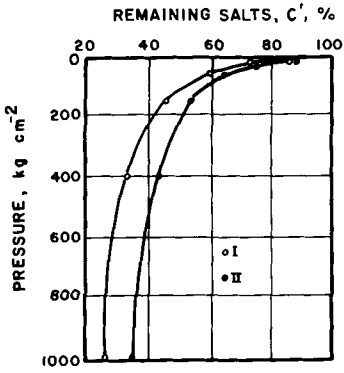
Fig. 55. Geostatic leaching curve showing the relationship between percentage of remaining salts and compaction pressure, based on experimental data. I = experiment no. 1, II = experiment no. 2. Remaining salts, C', % = (content after compaction, mg-equiv. 1^{-1})/(content prior to compaction, mg-equiv. 1^{-1}) $\times$ 100. (After Rieke/Chilingarian, 1974; from Kotova/Pavlov, 1968.)

Fig. 56. Relationship between remaining moisture content M' (% of original) and amount of remaining salts, C' (% of original). I = experiment no. 1, II = experiment No. 2. C', % = (content of salts after compaction, mg-equiv. 1^{-1}) / (content of salts prior to compaction, mg-equiv. 1^{-1}) $\times$ 100. M', % = (volume of pore water after compaction) / (volume of pore water prior to compaction) $\times$ 100. (After Rieke/Chilingarian, 1974; from Kotova/Pavlov, 1968.)
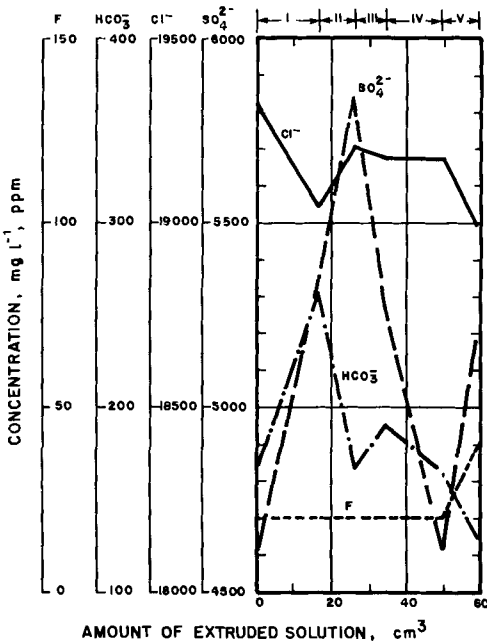
Fig. 57. Variation in concentration of anions with increasing compaction pressure in subsequent fractions of extruded solutions from montmorillonite clay saturated in sea water. (After Rieke/Chilingarian, 1974, fig. 138; from Sawabini et al., 1972.)
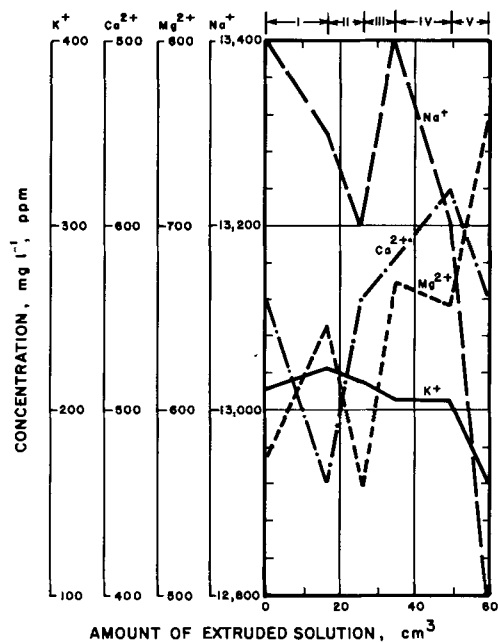
Fig. 58. Variation in concentration of cations with increasing compaction pressure in subsequent fractions of extruded solutions from montmorillonite clay saturated in sea water. (After Rieke/Chilingarian, 1974, fig. 139; from Sawabini et al., 1972.)
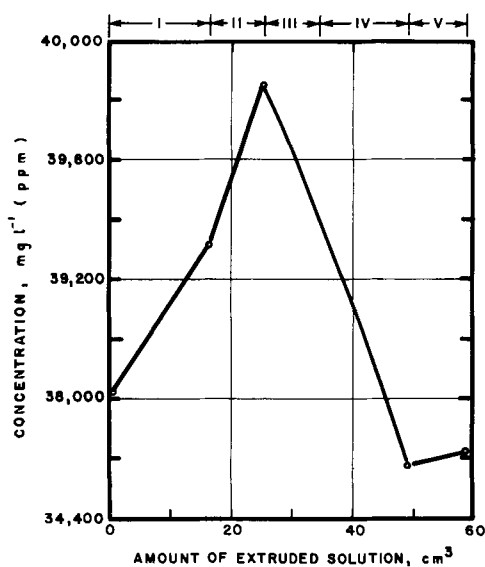

Fig. 59. Variation in total dissolved solids content with increasing compaction pressure in subsequent fractions of extruded solutions from montmorillonite clay saturated in sea water. (After Rieke/Chilingarian, 1974; from Sawabini et al., 1972.)

Note: Little data is available on the evolution of metallic elements in conjunction with the changes of formational fluids in sedimentary and volcanic basins.

Holland/Petersen (1979) discussed the conditions and processes of the dispersion and concretion of elements in relation to ore genesis, i.e., the physical, chemical, and biological mechanisms of endogenic and exogenic mineralizations, including
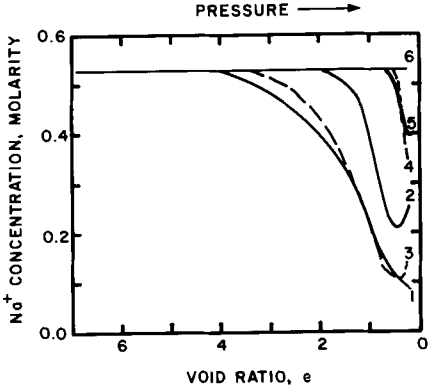
Fig. 60. Variation in Na$^+$ content of pore water expelled during compaction with increasing pressure (decreasing void ratio). *1* = bentonite, theoretical; *2* = bentonite, experimental; *3* = montmorillonite, experimental; *4* = illite, theoretical; *5* = illite, experimental; *6* = kaolinite. (After Rieke/Chilingarian, 1974, fig. 134.)
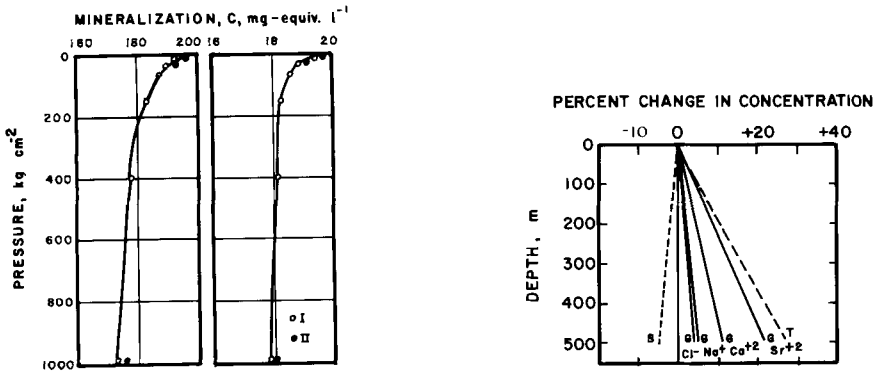
Fig. 61. Variation in mineralization of pore waters remaining in formation after application of overburden pressure. *I* = theoretical curve, *II* = actual experimental data. (After Rieke/Chilingarian, 1974, fig. 133; from Kotova/Pavlov, 1968.)

Fig. 62. Estimated changes in steady-state concentration of interstitial waters in a sediment column owing to various mechanisms. Starting solution is sea water. *G* = downward enrichment caused by gravitational settling of specific ions. *S* = changes due to *Soret migration* of ions toward cooler pole (thermal gradient = 3.3°C/100 m^{-1}; 0.01 *M* NaCl); *T* = approximate changes owing to the net movement of ions toward hotter pole in presence of cation-exchange media (thermal pumping). Total enrichment should approximate sum of *G* and *T*. (After Rieke/Chilingarian, 1974, fig. 121; from Mangelsdorf et al., 1970.)

diagenesis. Uranium in particular is used as an exemplar, but other elements are considered also, especially related to future low-grade resources.

Lewan/Maynard (1982) in their study of factors controlling V- and Ni-enrichment in bitumen of organic sedimentary rocks offered an excellent pH/Eh diagram (see pH section), a Ni-concentration overview (Fig. 63), and a graph showing the control of sediment thickness (see Depth).

Boudreau/Westrich (1984) demonstrated that sulfate concentration in marine sediments controls bacterial sulfate reduction.

NICKEL CONCENTRATIONS
(ppm DRY WEIGHT)
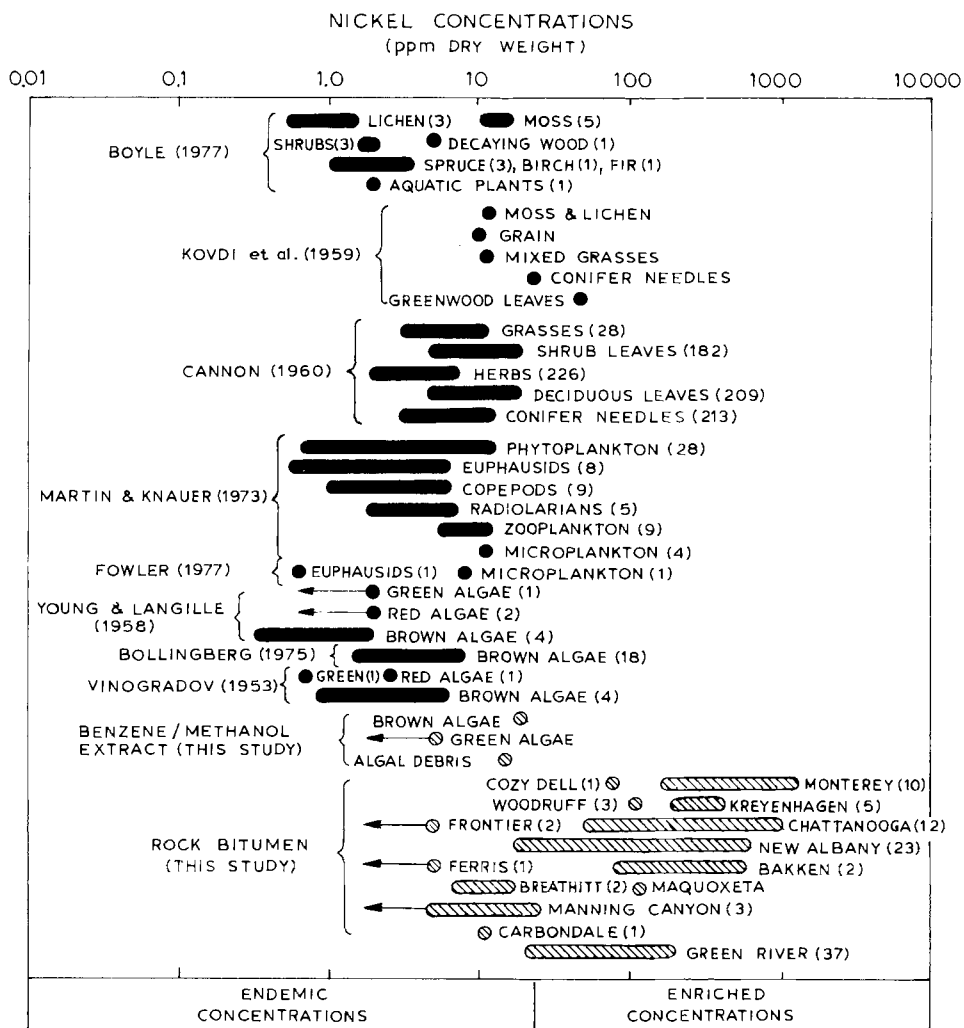
Fig. 63. Range of nickel concentrations in living matter and in bitumens extracted from sedimentary rocks. Number of samples given in parentheses. (After Lewman/Maynard, 1982.)

146

Stage	Facies						
	R	D	L	LG	T	SS	DS
Siderite							
Silica							
Pyrite							
Ankerite							
Calcite							

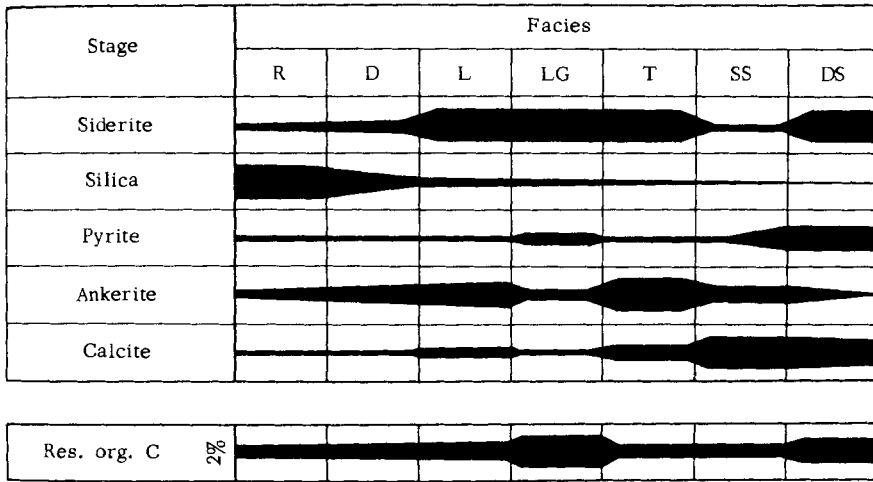| Res. org. C	2%						

Fig. 64. Occurrence of the various phases in the various types of facies. *R* = river beds; *D* = deltas; *L* = lagoons; *LG* = lagoon gulfs; *T* = talus sands; *SS* = shallow sea deposits; *DS* = deep-sea clays. (After Wolf et al., 1967; from Brovkov, 1964.)

Q A	Q A with siderite	A with Q and siderite	A C with siderite	Zones of diagenetic formation
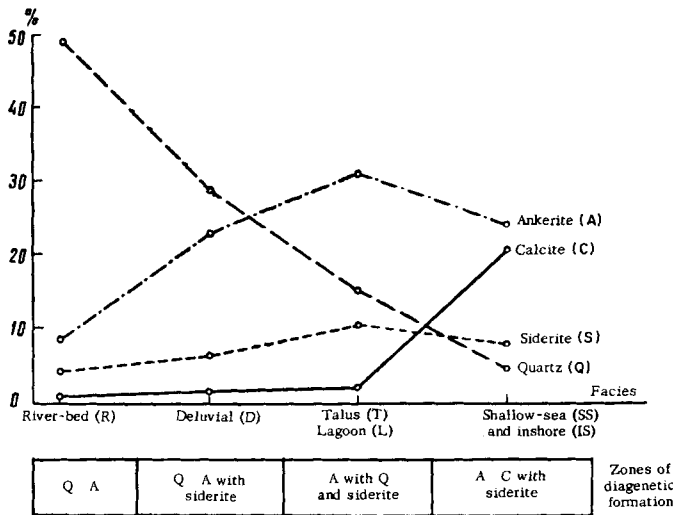
Fig. 65. Authigenic zones and relative proportions of quartz and carbonates in the cement of sandstones – siltstones of various facies. *Q* = quartz; *A* = ankerite; *C* = calcite. (After Wolf et al., 1967; from Brovkov, 1964.)

CONCRETIONS – NODULES

Brovkov (1964, in Wolf et al., 1967) and Weber/Williams (1965) offered two ex-
amples illustrating the use of detailed trace-element and mineralogical data in
reconstructing the original diagenetic processes and through them the depositional
environment. Weber and Williams studied the ranges of trace elements in so-called
syngenetic (?) nodules from shales and found that Si, Al, Mg, Ca, Ba and V are
useful indicators which separated the freshwater from the marine samples, but are
less useful in distinguishing brackish water shales. Brovkov, on the other hand,
recognized mineralogical changes in both cement types and concretions within ter-
rigenous clastic sediments (Figs. 64 – 66).

Berner (1969) studied the migration of Fe and S within anaerobic sediments by using
three alternative diagenetic models to explain the origin of pyrite concretions, layers
and pyritized fossils.

Fisher (1977) studied in detail the composition and origin of diagenetic geodes
characterized by sulfides and celestite/barite, believed to be linked with the origin
of Mississippi Valley-type ores. The geodes were formed by reactions involving
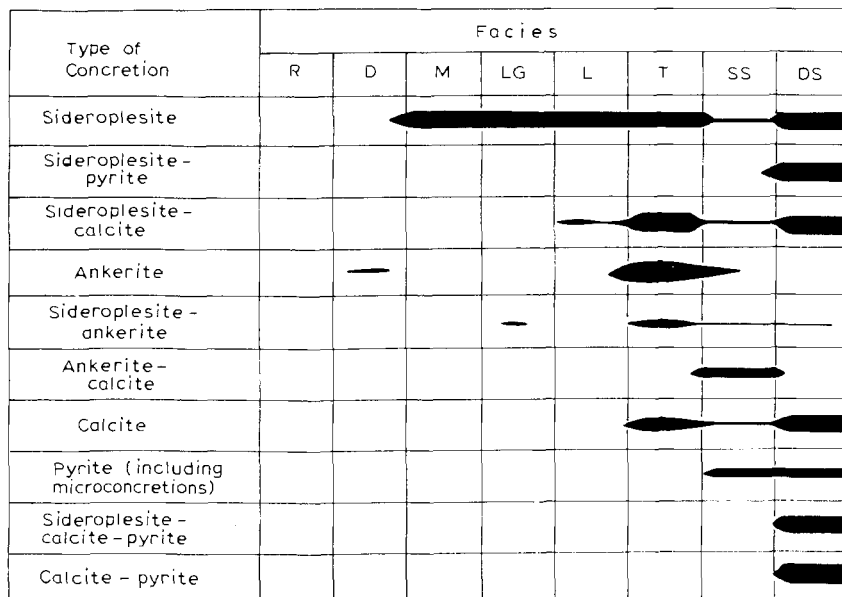meteoric water and upward-seeping formation fluids.

Type of Concretion	Facies							
	R	D	M	LG	L	T	SS	DS
Sideroplesite								
Sideroplesite – pyrite								
Sideroplesite – calcite								
Ankerite								
Sideroplesite – ankerite								
Ankerite – calcite								
Calcite								
Pyrite (including microconcretions)								
Sideroplesite – calcite – pyrite								
Calcite – pyrite								

Fig. 66. Occurrence of different types of concretions in the various facies. R = river beds; D = deltas;
M = marshy lakes; LG = lagoon gulfs; L = lagoons; T = talus sands; SS = shallow sea deposits; DS
= deep-sea clays. (After Wolf et al., 1967; from Brovkov, 1964.)

Hudson (1978): Petrographic and isotopic study of concretions revealing the diagenetic history of pore waters, paleotemperatures, compactional development, and origin of calcite, pyrite, and barite. A similar approach would be useful in the investigation of gangue and ore minerals of metalliferous deposits, e.g., Mississippi Valley-type deposits.

Yudovich (1980a) provided a useful compositional – genetic classification of concretions and rocks.

Coleman/Raiswell (1981) studied the isotope variations in concretions. Such investigations are important since many metal concentrations occur as concretions/nodules. Gautier (1982) discussed siderite concretions as indicators of early diagenesis. See Kaldi (1980) for nodular structures in limestones.

Skomyakova (1979), Halbach et al. (1981a,b, 1982), Reyss/Lalou (1981), Lyle (1982), and Kerr (1984), among many others (in journals and books) presented data of Fe – Mn nodules and associated trace/minor metals (e.g., Co), with numerous diagenetic mechanisms involved in their formation.

Pearson (1985) and Zachmann (1985) offered modern studies of concretions. The latter also investigated the metal elements concentrated by the concretions: the metals were derived by leaching from the hostrock (see Zachmann's model depicting proximal to distal changes).

Peryt (1983) and Augustithis (1982) summarized the data of the collectively called coated grains (see separate section) that include oolites, pisolites, sphaeroids, concretions, and related fabrics/structures of primary and secondary origins in all types of sedimentary, volcanic, plutonic, and metamorphic rocks, including concretionary-type ores.

Kidnadze (1984) found three types of diagenetic-to-catagenic sulfide concretions in the hostrocks of Cu-pyrite deposits and described their paragenesis and environment of formation. Boles et al. (1985) analyzed septarian concretions with vein-fillings and determined the Ca – Fe – Mn – Mg evolution in time and space. Such concretions may offer data revealing the control of hostrock environment in the origin of any associated larger economic ore concentrations. Concretions ought to be compared also with cements of the host and country rocks.

COPPER

Fleischer et al. (1976) and Jung/Knitzschke (1976) summarized the origin of the Zambian Copperbelt and Kupferschiefer deposits, respectively. These researchers, of course, have considered diagenesis. Chartrand/Brown (1984) compared a Canadian Cu-deposit with the Copperbelt occurrence; Samama (1976) provided a comparative review of the genesis of the Cu – Pb sandstone-type deposits using the
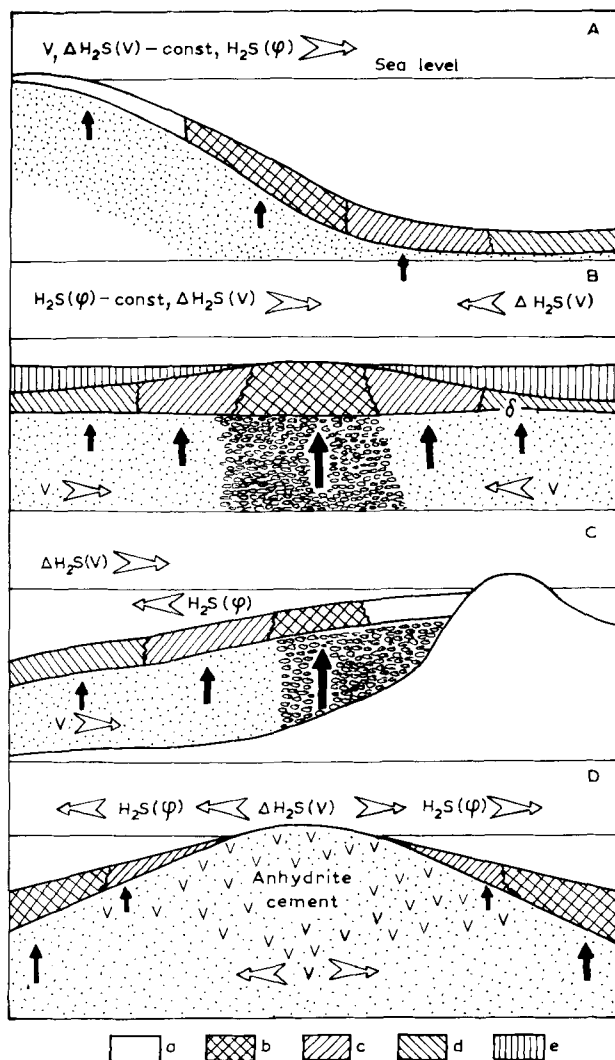
Fig. 67. Types of relation between sulfide zones and sedimentation conditions in a marine basin and the volume of the mineralizing solutions: (A) composition change in copper sulfides due to change in facies, with mineralizing solutions entering uniformly over the area (Beretyan deposit in Donbass); (B) change in copper sulfide composition due to change in volume of mineralizing solution per unit area, facies constant (Richelsdorf deposit in the Federal German Republic); (C) change in copper sulfide composition caused by changes in volume of mineralizing solution and facies, with the two variables acting together (Chambishi deposit in the Zambian copper belt); (D) change in copper sulfide composition due to change in volume of mineralizing solution and in facies, but with effects in opposite senses (Rudna mine at the Lubin-Seroszowic deposit). The vertical arrows show the intensity of entry of mineralizing solutions. The horizontal arrows are directed towards increase in the quantities denoted by the symbols: $a = Fe_2O_3$, $b = Cu_2S$, $c = Cu_5FeS_4$, $d = CuFeS_2$, $e = FeS_2$. (After Lur'ye, 1982.)
V = volume of mineralizing solution(s) entering per unit area; φ = facies; δ = impermeable bed; $H_2S(\varphi)$ = the H_2S content in interstitial water is dependent on the facies φ.

syngenetic, diagenetic and epigenetic models; and Rayner/Rowlands (1980), Němec/Holub (1980), Lange/Sherry (1983), Lambert et al. (1984), Perkins (1984), and Ripley et al. (1985) provided general data of stratiform/stratabound Cu, Cu – Zn, Cu – Ag ores, for example. Gablina (1981) presented new information of the Dzhezkazgan Cu-deposits considering facies distribution and mixing of reducing and oxidizing fluids. Knutson et al. (1983) deliberated the geochemical constraints on Cu-ore genesis.

Heggie (1982) proffered data on Cu in surface waters. How does metal concentration in surface waters control metals in interstitial solutions? Can such solutions eventually become ore-formers?

Brown/Chartand (1983) discussed the interaction of atmosphere, hydrosphere, biosphere, and lithosphere during the origin of stratiform Cu-deposits.

Nishioka et al. (1984) compared a number of paleohydrology hypotheses to explain the origin of Cu-occurrences in stromatolite facies.

Lur'ye (1982) related the Cu-ore composition to "conditions under which the interstitial water interacted with the mineralizing solutions, enabling us to distinguish four types of relations between the facies and the sulfide zones" (Fig. 67): (a) The mineralizing fluids entered uniformly over some area of the marine basin (equal volumes/unit area). Lur'ye's formula (p. 152) showed that the compositional change in the sulfides is entirely determined by the *change in facies*. (b) There are *no facies changes* in the ore-bearing marine sediments and H_2S is constant, so that the sulfides' composition in the ores is entirely controlled by the volume of the solutions per unit area. (c) The H_2S-contents of the interstitial waters and the volumes of metal-bearing solution entering are variable, but their effects on the redox potential (Eh) are in the same sense: both variables simultaneously increase or decrease Eh_s. Thus, the effects of mineralizing solutions emphasize the *lateral shift in facies*. (d) As in type c, both quantities are variable, but have opposite effects on the Eh-potential. Lur'ye provided more pertinent details, including examples of each of the four types of deposits.

COPRECIPITATION

Tsusue/Holland (1966) considered three types of research on the chemistry of ore-forming fluids: (a) fluid inclusions (e.g., Roedder, 1976) in ore and gangue minerals (the most direct approach); (b) phase equilibrium studies placing limits on the fluid's composition (but see Barton et al., 1963, on disequilibrium); and (c) the coprecipitation of ions in minerals in both ore and gangue that assist in reconstructing the chemistry of ore solutions. The authors discussed the coprecipitation of Zn with calcite and the influence of NaCl and HS^- in solution, the complexing of Zn^{2+} with Cl^-, and the temperature.
    The following should be considered: (a) The small amount of data that is

available on coprecipitation is discussed in terms of "hydrothermal" origin of the fluids and elements. Some of the information, however, was obtained at 25° and 50°C, for example, so that it can be applied to diagenetic – catagenetic conditions. In certain sedimentary basins, the temperature of hot formation waters exceeds over $90° - 100°C$ at greater depth. (b) More work is required on fluid inclusions in conjunction with coprecipitation investigations on early diagenetic to higher-grade late diagenetic and burial metamorphic minerals in basins. Possibly an answer can be found to the following questions: Can a *sequence* of coprecipitation of elements in minerals from the oldest to the youngest stratigraphic units be established? Is there a parallel change in the fluid-inclusion composition?

Baumann et al. (1968) – to mention a lesser-known publication – and many others (e.g., Loftus-Hills/Solomon, 1967) used trace-element characteristics of pyrite, galena, sphalerite, magnetite, and others to solve petrogenetic problems, e.g., to distinguish different environments of origin (see their numerous tables and figures). For example, it was possible to divide the minerals into kata-, meso- and epithermal sphalerite based on their In- and Ga-contents. The same was done with galena, sphalerite and pyrite by using a variety of other trace elements. The magnetite was divided into intramagmatic, contact pneumatolytic, hydrothermal (= intracrustal), submarine – exhalative, and sedimentary types as based on numerous trace-element contents. The trace-element distribution of the hostrocks around $Cu - Pb - Zn$ ore deposits of Japan were briefly summarized.

Note: (a) The precise mode of incorporation of the trace elements into their host mineral(s) was in most cases not established. Some trace elements were certainly taken up by coprecipitation, either syngenetically or diagenetically. (b) As to the "sedimentary" types of minerals, no distinction was made between syngenetic and early to late diagenetic types. Thus, in the future more detailed trace-element work is required to recognize the sub-types of "sediment-hosted" minerals, so that these in turn can be distinguished from the "hydrothermal – exhalative – sedimentary" varieties. (c) The use of "epithermal" has become ambiguous insofar as there may be igneous-, metamorphic- and sedimentary-processes-related epithermal fluids, all falling into the specific temperature – pressure range stipulated by the definition of "epithermal". Even late diagenetic and catagenic basinal fluids can be epithermal. This problem too has to be resolved. (d) Many of the uneconomic (low-grade) coprecipitated metals may be remobilized – transported – reprecipitated to form higher-grade ore deposits. The better understanding of syngenetic – diagenetic coprecipitation in sediments and volcanics would enhance recognition of potential source beds.

Popova (1961), Crocket/Winchester (1966), Ohde/Kitano (1980), Kitano et al. (1980), and Okumura et al. (1983) are merely a few of numerous researchers who have investigated the coprecipitation of trace/minor elements (e.g., Zn, F, Cu) with $Ca/Ca - Mg$ carbonates. Okumura et al. also studied anion-removal (F, Cl, sulfate, P, B, SiO_2) from seawater by carbonate precipitation. What elements are available for ore formation during diagenesis?

Urusov (1980) offered data on the energy of equilibrium co-crystallization.

Förstner (1982) discussed five major mechanisms of metal accumulation in sedimentary particles, as listed in Table 56. (See the original publication for details.) Much more data ought to be obtained from studies of Recent sediments and volcanics to understand the various processes in metal concentration during diagenesis.

Hallbauer/Kable (1982) established that coprecipitated trace elements in pyrite can be used to solve numerous problems, e.g., (a) allogenic clastic pyrite can be distinguished from authigenic – diagenetic or metamorphic pyrite (Fig. 68); (b) the provenance of clastic pyrite may be identified; and (c) various generations and/or different types of pyrite may be recognized. Coprecipitated elements should be distinguished from diagenetically – catagenetically – metamorphically replaced elements.

TABLE 56

Mechanisms of metal enrichment in lacustrine sediments, x – xxxx indicate relative significance of the process. C = substrate for coatings (Förstner, 1982, p. 192)

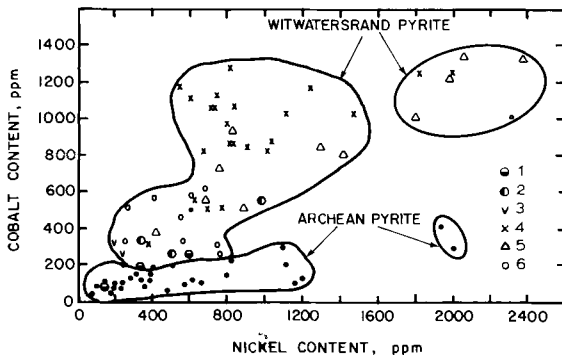|	Rock debris, solid waste material, etc. incl. organic	Metal – hydroxide – carbonate – sulphide	Organic substance (reactive)	Hydrous Fe/Mn-oxide autochthonous)	Calcium carbonate
Inert bonding	xxxx		x		
Adsorption	x			x	
Ion exchange	xx	x	xx	xx	x
Precipitation	C	xx		C	C
Co-precipitation				xxxx	xx
Flocculation			xx		

Fig. 68. Relationship between Co and Ni content for Archean pyrite and Witwatersrand pyrite. *1* = Basal reef; *2* = "B" Reef; *3* = Ventersdorp Contact Reef; *4* = Kimberley Reef, Evander; *5* = Kimberley Reef, Marievale; *6* = Vaal Reef, Klersdorp gold field. (After Hallbauer/Kable, 1982, p. 746.)

– See also Depth (e.g., Mo et al., 1973).

CRYSTALLOGRAPHY

Morgan/Wandless (1980) examined the RRE-distribution in hydrothermal minerals (barite, siderite, galena) as controlled by crystallography. Similar studies are required on diagenetic, catagenetic and all types of metamorphic minerals in combination with textural (micro-zoning) and isotope variation investigations.

Hartman (1982) considered crystal faces, i.e., their structure as related to genesis.

Walkden/Berry (1984) described the calcite crystal growth revealed by cathodoluminescence. The gangue minerals of M.V.-type ores ought to be similarly studied.

– See also Textures, and Zoning.
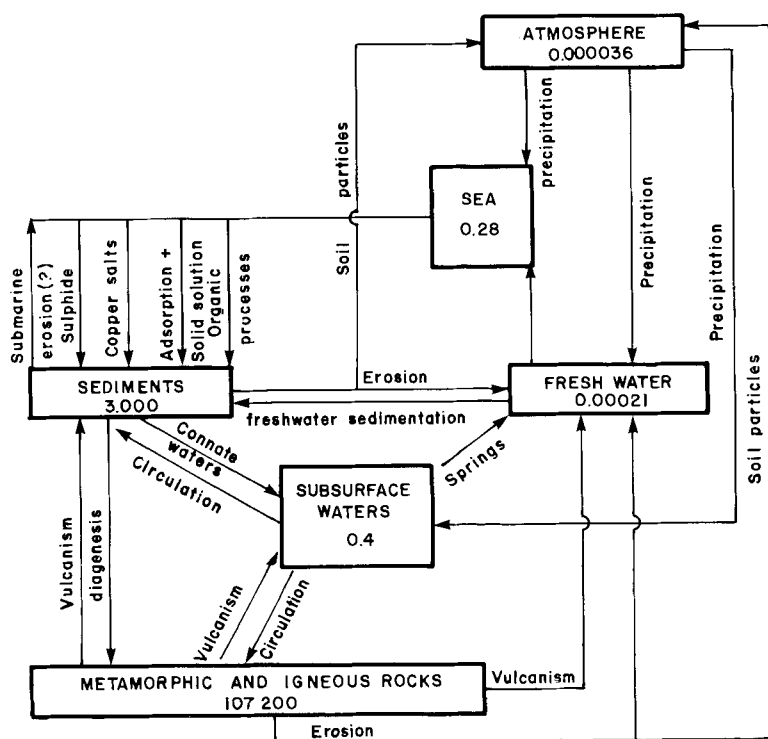
Fig. 69. Diagrammatic representation of the major units and relationships in the geochemical copper cycle. Figures refer to estimated masses of copper in metric tons. (After Rickard, 1970.)

CYCLES

MacIntyre (1970) studied the global cycles that remove and replenish more than seventy elements of the ocean. This paper is an important contribution on diagenesis.

Rickard (1970), Wolf (1976, 1981), and many others, modelized the cycles of elements (e.g., Fig. 69 of Cu and Fig. 70 of Zn).

Note: (a) Most of these cycles are still merely preliminary attempts highlighting the major features only and are qualitative, semi-quantitative, or pretentiously fully quantitative based on incomplete information. Even the qualitative (let alone the quantitative) cycles do not comprise all possible mechanisms of local, regional and
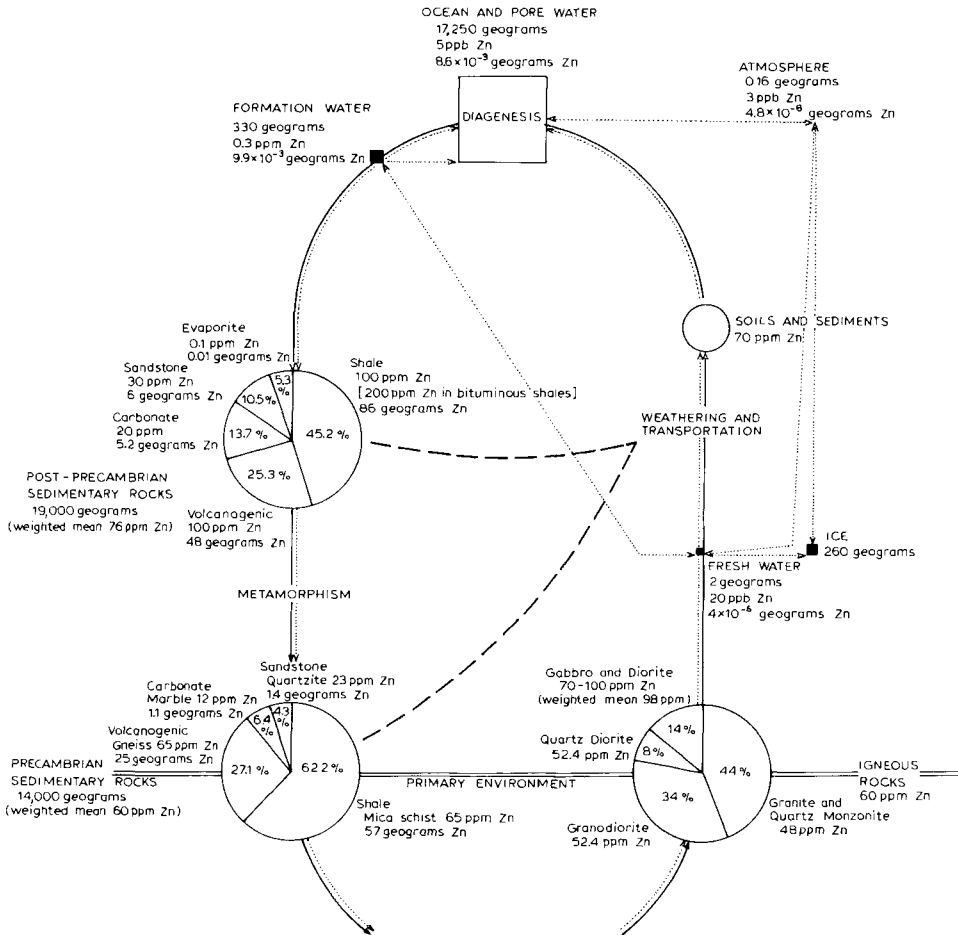
Fig. 70. Distribution of zinc in the secondary environment. (After Hitchon, 1977.)

global significance, either in the atmosphere, hydrosphere, or lithosphere. (b) An all-inclusive cycle of metals during syngenesis – diagenesis – catagenesis is still to be worked out in general, as well as for each chemical element, although preliminary attempts have been published. (c) As pointed out on several occasions (e.g., Wolf, 1981), one eventually should aim to determine the *intersections or overlaps* of the geochemical (or rock) cycles of those elements that constitute specific ore deposits. For example, the cycles of Pb – Zn – Ba – F and S must *intersect* (conceptually speaking) to produce a Mississippi Valley-type deposit. As to the Kupferschiefer-type concentrations, the cycles of the major elements Cu – Pb – Zn and several trace elements Ag – Co – Ni – V – Mo, and rare elements Se – Cd – Tl – etc., have to intersect. Considering the complexity of modeling all the elements' cycles and their innumerable possibilities for intersecting in nature, it is quite obvious that there is not yet enough data available for such exercises that would be of assistance in exploration. However, why not start with the major elements first, progress to the minor and then to the trace elements? (See Gabelman, 1977, for a fine example in U – Th exploration.)

Pilipchuk/Volkov (1974), Crecelius (1974), and Dean (1981) provided examples of specific-metal (e.g., Mo, As, Mn) and specific-environment cycles (e.g., lakes and seas), including inter-elemental relations (see also Saxby, 1969).

Lerman et al. (1975), Garrels et al. (1975), Lerman (1982), and Bulkin (1980) offered information on the modeling of geochemical cycles exemplified by P, concentration-equivalent of element-migration, sedimentary balance through time, and cycles and the global environment (including pollution). (See also Phosphates.)

Brinckman/Iverson (1975) discussed chemical and bacterial cycling in the estuarine system. Data on the cycling of pollution-supplied metals may be applicable to Recent diagenesis.

Ferguson/Gavis (1972), Sclater et al. (1976), Dehairs et al. (1980), Walsh et al. (1981), Garrels/Lerman (1981), Billen (1982), Froelich et al. (1982), Javoy et al. (1982), Sly (1982), Martin et al. (1983), Measures/Edmond (1983), Berner et al. (1983), Ivanov/Freney (1984), and Cutter/Bruland (1984) provided information on the cycles of As, Ni, Ba, C, CO_2, S, N, P, Be, Ag, carbonate – silicate, and Se. These cycles are related to specific milieus (e.g., natural waters, marine and open-sea environments, shelf sediments, Pacific waters, atmosphere); to particular geologic times (e.g., Phanerozoic, Recent); and/or to specific processes (such as geochemical/biochemical cycling, adsorption on suspended particles, chemical saltation, mineral reactions, trace element mobilization, and sedimentary-metamorphic mechanisms); or the cycles are treated in a general global context. Many conceptual models are offered. Bayer/Seilacher (1985) summarized the sedimentary and evolutionary cycles more recently.

Moore et al. (1980) described a local (lake) cycle of Mn involving an interaction of

the biota (algae, bacteria), sediment, Mn-nodules and Mn-coated sand grains, and Mn dissolved in the lake and interstitial waters. The following details have been offered: budgets of Mn in the lake indicate that a net loss of 23 t of Mn is due to Mn-nodule formation. Erosion of the nodules and Mn-coated grains in the well-oxygenated central part of the lake results in their transportation to adjacent deeper more reducing parts. The material sinks into the anoxic sediments and MnO_2 is reduced to Mn^{2+} – this produces a high Mn^{2+}-concentration in the pore waters of the sediments, and Mn^{2+} diffuses back into the watercolumn. Growth of the Mn-nodules alternates between periods of rapid accretion (>1 mm 10^2 yr^{-1}) and of no growth or erosion. Rapid growth may be enhanced by the "stripping" of Mn from the water by algae and bacteria. Periodic high algal productivity produces a high-pH high-O_2 environment, which is maintained throughout the water due to wind-induced mixing.

Claypool et al. (1980), Margaritz/Turner (1982), and Arthur (1984) offered age curves of S-, C- and O-cycles and discussed the controls of input/output fluxes, diagenetic overprints, etc.

Kay (1980) studied the cycling of elements in the context of the crust – upper mantle system (including volcanic arc magmas) (see models in his figs. 9 and 10), in which he included oceanic authigenic hydrothermal pelagic sediments.

Valklump/Martens (1981) described the biogeochemical cycling in organic-rich marine basins, including the flux of components, which is controlled partly by diagenesis (see model in their fig. 6). The system is influenced by pH/Eh and it, in turn, affects metal mobilization.

Zhabin (1981) attempted to define the 11-year solar activity cycle in sphalerite of a vein deposit!

Helbeck et al. (1981) studied the Calvin-Benson cycle and sulfide oxidation enzymes in animals from sulfide-rich environments.

Hallberg (1981) offered an example of recycling of metals in a specific, local to micro-milieu setting, i.e., along the redoxcline.

Honjo (1982) investigated seasonality influencing biogenic/lithogenic particulate flux into sedimentary basins.

Schidlowski/Junge (1981) and Garrels/Lerman (1984) examined the coupling (inter-relations) of the S, O and C cycles. Similar studies are to be carried out on all other elements emphasizing the *intersection/coincidence* of metal (Cu, Zn, Pb, etc.) and nonmetal (e.g., H, S, O, etc.) cycles. Such intersections of geochemical cycles is a prerequisite for ore genesis!

Lasagna (1980) treated the kinetics of geochemical cycles (e.g., linear and non-linear
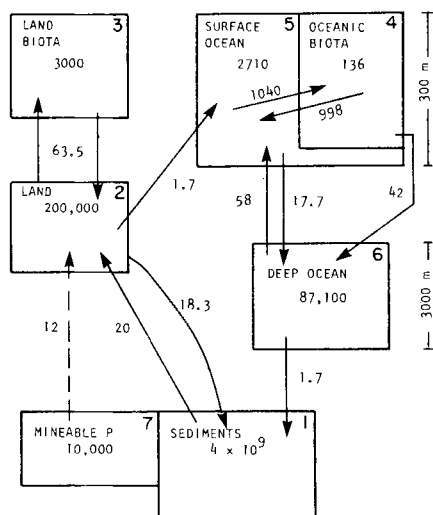
Fig. 71. The phosphorus cycle; phosphorus contents are in units of 10^6 MT of P, and transfer rates are in units of 10^6 MT P yr^{-1}. Assumed depths of reservoirs 5 and 6 are also shown. (After Lasagna, 1980.)
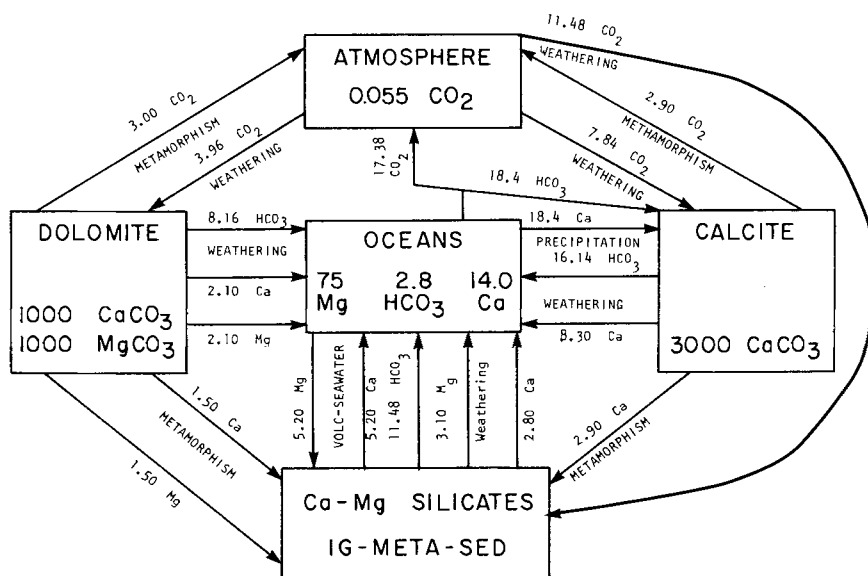

Fig. 72. Carbonate–silicate cycle for the present day. Fluxes of CO_2 and HCO_3^- are corrected for weathering via H_2SO_4 (from pyrite oxidation) and for sedimentary pyrite formation. Fluxes in 10^{18} moles m.y.$^{-1}$; reservoir sizes in 10^{18} moles. (After Berner et al., 1983.)

cycles), as exemplified by the C- and P-cycles (Fig. 71). (See also Evolution, Phosphates, Upwelling.)

Berner et al. (1983) modeled the carbonate – silicate cycle (Fig. 72): it includes the genesis of pyrite. Other sulfides must be similarly treated in the future; also the *interplay* of various hostrock types and sulfides, for example.

Garrels/Lerman (1984) elaborated on the evolution of S- and C-cycles during Phanerozoic time; their qualitative model is useful in general to larger-scale settings, but less applicable to the study of specific micro-scaled environments and processes, for example. The dominant exogenic redox system and cycle is complementary to the sulfide – sulfate – carbonate – organic carbon systems (see models in their figs. 1 – 7).

Walker/Brimblecombe (1985) reviewed the pre-biological (Precambrian) and Phanerozoic plus modern-earth geochemical cycles of Fe and S; to be considered in the examination of iron ore evolution and the development of any ore types that require sulfur.

Froelich et al. (1985) studied the geochemistry of inorganic germanium in natural waters. If trace elements, like Ge, are used in identifying the origin of mineral deposits, their geochemical cycle must be fully understood.

– See also Multi-factorial (Gabelman, 1977), Solubility (Finlow-Bates, 1979/1980), Time, and Zoning.

DATING

Godwin et al. (1982) subdivided the lead-isotope data of galena from syngenetic – diagenetic Ba – Zn – Pb, epigenetic Zn – Pb, and Ag-rich deposits into four distinct fields. This data, in conjunction with constraints imposed by stratigraphy, by K – Ar isotope dates, and by minor-element analyses of sphalerites, define three metallogenic events, two of which are of interest here: (1) "Old carbonate"-hosted Zn – Pb deposits, spatially associated with unconformities. A "karstic model" has been proposed, as shown in Fig. 73, which indicates a multi-stage origin of the ore. (2) The younger shale-hosted Ba – Zn – Pb mineralization is indistinguishable from the older carbonate-hosted Pb – Zn deposits (Fig. 74). These are believed to have originated from brines dewatered from the shale basin, where solutions were guided by faults, either within the basin (i.e., the shale-hosted Ba – Zn – Pb deposits formed along grabens near hinge lines close to the margin of the basin) or peripheral to and away from the basin (i.e., carbonate-hosted Zn – Pb deposits).
Note: (a) Of interest here is the methodology used in separating the three metallogenic events. If a less rigorous approach had been used, could it have been possible to equate the old and the two younger Zn – Pb deposits with each other as

of "epigenetic" origin in two different hostrock sequences? (b) As to the "karstic model", a number of questions arise in general – see Karst. (c) Assuming that the younger shale- and carbonate-hosted Pb – Zn deposits are genetically related, one may ask (Wolf, 1976): what are the late diagenetic conditions within the shale environment that *prevented* the removal of the Ba – Zn – Pb during compaction for example, and why did dewatering of the basin *allow* the movement of some of the Pb – Zn into the carbonate hostrock?

Godwin/Sinclair (1982) used the average age Pb-isotope growth curves in studying shale-hosted Zn – Pb deposits.

Segl et al. (1984) studied the ^{10}Be-dating of an oceanic Mn-crust and its implications for ocean paleocirculation.

Lalou et al. (1985) in their age dating of contemporary sulfides demonstrated that the distribution pattern, scale, size and location of the deposits need to be considered – this applies equally to hydrothermal – exhalative as well as to diagenetic processes and products.
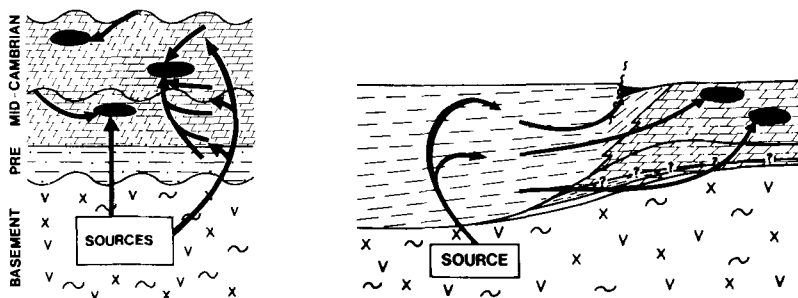
– See also Age, and Isotopes.

Fig. 73. Proposed genetic model for many old carbonate-hosted Zn – Pb deposits in the northern Canadian Cordillera. Sources represent crystalline basement of Hudsonian age. Heavy arrows are conceptual paths of lead transport, and the pattern of arrows is meant to imply residence time in Precambrian or mid-Cambrian rocks prior to extraction during karst development and deposition in mineral deposits at about 0.57 b.y. (After Godwin et al., 1982.)

Fig. 74. Proposed genetic model for young carbonate-hosted Zn – Pb deposits and shale-hosted Ba – Zn – Pb deposits in the northern Canadian Cordillera. The ultimate source of lead is thought to be crystalline rocks of Hudsonian age. Heavy arrows indicate bulk transport of sediments (and lead) into the Selwyn Basin and subsequent extraction and transport of lead during dewatering of the basin. Fluids from which syngenetic deposits formed within the basin are thought to be localized by intrabasinal faults and to be essentially contemporaneous with epigenetic mineralization in adjoining carbonates to the east in the Mckenzie platform. (After Godwin et al., 1982.)

160

Ludwig (1962a,b; see also Baumann et al., 1968) demonstrated the distribution of Cu, Pb, Zn and U in sediments as a function of the depth of the depositional basin (Fig. 75). (See Zoning.)

Note: Depth control of the original environment may determine both syngenetic and diagenetic processes via numerous mechanisms, e.g., changes in the proportion of carbon in seawater from the shore to the deep basin and Eh − pH variations, as in the Baltic Sea and the Black Sea.

Mo et al. (1973) established an interesting relation of uranium concentrations in marine sediments: (1) In estuarine basins the U concentration is directly proportional to the percentage of organic carbon deposited in an anoxic milieu. (2) In deep-sea Mn-nodules there is a direct relation between U- and Ca-concentrations, and both decrease with increasing depth of deposition. (3) Relatively high U-concentrations are present in carbonates in the deepest part of the Gulf of Mexico. A model was proposed where U-enrichment in nearshore environments occurs via an anoxic pathway, followed by redeposition in a deep-ocean environment with dilution, either by low-U-bearing forams or siliceous ooze or, along the continental margins, by dilution with high-U-bearing carbonate sands.

Note: Such data is required to determine the accuracy of studies of ages and rates of sediment accumulation, as well as of reworking − redeposition processes, for example.

Large (1981) and Plimer (1981) pointed out that shallow-water deposits most commonly contain stratiform Fe − Mn, Ba, Zn − Pb (usually pyritic) ore underlain by, or associated with, a footwall alteration zone of vein, disseminated, or stockwork ore. In deep-water settings, the stratiform Fe − Mn − Ba, Cu − Zn − Pb (commonly pyrrhotite-bearing), Sn and W ore is *not* usually underlain by a footwall alteration pipe, and the stratiform ore contains quartz, tourmaline, carbonate or fluorite. In shallow-water deposits, boiling, fluid mixing, or other mechanisms could cause a
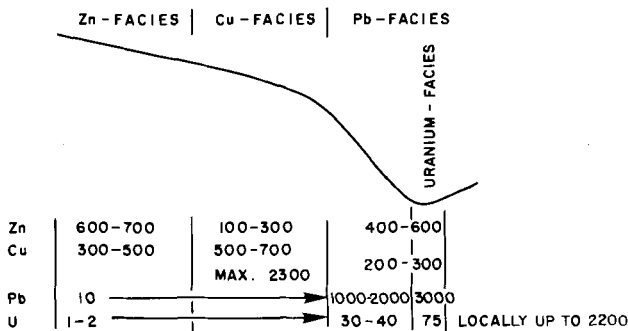

Fig. 75. Distribution of Cu, Pb, U and Zn in a clay-rich unit as a function of depth of the depositional basin. (After Baumann et al., 1968, p. 169.)

temperature decrease with resultant mineral precipitation beneath the seawater/rock interface. In deep water, fluid mixing with consequential temperature decrease takes place primarily in seawater and not beneath the seawater/rock interface. As an extrapolation of the above: all diagenetic processes are likewise controlled by depth, but precise data is missing.

Tarantsev (1981) discussed the depth to roots of ore-forming systems. Similar studies are needed to define the maximum depth of M.V.-type ore genesis, among others.

Halley/Schmoker (1983), Angevine/Turcotte (1983), and Shanmugam (1984), plus others, have studied the porosity changes controlled by burial, thermal gradient and depth. Such investigations must be undertaken on ores and their hostrocks, if they were formed by diagenetic – catagenic – metamorphic solutions passing through permeable rocks.

Halbach et al. (1983), Halbach/Puteanus (1984), Cowen/Silver (1984), and Bischoff/Rosenbauer (1984), among several others during the last few years, offered updated information of the control of water depth (e.g. in the oceans) on $Co - Ni$ concentration, metal fluxes, growth rates of $Fe - Mn$ nodules, carbonate dissolution, bioproductivity, laws of colloidal surface chemistry, diagenetic/bacterial remobilization, temperature distribution, etc.

Lakatos/Miller (1983) utilized fission-track data of apatite/zircon to define burial depth of sedimentary units. Is this applicable to ore hostrocks?

Lewan/Maynard (1982) prepared a graph depicting the thickness of an open sediment system necessary to assure different degrees of Ni-enrichment (Fig. 76).

– See also Pressure.

DIFFERENTIATION – FRACTIONATION – PARTITIONING

Krauskopf (1957) studied the separation of Mn from Fe in sedimentary environments. Note that under certain conditions the separation is either absent or incomplete, e.g., when Mn + Fe are associated in ferromanganese nodules in the contemporary oceans.

Fontboté/Amstutz (1980, 1981, 1982) discussed diagenetic differentiation/fractionation in the origin of "crystallization rhythmites" of several M.V.-type Pb – Zn ores. (See also in Wauschkuhn et al., 1984.)

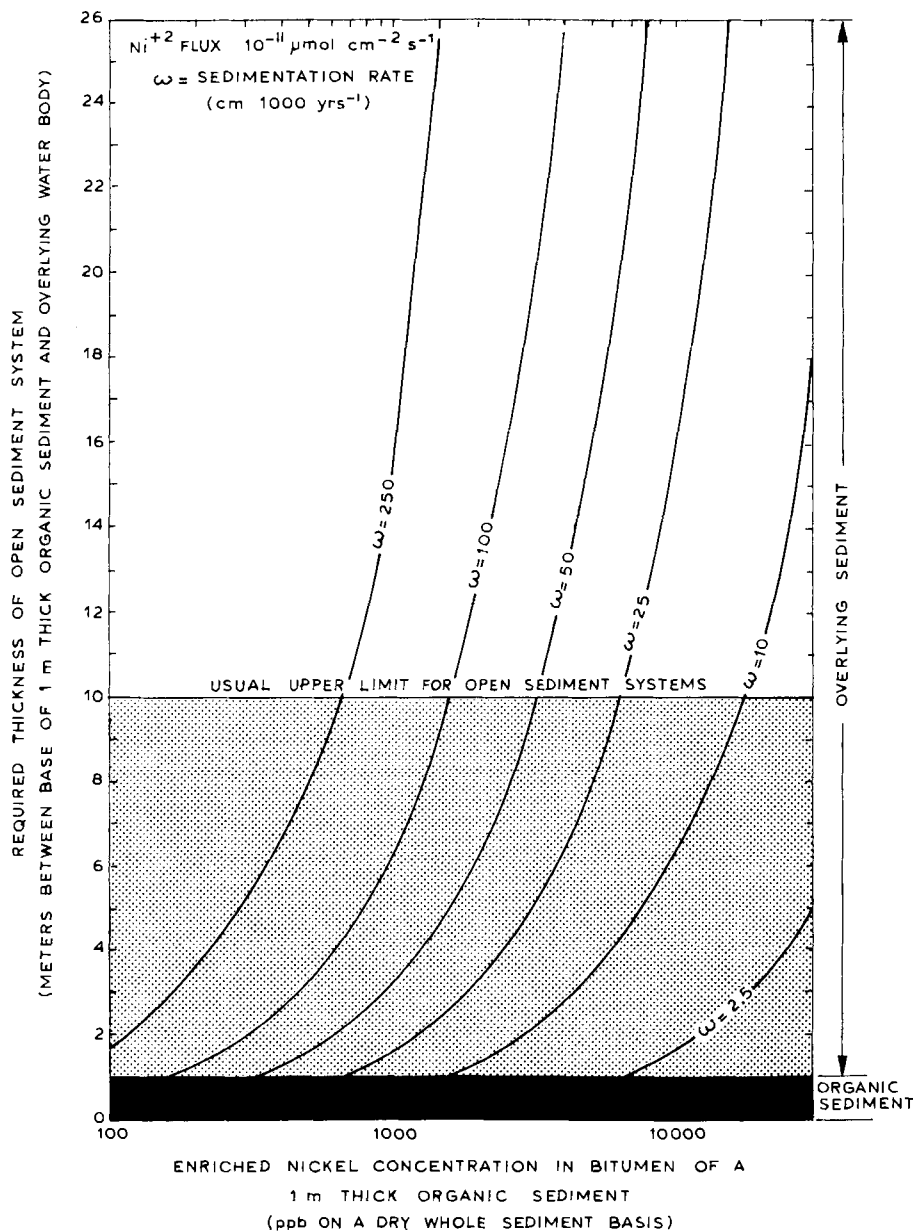Kramer (1980) described element fractionation controlled by pH.

Fig. 76. Graph showing the thickness of an open sediment system that is necessary to assure different degrees of nickel enrichment in the bitumen of a 1 m thick organic sediment at different rates of sedimentation. The calculations assume that all of the nickel that diffuses into the organic sediment forms metallo-organic complexes. Other considerations include a mean dry sediment density of 2.38 g cm^{-3} and a Ni^{+2} flux of 10^{-11} μmol cm^{-2} s^{-1}. The mean water content of the sediment is considered to be 50% by volume and compaction of sediment with burial is not considered. The dashed portions of the sedimentation rate curves indicate conditions under which nickel enrichment is completed by the end of the deposition of the 1 m thick organic sediment. (After Lewan/Maynard, 1982.)

Kitano et al. (1980) studied partioning of pollution-supplied heavy metals in a bay (see also Pollution).

Postma (1981) described siderite, vivianite and rhodochrosite formed by Mn-differentiation, for example, from pore waters in a recent bog sediment. There is a pH control on siderite – vivianite.

Moorby/Cronan (1981), Elderfield et al. (1981a,b), and Halbach et al. (1981a,b), among others, examined the distribution of elements between co-existing phases, differential diagenetic cycling of elements (e.g., RRE), and trace-element differentiation in hydrogenic and early diagenetic nodules – all related to the ferromanganese-concentrating systems.

Förstner/Stoffers (1981) described the fractionation of transitional elements in pelagic sediments.

Varnavas/Cronon (1981) and Frietsch (1982a) outlined the partition/differentiation geochemistry of sediments in hydrothermal mounds and volcanogenic – syngenetic Fe, Mn and sulfide ores. The source could have been a common one, but syngenetic – diagenetic environments caused variations. Therefore, one has to discriminate between primary (syngenetic, depositional) and secondary (diagenetic, catagenetic, etc.) differentiation in both sedimentary and hydrothermal ore genesis.
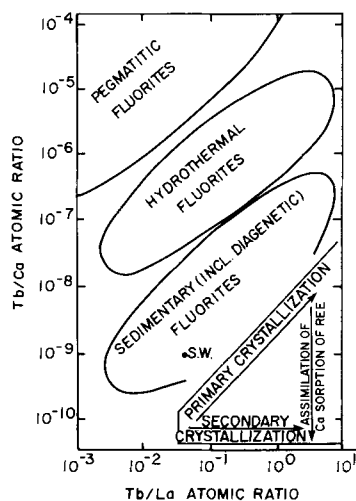

Fig. 77. Schematic Tb/Ca – Tb/La variation diagram for fluorite showing the fields for pegmatite, hydrothermal and sedimentary origins as compiled from various sources (after Möller et al., 1981). The arrows in lower right corner indicate often observed arrangements of data points in the variation diagram. Individual examples for primary and secondary crystallizations as well as interactions with country rocks are given in Möller/Morteani (1982). *s.w.* = seawater.

Calderoni/Ferrini (1984) outlined the diagenetic control on abundances and chemical fractionation of metals in limestones.

Li et al. (1984) discussed partitioning and adsorption of radiotracers between particles and seawater.

Kita et al. (1985) investigated O-isotope fractionation between amorphous silica and water at low to intermediate temperatures: hydrothermalism, diagenesis, etc., all controlled by temperature (among others) determined the O-isotope composition. (See also Silica, and Isotopes.)

Möller et al. (1981) and Götzinger/Weinke (1984), respectively, attempted a new approach in using trace-element concentrations in the study of ore genesis, as exemplified by their data of trace elements in various types of fluorites. That is, they considered Tb/Ca – Tb/La variations (Fig. 77) of hydrothermal vs. diagenetic vs. pegmatitic fluorites as based on a fractionation ("differentiation") index. Such study ought to be carried out on fluorites of various M.V.-type ores and others. What are the differentiation/fractionation potentials during sphalerite and galena genesis? And cassiterites in pegmatites in contrast to lower-temperatures types? Möller offered a Ga/Zn – Ga/Ge variation diagram for sphalerite demonstrating that fractionation also occurred during remobilization. Götzinger/Weinke delineated numerous carbonate minerals, in addition to the fluorites, by using the Na – Cl and Yb/Ca – Yb/La diagrams.

Majumder et al. (1982) studied the elemental differentiation or fractionation (comprising both diagenesis and supergenesis) of a banded iron formation (Figs. 78 and 79).

1. WHOLE ROCK BMQ   5. SECONDARY CHERT   9. SUPERGENE MAGNETITE
2. IRON MESOBAND OF BMQ   6. BISCUITY IRON ORE   IO. SUPERGENE HEMATITE
3. SILICA MATRIX OF BMQ   7. HIGH GRADE IRON ORE   II. SUPERGENE GOETHITE
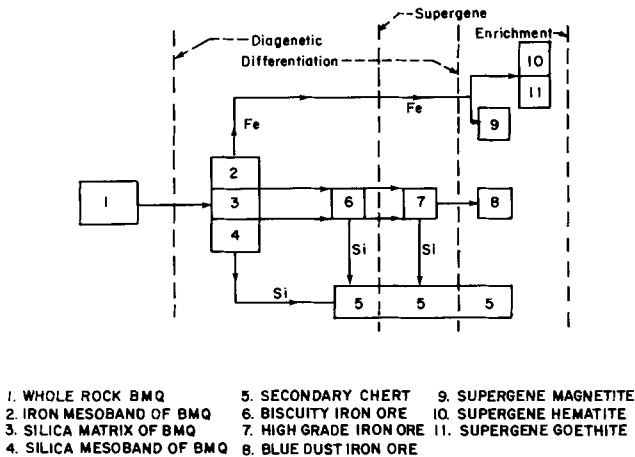4. SILICA MESOBAND OF BMQ   8. BLUE DUST IRON ORE

Fig. 78. Schematic diagram showing the trend of differentiation of elements in the BIF of Orissa and their various supergene products. (After Majumder et al., 1982.)
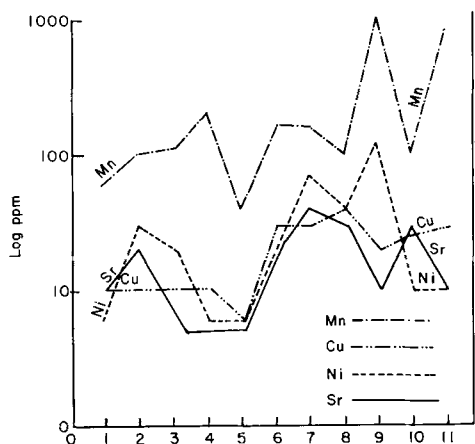
Fig. 79. Variation trend of Cu, Ni, Mn and Sr during fractionation of Orissa Banded Iron Formations. (After Majumder et al., 1982.)
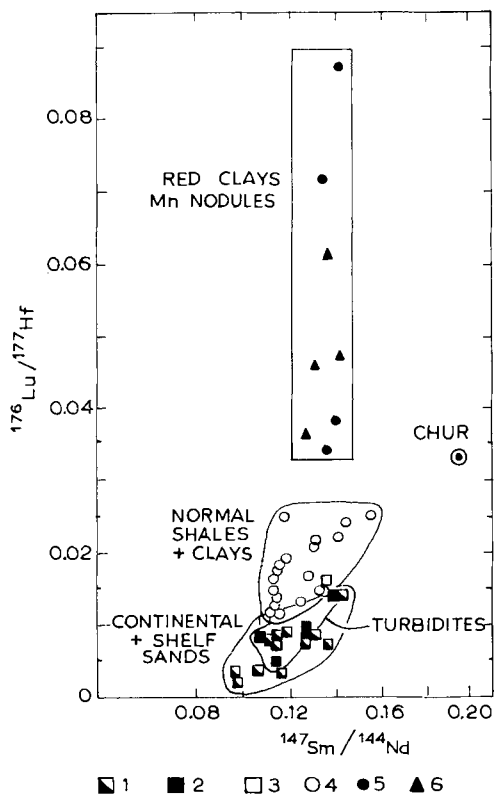

Fig. 80. ^{176}Lu/^{177}Hf versus ^{147}Sm/^{144}Nd plot of sediments of the study by Patchett et al. (1984). 1 = shelf/continental sandstone; 2 = turbidite sandstone; 3 = immature greywacke, volcanic source; 4 = normal shale/clay, any environment and age; 5 = recent REE-rich red clay; 6 = recent manganese nodules. The impure foraminiferal ooze lies off the top of the diagram. *CHUR* = present-day undifferentiated Earth. (After Patchett et al., 1984.)

Patchett et al. (1984) studied the Hf/RRE-fractionation in sedimentary systems and crustal recycling. Their fig. 3 shows the Lu/Hf-isotope distribution in pelagic – turbidite – shelf – continental sedimentary systems and their Lu/Hf vs. Sm/Nd plots in fig. 2 differentiate shales, sands, specific greywackes, etc. As an example, Fig. 80 given here shows that at least four depositional – diagenetic systems can be discriminated. What are the applications of this data to the study of various types of diagenetic ore-forming systems?

– See also Adsorption, Diffusion – Dispersion, and Pollution.

DIFFUSION – DISPERSION

Van Olphen (1963a, b) and Yariv/Cross (1979), among many others, provided general information on diffusion.

Boyle (1968) evaluated diffusion in the origin of Ag deposits and discussed four mechanisms.
   Note: Eventually, the similarities and differences must be established that exist between diffusion and related mechanisms during diagenetic, catagenetic, and metamorphic conditions; i.e., in unconsolidated and lithified deposits, as well as in open in contrast to partly open and "closed" systems.

Lavery/Barnes (1971) and Barnes/Lavery (1977) studied, for example, the dispersion of Zn in carbonate hostrocks adjacent to sphalerite ore zones. The extent, shape, and length depend on the size of the ore zone, concentration of metals in solution, and length of time of exposure of the hostrock to the solution.

Berner (1975, 1980a) described the effects of diffusion, deposition, compaction, adsorption, and chemical reaction upon depth distribution of dissolved elements.

Duursma/Hoede (1976) provided a general review of the principles of diffusion in sedimentary systems in reference to ore genesis.

Tzur (1971) and Lerman (1978), for example, discussed interstitial diffusion/advection of solute in accumulating sediments and chemical exchange across sediment/water interfaces. Such concepts have already been applied to ore genesis modeling, e.g., by Fontboté/Amstutz (1980, 1981, 1982; and in Wauschkuhn et al., 1984), listed under Differentiation.

Schöttler (1975, 1977) described "natural filtration" of heavy metals in association with pollution. Carignan/Tessier (1985) studied the diffusion of Zn in acid lakes. Many of the mechanisms described are most likely applicable to diagenesis as well.

Demin/Sergeyeva (1983) described interphase diffusion zones in ore minerals as in-

dex of intensity of transformation of massive sulfide deposits. Similar studies are to be applied to diagenetic ores.

– See also Differentiation.

DISTRIBUTION (of elements, etc.)

Fleischer (1953) is one of several researchers who have estimated the abundance (distribution) of elements in the Earth's crust. In general, such averaged-out data are less useful for specific-environment-type diagenetic studies, but they are invaluable in more broader-scope deliberations of the sources, remobilization, etc., of potential ore-forming elements, including those involved in syngenesis – diagenesis – catagenesis – metamorphism. (See geochemistry books for up-to-date information.)

Hirst (1962), Gorham/Swaine (1965), Leland et al. (1973), Nissenbaum (1974), Duinker et al. (1974), Lew (1981), Dinur et al. (1981), Loring (1982), and Harbinson (1984), are several of hundreds of researchers who have provided data on the distribution of elements in sedimentary deposits (many Recent in age). Among others, pH/Eh were considered by Gorham/Swaine; factors in general by Leland et al.; S-isotopes and a pyrite model by Lew and Dinur et al.; dispersal factors by Loring (cf. Rose/Wright, 1980, for other types of dispersal); and regional variations by Harbinson.

Goldberg (1965), Durum/Hem (1972), and Duchart et al. (1973), are a few among many who dealt with trace/minor elements in waters. The more data we have on the elemental composition (average, minimum and maximum values) of specific aqueous milieus and on the conditions that control this composition, the better we can reconstruct the diagenetic history of surface-pore-interstitial, and shallow-to-deep subsurface fluid patterns and developments. See also Horn/Adams (1966) for geochemical balances and element abundances, and more modern similar treatments.

Gordeyev/Demina (1979) and Li (1982a) proffered publications dealing with the distribution of elements in Recent ocean-floor hot springs and abyssal ferromanganese nodules.

Rose/Wright (1980) offered dispersion models for sedimentary U-deposits employed during geochemical exploration (see also numerous exploration geochemistry books). Note that much information on dispersion is only indirectly applicable to diagenesis, but certain concepts are concerned with processes useful in the investigation of diagenetic ores.

Maynard (1981) examined C-isotopes as dispersal-pattern indicators.

Peryt/Wazny (1980), Osczepalski (1980), and Fleischer et al. (1976) offered data on elemental distribution of ancient ore deposits, including the Kupferschiefer, whereas Carr (1984) described the primary geochemical and mineralogical dispersion of one Zn – Pb – Ag deposit [e.g., pyrite, siderite and dolomite are common in hostrocks: pyrite is syngenetic/diagenetic and the siderite halo is of secondary (diagenetic?) origin precipitated from basin brines, which indicates that the gangue minerals are of *several* different types].

Vinogradov/Lisitsyn (1983) studied the global distribution of life as reflected in bottom-sediment composition. More work is required on the numerous complex relations between organisms, composition and secondary alterations on a world-wide scale.

Butyzova/Lisitsyna (1983) described the ore geochemistry and destribution pattern of metal deposits in the Red Sea basins: there are differences between sub-basins controlled by *local* variables.

– See also Environments, Facies, General aspects, and Zoning.

DOLOMITIZATION – DOLOMITE – DEDOLOMITIZATION

Murata et al. (1972) studied the alteration history of deeply buried marine sediments as revealed by the chemical and isotopic compositions of secondary dolomites.
   Note: Similar detailed studies ought to be carried out on dolomite gangue minerals of ore deposits. It is necessary to differentiate various genetic types of dolomites, e.g., sedimentary – diagenetic versus hydrothermal dolomites.

Roberts (1973) pointed out that those factors which were significant in the formation of dolomite were also important in the genesis of the Woodcutters ore deposit (N.T., Australia): (1) An evaporitic environment favouring dolomite formation concentrated Pb and Zn in the overlying solutions. (2) The base metals were further concentrated and fixed in the sediments by coprecipitation, the precursors being dolomite, Mg-calcite and/or aragonite. (3) The diagenetically formed dolomite underwent a structural change in the case of aragonite, or an ordering if the precursor was Mg-calcite. Dolomite was unable to accommodate the large amount of base metals, so that during dolomitization they were released to the pore fluids, where they may have complexed with organic matter, thus remaining in solution during lithification. During folding, the metal-enriched solutions were transported to fractures, and metal sulfides precipitated when the organic complexes became unstable.

Zenger et al. (1980) and Chilingar et al. (1979) provided data on early and late diagenetic dolomitization, including its controls and evidence – frequently, the brine – reflux mechanisms were invoked. Similar investigations are needed on dolomites hosting ore mineralization.

Beales/Hardy (1980) concluded that dolostones, being the favoured hostrocks of low-temperature Pb – Zn ore deposits, were probably formed in evaporitic environments. In turn, sulfates provided a local sulfur source that probably enhanced the chance of ore mineralization. Saline solutions from the evaporites may have been ore-formers. Consequently, the recognition of both dolostones and evaporites (or the former presence of evaporites because they are easily removed), is important in research and exploration. Gypsiferous vugs, fluid inclusions, and solution-collapse breccias may be evidence in favor of former evaporites.

Mattes/Mountjoy (1980) classified the types of dolomites and the genetic mechanisms in their origin (Table 57).

Note: Which types of dolomites and which mechanisms are most likely associated with the numerous types of ores?

Chilingar et al. (1979) and Morrow (1982), for example, provided general reviews of dolomitization.

Fairchild (1980), M'Rabat (1981), Tucker (1982), Makhnach (1982a, b), Ricketts (1983), Zenger (1983), Back et al. (1983), Randazzo et al. (1983), Simms (1984), Gregg/Sibley (1984), and Saller (1984) treated various selectively/preferentially chosen aspects of dolomites: stages in dolomitization, cement vs. replacement textures (in some cases 4 – 5 different types), isotopic and elemental evidence, karst development, dedolomitization, diagenetic-to-catagenetic (eo-, meso-, telo-genetic) types, hydrology, evaporite influences, temperature control, physicochemical/ thermodynamic controls, etc. Like the "six blind men describing the elephant and seeing only certain parts but not the whole" — so it is with the study of dolomitiza-

TABLE 57

Dolomite types and mechanisms (after Mattes/Mountjoy, 1980)

Relative Timing of Process		Mechanisms and/or environments
Primary precipitation		1. Hypersaline lakes
Penecontemporaneous		2. Sabkha
	Early	3. Freshwater-seawater mixing (Dorag)
		4. Organic dolomites
		5. Reflux
		6. Cannibalization
Secondary	Intermediate to late	7. Burial (inorganic)
		a) pressure solution
		b) compaction brines
	Late	8. Hydrothermal
		9. Metamorphic

tion; but eventually we will succeed in solving the numerous enigmas. The origin of dolomite hostrocks and gangue minerals is fundamental in unravelling the genesis of the M.V.-type ores, among others. (See also M.V.-type ore, Carbonates, and Limestones.)

Clark (1980) presented information on dolomitization, dedolomitization, halitization, anhydritization, calcitization, porosity genesis, rock evolution models, and diagenetic history models. Similar studies are to be performed on ore hostrocks.

Lagny et al. (1980/1) and Macquar/Lagny (1981), among many others, investigated the relations between dolomitization and ore genesis – yet too many investigators have ignored this possible connection.

Fruth/Scherreiks (1982) investigated anaerobic dolomitization and celestitization (see models in their figs. 6 and 7). For example, they outlined the relation between depth of burial (and time, therefore), pore-space reduction, organic matter depletion and calcite–dolomite compositional changes (i.e., material balance).

Erikkson/Warren (1983) provided a paleohydrologic model for early Proterozoic dolomitization and silicification.

Sperber et al. (1984) modeled some aspects of dolomite genesis: e.g., open vs. closed and deep-burial vs. shallow-burial systems, among others.

Land (1985) offered models depicting the genésis of massive dolomite and discussed the sedimentary (diagenetic) and epigenetic types. Inasmuch as many dolomite ore hostrocks are of the massive "epigenetic" variety, this is a pertinent publication for those researching the M.V.-type ores.

Hennessey/Knauth (1985) studied in detail the isotopic variations of dolomitic concretions. Similar such precise, in-depth isotopic investigations are required on dolomitic hostrocks and/or associated gangue minerals. One conclusion is relevant: single (or a few) specimens are insufficient for isotopic studies; multiple sampling is required. Like in other geochemical work (e.g. on trace elements), a statistical treatment of the isotope data is needed to enable the most plausible interpretation and establish the degree of reliability.

Richter (1985) presented another excellent study of evaporite- and dolocrete-playa dolomites.

Leuchs (1985) offered a rare investigation of the relation between silicification and dolomitization of a reef limestone – a good model is given of hydrothermal dolomite/silica veins formed by convection cells.

Randazzo/Bloom (1985) discussed dolomitization in the freshwater/saltwater mixing zone of a coastal aquifer; the process is rock-selective. Could dolomitization *and*

ore mineralization (including zoning of the gangue and metalliferous minerals) be controlled by such hydrologic factors?

Eh-CONTROLS (OXIDATION, REDUCTION)

Baas-Becking et al. (1960) outlined the pH – Eh limits of most major natural environments (see Solutions; Fig. 81).

Manheim (1961), like many others, demonstrated the distribution of trace elements (Zn, Cu, Mo, U, Ag) according to depth, Eh, and pH in the Baltic Sea. Similar data has been obtained from many recent and fossil milieus, e.g., Black Sea.

Tischendorf/Ungethüm (1964, 1965) (to mention a couple of lesser-known publications, and of course many English-language papers and books) stressed the application of Eh – pH relations to geological problems in regard to local (micro- to macro- and mega-) and regional environments (see also Solutions). The figures presented here provide some examples:

   (a) Lithologies and ores (and their environment of precipitation, therefore) can be divided according to pH – Eh diagrams in fine details based on the minerals (e.g., the Fe – Mn ores in Fig. 82). If the mineralogical paragenesis is known, then the geochemical paragenesis (in this case the Eh – pH paragenesis), and finally the changes in fluid composition with time, can be reconstructed.

   (b) The trace- or minor-element composition of specific minerals, like sphalerite, may be controlled by pH (and other variables). Figure 186 shows the MgO-dependence of siderite on the pH. (See pH.)

   (c) The Fe^{3+} : Fe^{2+} -relations in sedimentary, as well as in magmatic rocks, can
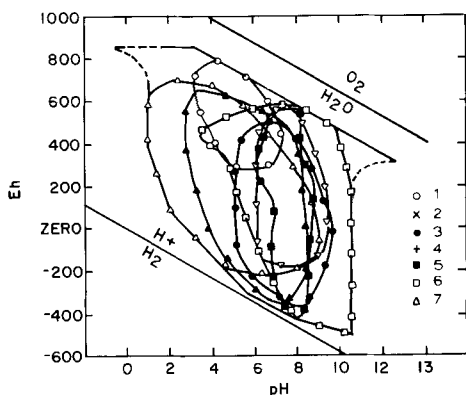

Fig. 81. Approximate "areas" of Eh and pH for some natural environments studied by Baas-Becking et al. (1960, p. 278). The "area" for each environment is bounded by a different symbol: *1* = meteoric water; *2* = peat bogs; *3* = marginal marine sediments; *4* = sea water; *5* = open-sea sediments; *6* = evaporites; *7* = geothermal environment.
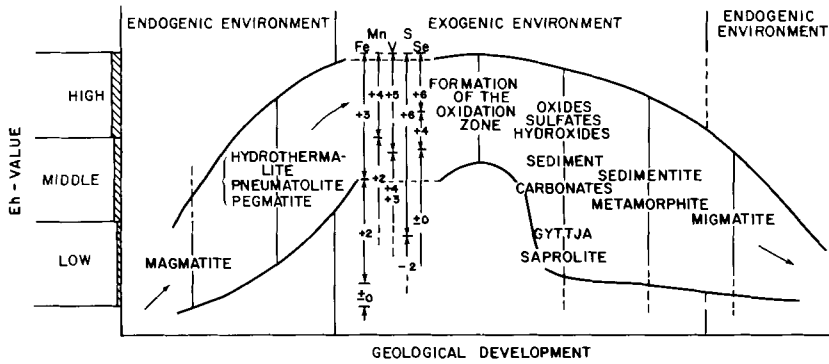
Fig. 82. Schematic diagram of the endogenic and exogenic realm related to the geologic evolution of reducing – oxidizing conditions. For comparison purposes, the stability boundaries of the exogene environment are given for specific valency phases of Fe, Mn, V, S and Se, as related to pH 7. (After Tischendorf/Ungethüm, 1964.)
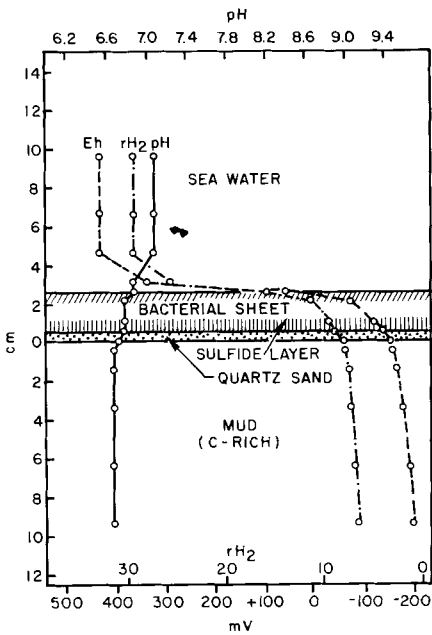

Fig. 83. Eh – pH characteristics of a seawater – muddy sediment medium with a *sulfuretum* colony: precipitation of heavy metals occurred during a 48-h experiment. (After Tischendorf/Ungethüm, 1965.)

be a useful redox indicator, so that geochemcial facies can be outlined. In sediments, four geochemical facies can be established:

I.   oxidizing $- Fe^{3+}$ $> Fe^{2+}_{HCl}$ $\gg Fe^{2+}_S$

II. weakly oxidizing $- Fe^{2+}_{HCl}$ $> Fe^{3+}$ $> Fe^{2+}_S$

III. reducing $- Fe^{2+}_{HCl}$ $> Fe^{2+}_S$ $> Fe^{3+}$

IV. strongly reducing $- Fe^{2+}_S$ $> Fe^{2+}_{HCl}$ $\gg Fe^{3+}$

Fe^{2+}_{HCl} refers to the iron with valency of two fixed in HCl-soluble minerals; whereas Fe^{2+}_S is bound to sulfide. The $Fe^{3+}:Fe^{2+}$ ratio is the most important for the Eh relations, whereas $Fe^{2+}_{HCl}:Fe^{2+}_S$ ratio is not only Eh but also pH dependent because of the influence of the anion activity.

  (d) Figure 83 illustrates the Eh – pH changes in a seawater – mud environment with a *sulphuretum* bacterial colony and heavy-metal precipitation during a laboratory experiment (after 48 h).

  (e) The importance of Eh – pH on the sulfur-containing complexes is shown in Fig. 84 (presented also in many other papers and books).

  (f) Figure 85 provides the stability fields between several Fe-compounds. Note the Eh – pH limits of the heterotrophic organisms.

  (g) Figure 86 shows the physicochemical characteristics of some ore and rock minerals.

  Note: Tischendorf and Ungethüm (1964, 1965) applied the Eh – pH study to the following systems (bacterial oxidation and reduction): $Fe - Mn - S - CO_2 - H_2O$, $U - Se - H_2O$ (e.g., origin of sandstone-hosted U-cells of the Colorado Plateau-
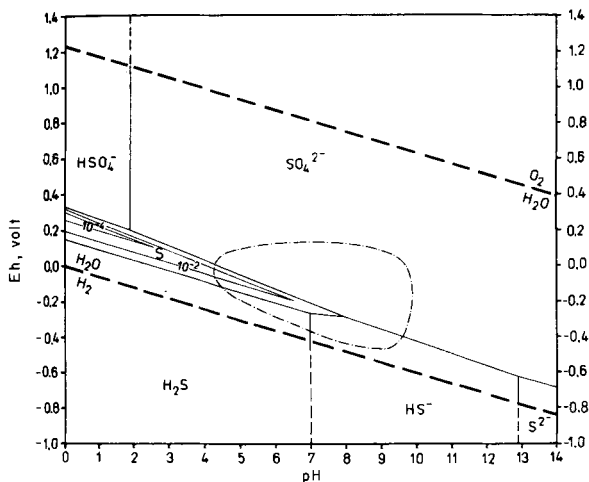

Fig. 84. Predominating fields of S-containing compounds at $\Sigma S = 10^0$ (i.e., 10^{-2}, 10^{-4}), 25°C, 1 atm total pressure, and with the Eh – pH characteristics of the *desulfuricum* bacteria (after Baas-Becking et al., 1960). At $\Sigma S = 10^0$, the H_2S activity in the H_2S field is only about 10^{-1} because of its limited solubility. (After Tischendorf/Ungethüm, 1965.)

174

type), $Cu - Pb - Zn - Fe - S - H_2O$ (e.g., applied to the Kupferschiefer's differentiation of $Cu - Ag$ and $Pb - Zn$), $Pb - Ba - S - H_2O$, and non-ferrous metals $(S - Se - H_2O)$.

Curtis (1967) studied the diagenesis of iron minerals and concluded that it is "particularly difficult to equate differing diagenetic iron mineral assemblages with variations in pH and Eh of the growth environment." Hence, a simplistic "mineral-to-
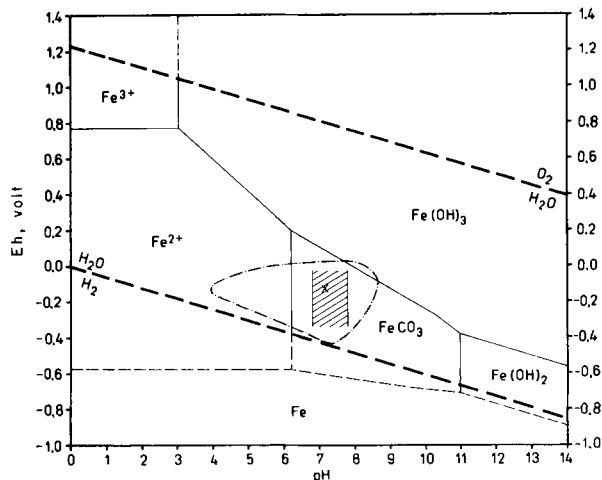

Fig. 85. Stability relations between a Fe-compound in the system $Fe - CO_2 - H_2O$ at 25°C and 1 atm total pressure. Total activity: $\Sigma Fe = 10^{-4}$, $\Sigma[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 10^{-2}$. The $Eh - pH$ characteristics of heterotrophic organisms (after Baas-Becking et al., 1960) have been added. (After Tischendorf/Ungethüm, 1965.)
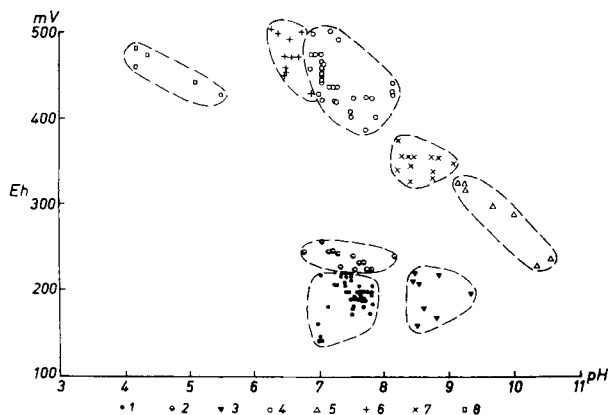

Fig. 86. Physicochemical (pH – Eh) characteristics of ores and hostrocks of the Beresowsk deposit. (After Tischendorf/Ungethüm, 1965.) *1* = siderite; *2* = siderite with hydrogoethite; *3* = siderite with calcite; *4* = hydrogoethite; *5* = dolomite; *6*= carbonate-free clay/mud; *7* = carbonate-containing clay/mud; *8* = siliceous – argillaceous rocks.

Eh/pH" correlation should not be undertaken without having considered all other potentially controlling alternative factors.

Spencer et al. (1968) discussed factors controlling element distribution in sediments. They concluded that single variables are not independent but will interact with many others to a varying extent throughout time to control diagenesis and element distribution; Eh and pH are only two variables. Figure 87 shows the oxidizing – reducing environments in a recent milieu.

Strakhov (1969): Figure 88 depicts oxidation and reduction zones in basin sediments and the products thereof in an ocean and in a lake. (See also Fig. 89.)

Yariv/Cross (1979) provided some basic data on both Eh and pH related to colloid systems.

Bølviken (1979) examined the Eh-potential field of the Earth (Figs. 90 and 91). Such information is required in the studies, of, among others, electro-diagenetic and electro-supergenic mechanisms.

Yakhontova et al. (1981) offered new data on the influence of Eh (oxidation, etc.) on galena and sphalerite. See also many other books and journal articles in regard to Eh/pH control of specific diagenetic (low T/P) minerals. This applies not only
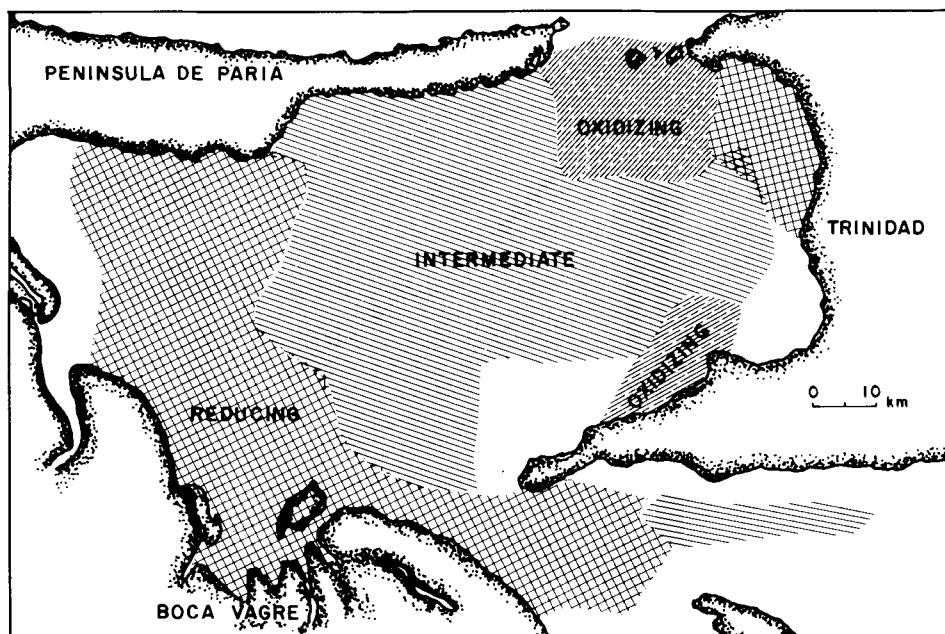

Fig. 87. Distribution of oxidizing and reducing environments in the surface layer of a recent bay. (After Spencer et al., 1968 – see for original source of data therein.)

to ore minerals but also to the gangue and/or hostrock components, e.g., chlorite. Kalogeropoulos (1983b) described the Eh-dependence of chlorite from tuffaceous exhalites associated with sulfide ore. How can other varieties of chlorite (diagenetic, burial and regional metamorphic types) be discriminated?

Klinkhammer et al. (1982) studied numerous processes related to metal diagenesis in oxic (Eh-controlled) marine sediments.

Hallberg (1982) proposed that diagenetically accumulated metals may be indicators of Eh conditions. Thus, the $(Cu + Mo)/Zn$ ratio is believed to be a paleoecologic/ paleoenvironmental indicator of ancient redox milieus.
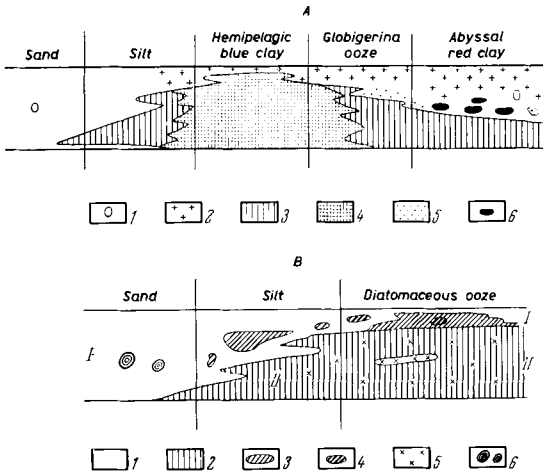

Fig. 88. Oxidation and reduction zones in basin sediments.
    A. Section through the ocean: *1* = oxidation zone of the sediments; *2* = iron oxides, staining the oxide zone brown; *3* = weakly defined reduction zone; *4* = strongly defined reduction zone; *5* = zones enriched in iron and manganese; *6* = iron — manganese concretions.
    B. Section through Lake Baikal: *1* = oxidation zones (*I*); *2* = reduction zone (*II*); *3* = uniformly stained slightly ferruginous rusty spots; *4* = manganese (black) spots; *5* = vivianite spots; *6* = iron — manganese concretions. (After Strakhov, 1969, vol. 2, p. 446.)
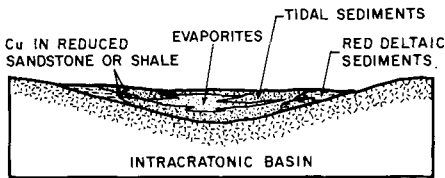

Fig. 89. Loci of deposition of Cu mineralization at the interface between oxidized, hematitic sandstones or shales and reducing sediments, in vicinity of evaporites. (After Barnes et al., 1984.)
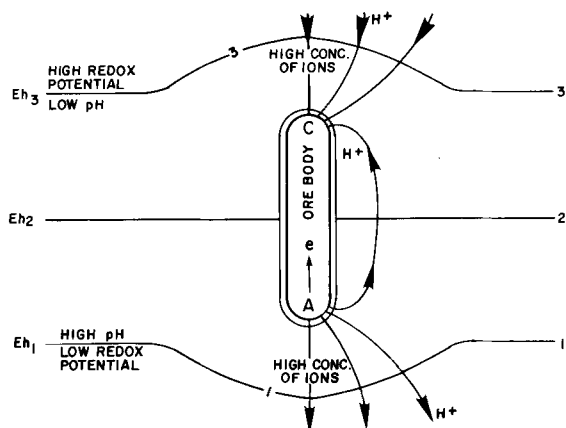
Fig. 90. Schematic model of an ore body as electrode in a primary redox potential field. The lower end develops into an anode (*A*) and the upper into a cathode (*C*). Direction of positive electricity (cations) in the electrolyte are indicated with arrows. Arrow inside ore body shows the direction of electron flow in the ore. Thin lines: equipotential surfaces. Deviation from linear isopotential curves show the local secondary redox potential field causing increased potentials around the anode and decreased potentials around the cathode. Species oxidized at the anode will migrate outwards from the anode and be reduced by species moving towards the anode. Species reduced at the cathode will migrate outwards from the cathode and be oxidized by species moving towards the cathode. (After Bølviken, 1979.)

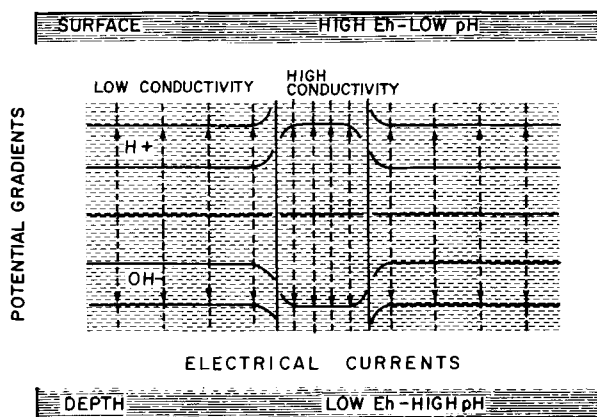Fig. 91. Schematic representation of a vertical rock formation of high conductivity in a country rock of relatively low conductivity. Horizontal lines: isopotential curves. Vertical lines: current direction. The current directions are relative and do not show the absolute direction of flow. Potentials will be relatively low and pH high in the upper part of the higher conducting zone. (After Bølviken, 1979.)

Trüper (1982, in Holland/Schidlowski, 1982) discussed the S-transformations in *sulphuretum* bacteria (see model in his fig. 4) in the oxic – redoxcline – anoxic zonal setting.

Trudinger (1982) studied the geological importance of sulfur oxido-reduction by bacteria (see Bacteria).

Sverjensky (1984b) discussed the euopium redox equilibria and the Eu-content of sedimentary, hydrothermal and metamorphic systems. Can barite-types be distinguished by Eu?

Piper et al. (1984) outlined the oxidation state of Mn nodules.

– See also Organic matter, pH (e.g., Goleva, 1980), Mobility, and Reducing.

ELECTRODIAGENESIS

Serruya et al. (1967) proposed "electrodiagenesis", e.g., the role of natural electric currents and potentials influencing secondary processes that can control any ionic exchanges and vice versa (?). They discussed in this context numerous minerals (both gangue and ore forming varieties) occurring as authigenic and open space-filling (cementing) products. Certain trace-mineral variations, micro- to macro-zoning, etc., could have been the consequence of electrodiagenesis.
   Note: An alternative term may be "galvanic diagenesis" or "galvanodiagenesis" because "galvanism" means electricity developed by chemical action. However, this type of process could be merely one variety of electrodiagenesis comprising several sub-types.

Pravdic (1970) and Neihoff/Loeb (1972) described the surface charge of particulate matter and sediments. With some extrapolation it seems reasonable to assume that electrodiagenesis influences the surface charge of all particles.

Sivenas/Beales (1982) discussed "natural geobatteries" associated with sulfide deposits. This concept too might be applicable to specific diagenetic settings in pyrite-containing sediments.

Morris (1985) described a supergenetic "electrochemical model" which ought to be considered in diagenetic electrochemical processes.

– See also Adsorption.

ENERGY

Fyfe (1964), Mason (1965), and Rösler/Lange (1972) offered general data on energy and related aspects. Van Olphen (1963a, b) and Yariv/Cross (1979) provided basic

information on energy of colloidal systems; and Spry (1969) discussed briefly energy related to metamorphic textures.

Sharp (1977) treated the energy-transport in basins and their role in petroleum and ore genesis. The dynamic processes in sediment genesis are: (1) momentum (viscous flow) transport; (2) energy (heat) transport; and (3) mass (chemical) transport. The latter occurs by (a) conduction, (b) dispersion, (c) free and forced convection, (d) physical, and (e) chemical reactions. The most prominent mechanisms are conduction and forced convection by moving pore fluids through compaction. Pressure and temperature history must be considered simultaneously. Delayed compaction can produce a vast reservoir of high-temperature fluid. In some cases, the temperature history was not conducive to oil generation, but can account for Pb – Zn ores formed by discrete pulses of hot pore fluids, generated through (compaction-induced in some cases?) faulting of geopressured sections.

Timofeev et al. (1981) and (1983), among several other Soviet scientists, have studied the "energetics" (i.e., energy exchanges, energy transformations, potential energy systems, etc.) of sedimentary complexes. For example, Table 58 lists the

TABLE 58

Levels of energy exchange of principal hypergenetic processes (from Timofeev et al., 1981)

Particle size (cm)	Energy system	Principal processes	Total energy potential (W)
10^{-8}	Atoms, ions, molecules	Lixiviation (dissolution)	
10^{-7}			$n \cdot 10^{11}$
10^{-6}	Colloids Protein molecules		
10^{-5}		Hydration of minerals	
10^{-4}	Clay	(chemically bound water)	$n \cdot 10^{11}$
	Cells		
10^{-3}	Loam	Wetting (physically bound	
10^{-2}		water)	$n \cdot 10^{11}$
10^{-1}	Sand – loam Organisms		
	Sand		
	Gravel	Disintegration	$n \cdot 10^{12}$
10^{0}			
	Scree		
10^{1}			
	Boulders		
10^{2}		Photosynthesis	$n \cdot 10^{12}$
10^{8}	Earth surface	Endogenous thermal flux	$n \cdot 10^{13}$
10^{9}	Biosphere		
	Atmosphere	Cycle of moisture	$n \cdot 10^{16}$
10^{22}	Galaxy	Solar heat flux	$n \cdot 10^{17}$

energy-exchange levels of the chief hypergenetic processes in nature; Figs. 92 and 93 provide flow-chart-like energy-transformation pathways/cycles. Note that diagenesis, among numerous others, is important in these systems. Qualitative, followed by quantitative, models of the energetics involved in ore genesis must be prepared.

Timofeev et al. (1985) continued their investigations in energy aspects of ocean sedimentogenesis (see their new model and integrate with earlier ones). The Soviet geologists seem to have taken the energy requirements quite serious. For a western approach see Parker (1985) who contemplated buffers, energy storage and temperature of geologic events: i.e., compared energy vs. time vs. processes; energy storage vs. release; and when time is included, he was compelled to contrast gradualism with catastrophism! How do these aspects control diagenesis and how can diagenetic products indicate energy conditions? Can we eventually develop "energy parageneses" by studying ore and gangue mineral associations?

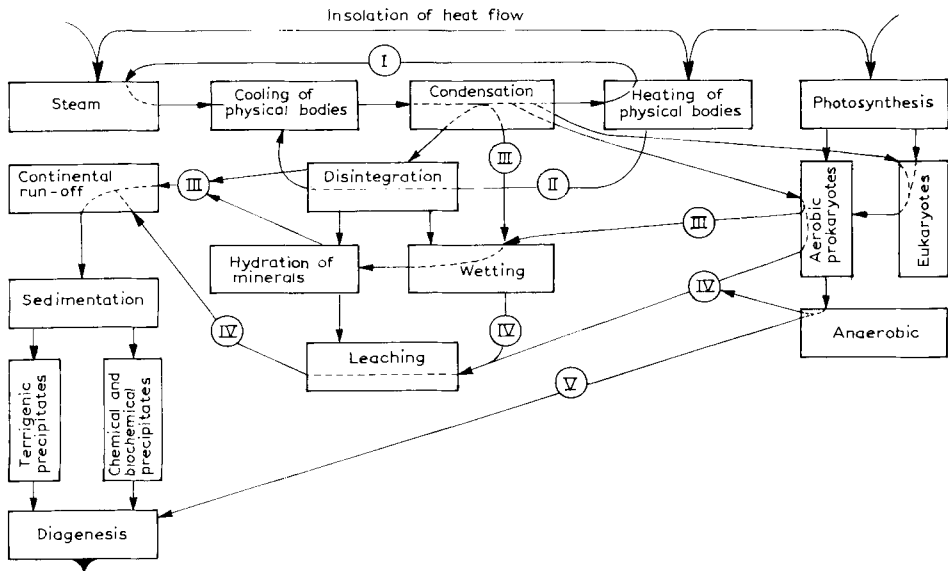− See also Bacteria, Temperature, and Thermodynamics.

Fig. 92. Transformation mechanism determined by periodic temperature fluctuations. I = Water evaporation and condensation (4.04×10^{16} W); II = mechanical destruction of rocks ($n \times 10^{12}$ W); long geologic transformation cycles; III = run-off of suspended matter (8.42×10^{11} W); IV = run-off of dissolved matter (5.4×10^{11} W); V = residual products of vital activities of organisms (3.7×10^{11} W). (After Timofeev et al., 1981.)
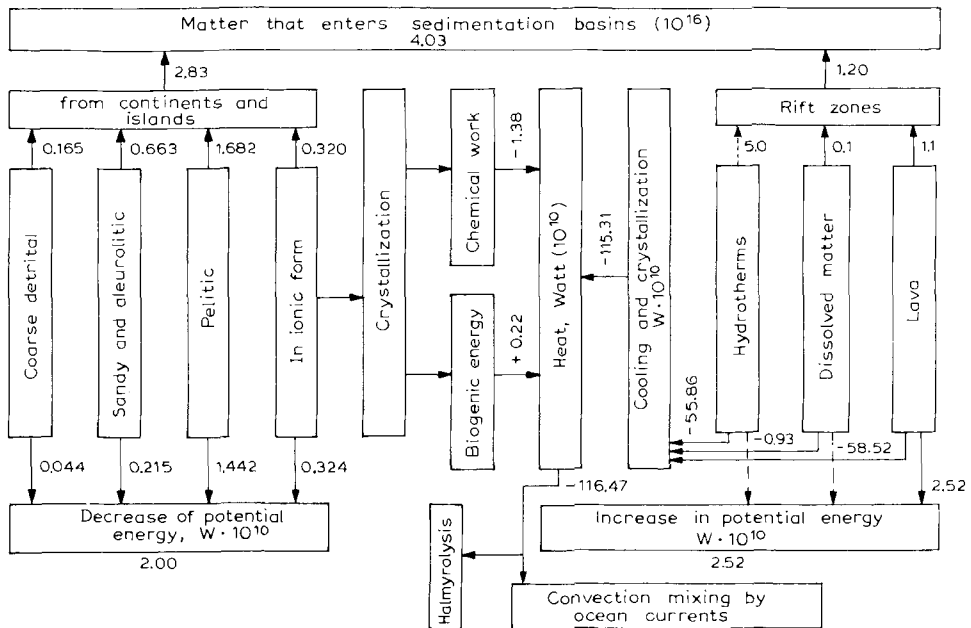
Fig. 93. Flow-chart of quantitative evaluation of matter that enters the oceans and the transformation of potential energy. (After Timofeev et al., 1983.) The numbers at the top, associated with arrows pointing upwards, represent material accumulated or settled in units of g yr^{-1} × 10^{16}; whereas those near the bottom, as well as those with positive and negative signs, represent potential energy in units of W × 10^{10}, where W = Watt.

ENTROPY[1]

Mason (1958), Van Olphen (1963a, b), Fyfe (1964), Garrels/Christ (1965), Berner (1971), Rösler/Lange (1972), Krauskopf (1979), and Yariv/Cross (1979) offered general basic information on entropy and related topics. Spry (1969) dealt with entropy related to metamorphic systems.

Finlow-Bates (1979) has applied the concept of entropy to the association and/or paragenesis of metals or minerals (galena, pyrite, dolomite, and sphalerite), their zoning, styles of cycles, variations from ideal cycles, and different depositional sedimentary environments (Fig. 94).

Note: As pointed out in the first part of this chapter, diagenesis ought to be eventually classified into various categories based on the sedimentary environments. These, in turn, offer different biological – chemical – physical conditions as reflected in different types of diagenetic systems. Possibly, entropy can be used as one of the parameters for the subdivision of diagenesis.

– See also Energy, Thermodynamics.

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[1] The concept of entropy has far-reaching implications not only in strictly scientific (e.g., physiochemical) studies, but also in numerous non-scientific fields of endeavour (yet still based on the "Laws of Thermodynamics"), as outlined by Campbell (1982), Rifkin (1980) and Wolf (1985a, b).

ENVIRONMENTS (DEPOSITIONAL)

Wolf (1976, 1981, 1985, 1986) issued a 14-volume Handbook that includes, among many other topics, diagenesis related to ore formations, and many conceptual models are presented. Campbell/Ethier (1983) and Taylor (1984) contributed two additional publications illustrating environmental interpretations of ore deposits.

Berner (1981) offered a new geochemical classification of sedimentary environments, whereas Kingston et al. (1983a, b) provided a global basin classification system and associated hydrocarbon plays. Can all diagenetic processes be similarly classified? Which diagenetic systems are restricted to which types of basins; how does tectonism control regional diagenetic facies? For example, Seslavinskiy (1981a, b) and Seslavinskiy/Gel'vi (1981) demonstrated an effect of sedimentation rates (no doubt controlled by tectonism, among others) on the composition of sediments, stratigraphy and age determinations – and thus also affecting diagenesis. Windley (1980) provided evidence of land emergence plus transgressions – regressions controlling red-beds, chemical weathering, and the origin of banded iron-formations, $U - Au - $ pyrite ores, and $U - V - Cu$ ores. Klein (1982) postulated a sequential arrangement of depositional systems on cratons, whereas Vinogradov/Lisitsyn (1983) described global features of the distribution of life in the ocean as reflected by bottom-sediment composition, all of which will control diagenesis in both space and time.

Boulton (1976), in a symposium on diagenesis of till deposits, proffered a genetic classification of tills and criteria to differentiate various types. Insofar as climate
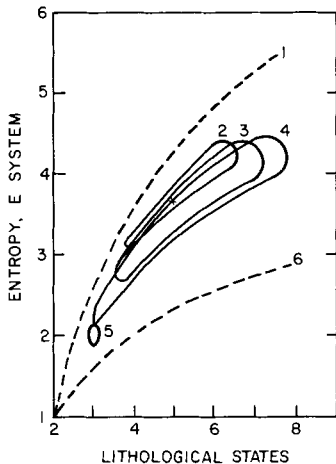

Fig. 94. Relationship between entropy and depositional environments of lithologic sequences redrawn from Hattori (1961). (After Finlow-Bates, 1979.) *1* = Maximum possible entropy for a system at each state. Entropy for coal-measure successions (*2*), fluvial – alluvial successions (*3*), neritic successions (*4*), and flysch sediments (*5*). Entropy for the Mt. Isa (Australia) ores marked with a star. *6* = Minimum entropy possible for a system at each state.

controls diagenesis and ore genesis, the recognition of glacial periods is fundamental.

Reineck/Singh's (1973, 1980) and Reading's (1978) contributions are highly recommended as general references to clastic sedimentary environments and facies. Scholle/Spearing (1982) treated the sandstones environments and J.L. Wilson (1975) and Scholle et al. (1983) the carbonate facies.

Kuznetsov et al. (1979) and Coveney/Martin (1983), for instance, offered data on specific elements useful in environmental interpretations (upwelling, mixing zone, Eh, etc.). Alvarez et al. (1980, and other publications by him) studied trace-element concentrations that may have caused the Cretaceous – Tertiary extinction of certain animal groups; i.e., an extraterrestrial cause is invoked. How was diagenesis affected by these element concentrations?

Gross's (1980) classification of Fe-formations based on depositional milieus must eventually be supported/supplemented by several types of additional models and facies concepts: textural, structural, geochemical, diagenetic, etc.

Bull et al. (1980) described chattermarks as a paleoenvironmental indicator. Many other surface features have been investigated that are believed to be indicative of a number of depositional and diagenetic conditions (see sedimentological books on textures and structures revealed by the electron-microscope).

Chambers (1982) and Piepgras/Wasserburg (1982), among many researchers, demonstrated the use of isotope information to reconstruct the original environment; sometimes merely of the hostrock or of both the ore and the hostrock environment. (See Isotope.)

Leventhal (1983) and Thisse et al. (1983) described certain aspects of the Black Sea and Red Sea (for additional publications see references in Wolf, 1976, 1981, 1985, 1986). These two seas are "natural diagenetic laboratories" – others ought to be formally recognized. (See also Estuaries.)

Hollister/McCave (1984) discussed sedimentation under deep-sea storms; Powell (1984) the glaciomarine processes and lithofacies modeling; Handford (1981) the process-sedimentary sabkha modeling; and Neudert/Russell (1981) the hypersaline features. Warren/Kendall (1985) contrasted modern and ancient sequences formed in marine sabkha (subaerial) and saline (subaqueous) settings. All supply information useful in reconstructing the history of ore and hostrock: e.g., storm-reworked ore and hostrock breccias, diamictite/tilloid-type hostrocks, sabkha-sediment-hosted Cu-deposits, etc.

– See also Depth, Eh, General, pH, Pressure, and Temperature.

EPIGENESIS

Waschkuhn et al. (1984), in a book on syngenesis/epigenesis, and Wolf (1976, 1981, 1985, 1987) offered much data on epigenesis, which was put in context with diagenesis, catagenesis, syngenesis, and metamorphism.

Smirnov (1972) examined the syngenetic – epigenetic relations during ore formation.

Bernard/Samama (1976) discussed a number of concepts related to epigenesis vs. syngenesis (and diagenesis) of the French School.

ESTUARY ENVIRONMENTS

Phillips (1972), Burton/Liss (1976), Burton (1976), and Olansson/Cato (1980), for example, treated the chemical processes in estuaries or the estuarine chemistry and biochemistry. Estuaries, like fjords and the Black Sea and Red Sea, are "natural diagenetic settings".

Turekian (1975, 1977), Carpenter et al. (1975), Elderfield/Hepworth (1975), Luther et al. (1980), Bopp/Biggs (1981), and Gordeev et al. (1983) treated the fate of metals and processes involved in estuaries (see also Pollution).

EVAPORITES – EVAPORATION

Wolf (1976a, fig. 38, pp. 69 – 72; 1976b, fig. 5 – 92, p. 644) offered a conceptual model of ore genesis that includes evaporites as a potential source of brines and/or metals (?), mobilized during basin sediment compaction, for example.

Davidson (1965, 1966), Dunham (1970), Tooms (1970), Bush (1970), Renfro (1974), and several others before and since the quoted dates, have discussed the relationship between evaporites, evaporitic environments (e.g., sabkha), and brines, on one hand, and syngenetic – diagenetic – epigenetic ore genesis, on the other. [See also the discussions following many of the above papers in Trans. Inst. Min. Metall., Sect. B, 80(771) (1971): 50 – 74.]

Crick/Muir (1980) described a multi-stage origin of the evaporite-associated U and base-metal ores.

Pagel et al. (1980) advocated a diagenetic origin for the Saskatchewan U deposits. The evaporitic-type sedimentation was characterized by high $Mg – Li – B$ and organic matter at the beginning of sedimentation; during diagenesis a highly concentrated brine was present in the sandstone facies. A hydrothermal alteration at a temperature of about 200°C along the boundary between the basement and the

cover was reconstructed from fluid-inclusion and isotope studies. All evidence indicated that the U-ore precipitating fluids were very similar to the diagenetic brines.

Longinelli (1979/80), Kesler/Jones (1981), Harwood/Coleman (1983), S.R. Taylor (1983), and Cameron (1983a, b) employed isotope geochemistry in environmental studies of evaporites (e.g., meteoric influx recorded) and concluded that bacteria caused reduction, anhydrite recorded S-isotope partitioning in Precambrian oceans, etc.

Harwood (1980) and Sighinolfi et al. (1980) described, respectively, calcitized anhydrite and associated sulfides and the geochemistry and origin of sulfide – anhydrite-bearing Archean carbonate rocks.

Gibbs (1971), Gac et al. (1979), Anderson/Kirkland (1980) and Kushnir (1982) proposed that the evaporative crystallization mechanism controlled world water chemistry (and the evolution thereof?). They also discussed a chemical model of elements in salts and brines, dissolution of salt by brine density flow, and the composition and origin of brines as deduced from coprecipitated ions with gypsum/anhydrite (marine vs. continental brines, regional differences). More data is required on the metal contents of subsurface brines.

Moine et al. (1981) suggested the geochemistry of evaporite rocks as a guide to recognizing meta-evaporites. More information is needed about diagenetic-to-catagenetic modifications of evaporites to elucidate the origin of ore-forming brines and the possible supply of sulfur, metals, and organic matter.

Roulston/Waugh (1981) and Brodtkorb et al. (1982) described borate and celestite – barite in evaporitic sequences; of the latter there are three types, namely syngenetic, diagenetic – epigenetic due to in-situ remobilization, and epigenetic vein types. Also, stalactites filling cavities were observed.

Arakel/McConchie (1982) and Leach et al. (1980) studied calcrete and gypsite lithofacies (formed in playa evaporative lakes) and their associated uranium mineralization (see their classification scheme). More data is needed on the diagenesis in playas.

Makhnach (1982a, b) and Zharkov et al. (1983) dealt with the global evolution of evaporites and the classification of salt-bearing associations based on composition and spatial patterns. That all these variables involve diagenesis (even if indirectly only) seems clear enough. Khrushshov (1979) discussed the evolution of saliferous basins as based on elemental composition. Parrish et al. (1982) correlated rainfall patterns with the distribution of coals and evaporites in the Mesozoic and Cenozoic.

Goudie/Pye (1983) summarized the ore-mineral evaporative environmental settings (e.g., U-bearing calcrete, chemical sedimentation in non-marine and lacustrine milieus).

Shearman (1966), Kirkland/Evans (1981), and Hardie (1984), for instance, discuss-
ed evaporite mineral diagenesis, source-rock potential (e.g., of organic matter),
classification of marine/non-marine evaporites, etc. Sonnenfeld (1984) reviewed
evaporites and brines. There is little doubt that evaporite minerals (from small
disseminations to larger concentrations) and as mono-mineralogic units are impor-
tant controls in ore genesis (see Bogashova, 1984, below).

Bogashova (1984) offered a rare study of metalliferous interstitial water in
evaporites. These brines may be analogous to the thermal fluids of the Red Sea
brines. Brines concentrated in clays within and under salt deposits at low-
temperature conditions can become heated at greater depth to resemble "hydrother-
mal" fluids.

Nature (1985) offered data on gypsum precipitation from cold brines in an anoxic
basin.

Sonnenfeld (1985; see also 1984) considered the possibility of evaporites as oil – gas
source rocks, and thus as the source of brines as well. Combining his ideas with
those of others, can we find the answer to the question as to whether in some cases
there is a meaningful relation between evaporite – hydrocarbon, evaporite – ore,
hydrocarbon – ore (with evaporite-derived brines), and evaporite – hydrocarbon –
ore associations? Can evaporite be the source of either one, or two, or all of the
following: brines (yes!), organic matter (possibly) and/or metals (not enough data
as yet?)?

– See also Dolomitization (e.g., Beales/Hardy, 1980).

EVOLUTION – DEVELOPMENT – TRENDS (various types)

Garrels/Mackenzie (1971) reviewed in an excellent book the evolution of sedimen-
tary rocks.

Ronov (1972) and Strakhov (1969, vol. 2), Boyle (1976) and Lambert/Groves (1981)
presented information on the evolutionary trends; see for example figs. 145 and 178
in Strakhov's volume 2, and fig. 26 in Lambert/Groves (1981), which depict the
evolution of organic material accumulated during the Earth's history and the
development of chemical – biogenic rocks.
   Note: (a) Is it unreasonable to propose that if there was an evolution in both
chemical – biogenic rocks and in biological processes, for instance, there was also
an evolution in the composition of surface waters, which in turn affected the subsur-
face basinal formation fluids? Also, implicitly, was there an evolution in the type,
intensity and distribution of diagenesis? (b) Insofar as some researchers believe that
the composition of the world's ocean waters has remained constant throughout the
Upper Precambrian and Phanerozoic, how can the evolution of chemical – biogenic
rocks formed in the marine environment be explained? Does this evolution reflect

only local changes superimposed on the compositionally average constant oceans? (c) In the studies of the evolution of ore and other deposits one ought to evaluate concomitantly the usefulness or applicability of the classification schemes of ores. For example, in the case of the Mississippi Valley-type ores hosted in carbonate rocks, the metal supply, precipitation, etc., may have remained constant in contrast to the evolution of the hostrocks. When no carbonates were formed, were the Pb and Zn concentrated in other lithologies, like shales? The same metal-precipitating mechanisms may be operative in different clastic and chemical environments, so that in one milieu the Pb – Zn may accumulate in a sand – mud – clay sequence, whereas in others they might be concentrated in a limy deposit. Also, can the same diagenetic processes occur within different hostrocks; or can different diagenetic mechanisms be operative in the same lithologic environment? (d) In evolutionary investigations of ores, one should also consider those types of deposits that are consistently *absent* during specific geological periods (see Boyle, 1976, pp. 37 – 38, for example). What are the reasons for certain sediment-associated deposits being absent or rare during the Archean? Is this related to the source, to the depositional environment, or possibly to the absence of certain diagenetic settings? If the latter query is in the affirmative, one has to wonder whether or not the diagenetic systems evolved from the Precambrian to the Recent.

Veizer (1973, 1976) and Veizer/Jansen (1979) have provided semi-quantitative to fully quantitative data that eventually will be useful in outlining the "diagenetic evolution" associated with the development of the sedimentary environment(s) since the early Precambrian (see for example figs. 6 and 9 in Veizer, 1976). In many tables and diagrams, Veizer depicted the evolution of basements and platforms, sediment thicknesses, sediment distribution, and metallic ores (Pb, Zn, Cu, Au, Cr, Ni, Mo, Sn, etc.), and discussed the importance of recycling. He also treated crustal fractionation and cratonization, and the changes of genetic types of sedimentary iron ores with geologic time. The Minette, Clinton, Superior, and Algoman iron ores are distinguished by several features that clearly reflect different syngenetic and diagenetic conditions. Whatever the more fundamental factors were that controlled the evolution of these sedimentary iron ores (including recycling, see Veizer/Jansen, 1979), the diagenetic environment seems to have changed also!

Mookherjee (1976) presented a good summary of the "metamorphic" ores, including the temporal and genetic relationship of mineralization formed during basinal evolution. Mookherjee's fig. 10, for example, traces the development and transformation of compactional – diagenetic – metamorphic mobilization of basinal fluids and the ore-fluid-generating potentialities of various lithologies. It should be noted that one has to distinguish several types of evolution in regard to syngenesis – diagenesis and their effects on ore genesis, namely, evolution on a grand worldwide all-pervasive scale from the Precambrian to the Recent, and development on a more local scale, such as within one basin or platform.

Hutchinson (1981) discussed ore genesis related to supracrustal evolution of the Earth, offering numerous tabular and diagrammatic models and comparisons, thus

listing the differences and similarities of ore types and their changes through geologic time.

Note: (a) Publications such as these usually do not treat diagenesis, because the authors predominantly concentrate on the major features and major processes. In any case, in most of the Precambrian terranes the diagenetic features have been obliterated, but there are important exceptions, such as the oolitic iron ores with well-preserved grain types, matrix and cement. Nevertheless, the "evolution of diagenesis" may be best preserved in the Phanerozoic to Recent deposits. However, some preliminary attempts have been made to investigate such evolution. (b) Inasmuch as it has been shown that the major lithologies evolved in geologic time and the diagenetic milieus within various rock types differ, it seems reasonable to assume by extrapolation or projection that the diagenetic systems evolved in a more-or-less parallel fashion with the lithologies. How this affected ore genesis is unknown at present. (c) As an example of metallogenic evolution, Hutchinson listed the differences between the Archean, Proterozoic and Phanerozoic iron-rich sedimentary rocks as based on rock associations (volcanic, sedimentary), depositional environment (deep basin – eugeosynclinal, shallow shelf – miogeosynclinal, littoral), extent, texture (fine-grained, oolitic, and both), facies (low to high Eh; rates of change, oxide/magnetite/hematite, carbonate, sulfide, silicate), and associated deposits (Cu – Zn, Au, Ni). This quick overview suggests distinct differences in both syngenetic and diagenetic environments that, together with the other geological conditions, changed with time.

Tugarinov (1979), Lambert/Groves (1981), and Meyer (1981, 1985) summarized the evolution of ore genesis systems in context of the evolution of the Earth as controlled by tectonism, photosynthetic generation of O_2 and C, Eh in sedimentary systems, igneous processes, source of metals, etc. When more data is available, the development of diagenetic systems throughout Earth's history will be reconstructed.

Sato/Sasaki (1980) reconstructed the ore-Pb evolution of the Besshi-type deposits using Pb-isotope information.

Veizer (1979), Williams (1981), McLennan (1982), Timofeev et al. (1983b), Davidson (1983), and Ronov (1984) summarized the data on secular variations in the chemical composition of sediments, evolution of depositional basins and of sediments on continents, and the sedimentary shell in general (see the many tables). Davidson (1983) provided evidence of the role of subducted sediments in island arc magma genesis: how does sedimentary recycling affect global geochemical evolution and in a very indirect, yet important, way control future secondary processes in sedimentary environments?

Nagy (1983) supplied ideas on the development and interactions of the Precambrian atmosphere, lithosphere and biosphere: the 23 articles offered many data on diagenesis, e.g., on biogeochemical cycles, BIF models, chemical weathering; pedogenetic and diagenetic fabrics in carbonates; REE unaffected by diagenesis, oxidizing-reducing milieus; bacterial processes; organic evolution (for their applica-

tion in ore genesis studies, see Brown/Chartrand, 1983, and Mossman/Harron, 1983). Other publications dealt selectively with the evolution of the atmosphere, e.g., Budyko/Ronov (1979), Kulish (1979), Junge (1981; see data on sediment – organism relations and on metals, sulfides, etc.), Walker (1982a), Clemmey/Badham (1982, on oxygen using geological criteria), Henderson-Sellers/Cogley (1982), Canuto et al. (1982, on UV-radiation during prebiological paleoatmosphere: it reconciles the co-existence of oxidized Fe and reduced uranium, etc.), Hattori et al. (1983, on S-oxidation in continental environments), and Robinson/Spooner (1984a, on uraninite-bearing conglomerates vs. O-content of the atmosphere).

Lopatin (1980), Skyring/Donnelly (1983), Schopf (1983), and Steele (1985) reviewed the evolution of the biosphere/organic systems and fossil fuels, the role of sulfite in the evolution of biological sulfate reduction (based on S-isotopes), and compared terrestrial and marine ecological systems evolving through geologic time. There is no doubt: with these developments, the diagenetic systems evolved also. Lopatin, for example, offered a model in which he demonstrated the "timing" of uraninite and iron ore formations. Holland/Schidlowski (1982) provided many models connecting the evolution of mineral deposits with the biosphere.

Cairns-Smith (1982) outlined in his "Genetic Takeover and the Mineral Origins of Life" a unique innovative hypothesis depicting the transition and link between matter (colloidal mineral crystallites, clays, etc., as part of a Precambrian inorganic system) and the earliest organisms. He advocated that inorganic materials, like organisms, are controlled by *natural selection* at all levels of organization, have their own heredity, and engage in competition. The earliest solid-state biochemistry was used in mineral crystallography, according to his hypothesis, and this "inorganic biochemistry" gradually evolved. How did this affect early Precambrian exogenic (diagenetic) ore genesis?

Jones/Risader (1980) presented data on the geochemical evolution of brines; Edmunds et al. (1982) on the hydrochemical development of sandstone aquifers; and Moore/Druckman (1981) described burial diagenesis and porosity evolution. How can these and other data be combined in the study of basin analysis as applied to the investigation of sediment-hosted ores?

Heinrichs et al. (1980), Schidlowski/Junge (1981), and Burkov/Rundquist (1979) discussed some geochemical aspects of indirect application to chemical cycles and evolution of elements.

Vidal et al. (1981) outlined the evolutionary history and isotope geochemistry of coastal submarine hydrothermal activity; but what are the controlling variables? What are the effects on metal-precipitation in sediments?

Holland/Schidlowski (1982) offered a diagram depicting the temporal distribution of phosphorites, and sedimentary (iron ore, glacial, evaporitic), organic, and tectonic events (Fig. 95). Diagenesis certainly must have evolved concomitantly.

Veizer et al. (1982), Smith (1982), Burke et al. (1982), Maisonneuve (1982), Turner/Liss (1983), Van Andel (1983), Berry/Wilde (1983), and Lafitte/Maury (1983) discussed mantle buffering of early oceans (i.e., the evolution of oceans controlled carbonate sedimentation, geochemical patterns, etc.); compared Precambrian to younger seawater; mentioned the Sr-isotope variations in seawater during Phanerozoic, the sulfur-budget, evolution of organic carbon-fixation in primitive anoxic ocean, and the evolution of the stoichiometry of sulfides in regard to pyrites, chalcopyrites and sphalerites from early terrestrial and ocean environments. Drozdovskaya (1985) outlined the chemical (sedimentogenic) evolution of the oceans.

Nagy (1983) in a multi-authored review of the Precambrian atmosphere, lithospere and biosphere and their interactions offered much for the diageneticist: e.g. data on biochemical cycles, BIF models, pedogenesis, diagenetic fabrics/textures, REE data, Eh controls, bacterial processes, etc.; and Brown/Chartrand (1983) and Mossman/Harron (1983) applied such concepts to ore genesis.

Laskowski/Kröner (1985) in their study of the evolution of the continental crust described cannibalistic recycling of older crustal sources, including diagenetic material such as trace metals in shales, for example.
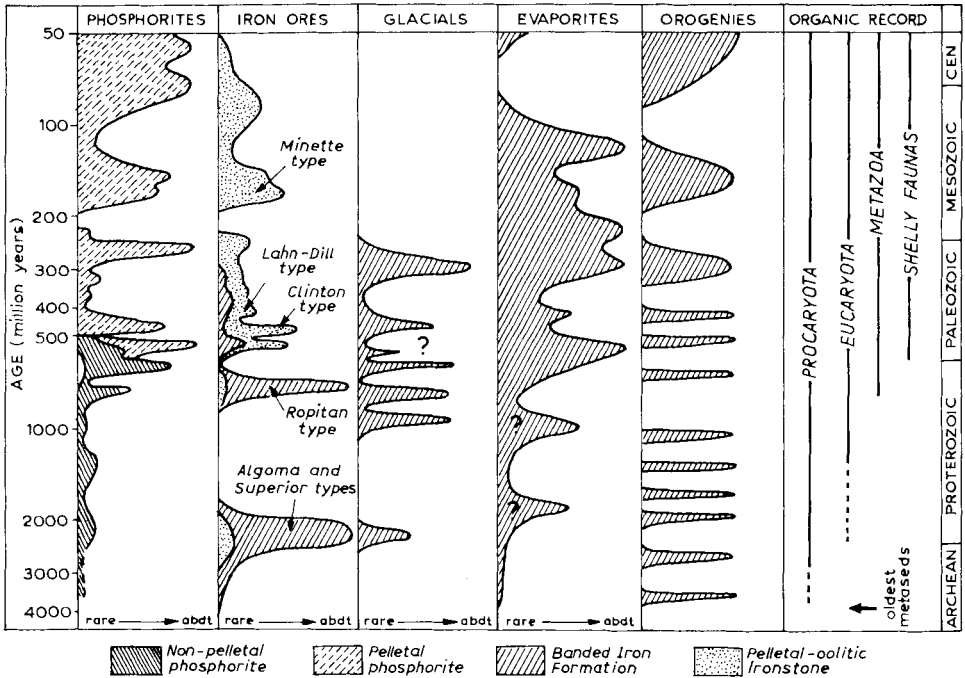

Fig. 95. The temporal distribution of phosphorites and sedimentary, organic, and tectonic events which may influence phosphogenesis. (After Holland/Schidlowski, 1982; from Cook/McElhinny.)

Rathmanov (1983) described the periodicity in global Mn-precipitation during the evolution of the Earth.

Schwartz (1983), Campbell (1983), and Rietmeijer (1985) deliberated chemical evolution in the remote geological past, discussed the exogenic systems' evolution, and offered a model of diagenesis in protoplanetary bodies!

Lewin (1984a) outlined a "thermal filter to extinction", i.e., he discussed periodic global refrigeration causing extinction. Is there any record in the sedimentary and *diagenetic* deposits? He recognized the following cooling periods: 1 major in the Permian, 4 intermediate and 10 lesser periods.

Ronov's (1984) book "Earth's Sedimentary Shell" offers 53 charts/tables depicting the quantitative patterns of the structure, composition and evolution of sediments and volcanic rocks. How did diagenesis evolve with these "depositional shells"? Is there a difference between the development of "ordinary", barren sedimentary rocks in contrast to those that host ores? Such questions must be attempted to be answered by detailed analyses in support of the larger-scale paleoenvironmental reconstructions. For example, Maack's (1981) paleogeographic study of the evolution of ancient oceans ought to include the development of diagenetic milieus in conjunction with the lithogenetic and geochemical environments.

Shaw/Wasserburg (1985) investigated the $Sm - Nd$ in carbonates and phosphates as a function of time, among others (see their figs. 3 and 4).

– See also Multi-factorial, Multi-stage, and Time.

FACIES

Teodorovich (1947 and thereafter): In several of his publications he has presented in tabular comparative fashion the "Geochemical Sedimentary Facies" based on $Eh - pH$ and other variables. These implicitly incorporate the following syngenetic and diagenetic facies: sodic, calcareous, evaporative, dolomitic $+$ FeS_2, pyritic – bauxitic – siliceous, kaolinitic, sulfuro-sideritic, leptochloritic, glauconitic, mangano-ferro-siliceous, and others.
   Note: (a) An updated, expanded, and especially adopted for diagenesis comparative/contrastive-type scheme of the geochemical facies is required. (b) A different approach was offered by Perel'man (1967) as mentioned below. (c) See also Larsen/Chilingar (1967a).

Perel'man (1967) dealt in his book mainly with "epigenetic – pedogenetic" processes, but a fair amount of the geochemical data and concepts has been applied to diagenesis.
   Note: (a) Teodorovich (1947) divided the "sedimentary geochemical facies" according to Eh-pH, for example. On the other hand, Perel'man (1967) gave a list of

physicochemical barriers (and/or boundaries between depositional facies) that cause the precipitation of elements. These syngenetic to diagenetic – catagenetic barriers are of the following types:
- oxygen barrier for Fe, Mn, Co, and S;
- hydrogen sulfide reducing barrier for V, Fe, Cu, Co, As, Se, Ag, Ni, Zn, Cd, Hg, Pb, and Cu;
- sulfatic- and carbonatic-type barrier for Ca, Sr, and Ba;
- alkaline barrier for Ca, Mg, Sr, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb;
- acid barrier for SiO_2;
- evaporate-type barrier for Li, N, F, Na, Mg, S, Cl, K, Na, Ca, Zn, Sr, Rb, Mo, I, and U; and
- sorptive barrier for Mg, P, S, K, Ca, V, Cr, Co, Ni, Cu, Rb, Mo, Zn, Ag, Hg, Pb, Ra, and U.

Questions: (a) Are there not also biological and temperature threshold barriers, and others, e.g., based on common-ion effects, fluid mixing, etc.? Is the pressure-barrier the least effective, say, during burial of sediments? (b) Can facies be classified according to solubilities? Teodorovich provides data on this, indirectly applicable to the division of diagenetic facies. (See also Solubilities.) (c) Teodorovich presented other data of interest (see his tables 27, 32, 33): basic geochemical types of epigenetic – pedogenetic processes, their identification, and the paleohydrochemical reconstructions on the basis of epigenetic rock alteration.

Hirst/Kaye (1971) chose a relatively unmineralized section of the hostrock to study the controlling factors of mineralogy and chemistry of the sediments. Four factors related to the depositional processes (sorting of clay vs. quartz, rate of deposition, proximity to shoreline and source of clastic matter, and pH of the environment), and two related to diagenesis (indicated by siderite and pyrite, with Fe, Mn, Mg, Na, Pb, and F variations) were identified. Overprinting by mineralizing fluids was considered.
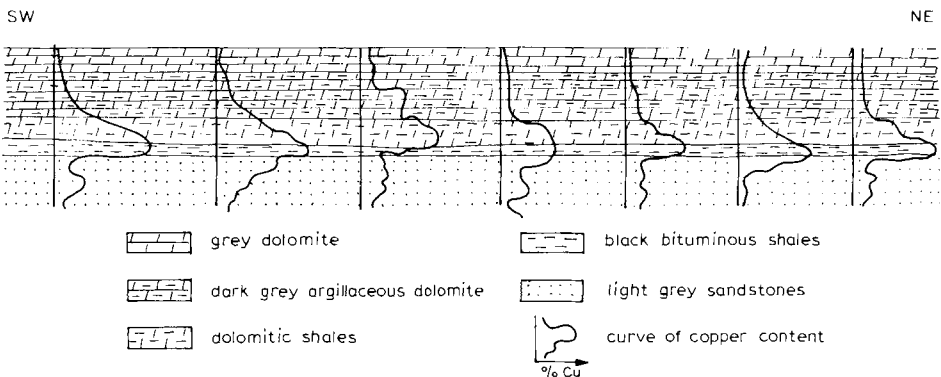

Fig. 96. Variations of copper-mineralization in vertical sections of the Pre-Sudeten monocline deposits (Lublin mine). (After Konstantynowicz, 1972.)

Konstantynowicz (1972) described the areal and vertical distribution patterns of Cu-bearing minerals, pyrite, galena, and sphalerite, as controlled by stratigraphic – lithologic, facies, and bitumen-content variables. The vertical variations in Cu, and Cu – Pb – Zn are given in Figs. 96 – 98.
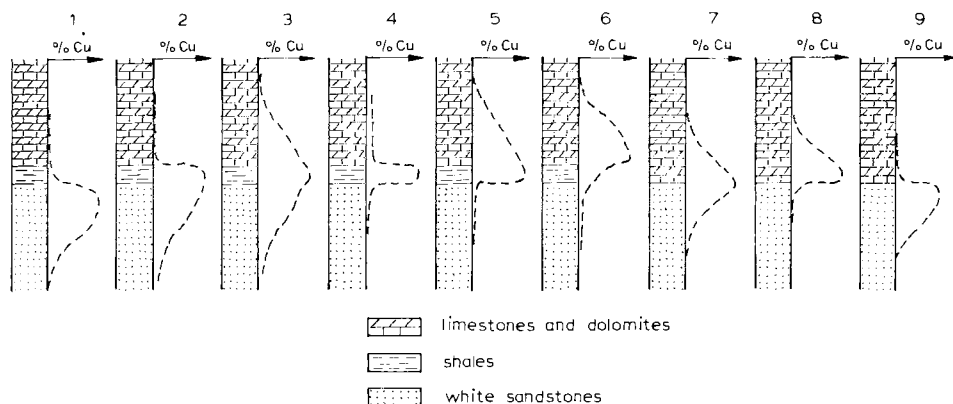

Fig. 97. Types of copper mineralization in Pre-Sudeten monocline deposits. (After Konstantynowicz, 1972.)
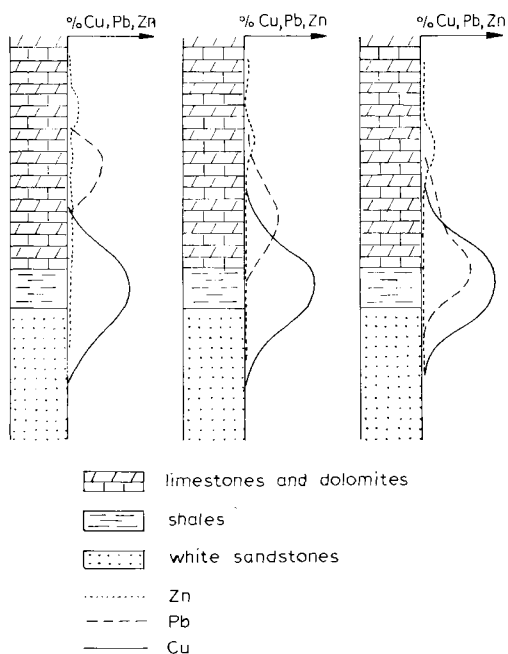

Fig. 98. Occurrence of Cu, Pb, Zn ores in a vertical section of the Pre-Sudeten monocline deposits. (After Konstantynowicz, 1972.)

Hackett/Bischoff (1973), and numerous others divided the metal deposits in the Red Sea Atlantis-II Deep into seven laterally correlative facies, namely: (a) detrital, (b) iron – montmorillonite, (c) goethite – amorphous, (d) sulfide, (e) manganosiderite, (f) anhydrite, and (g) manganite (see Fig. 99).

Note: (a) Referring to the "suspensate-type diagenesis" (see Suspensate) by Hartmann (1973) and Degens et al. (1972), for example, the following questions arise as to the *precise* syngenetic and diagenetic origin of the above-listed chemically and biologically (?) formed phases. Were all of them formed as suspensates, which settled to accumulate at the bottom? (b) Are the intrastratal fluids different in these facies, so that diagenesis would also be variable? (c) During compaction, do these variable fluids expell to mix and thus form a new diagenetic system? (d) What are the factors that controlled the changes of facies, both horizontally and vertically?

Monseur/Pel (1973) made a comparative study of 33 Pb – Zn – Cu – Fe (Ba, F, Mn) stratiform ore deposits from various continents, ranging in age from the Precambrian to the Cretaceous. This study resulted in the recognition that sedimentary rhythms or cycles controlled the mineralization and their association with the carbonate reef complexes, as demonstrated by the paleogeographic and environmental facies distribution of the ores (see Fig. 100).

Note: If one assumes that syngenesis and diagenesis influenced the origin of the metalliferous deposits, a very detailed *comparative* study of all these deposits ought to be performed.

Eichler (1976) described the four types of banded iron-formation's facies (see his figs. 3, 4, 5, 7; and tables II and III): oxide (hematitic, magnetitic), silicate, carbonate, and sulfide. He also outlined the diagenetic, pre-metamorphic mineral assemblages (table III). (See also Dimroth, 1976, in Textures.)
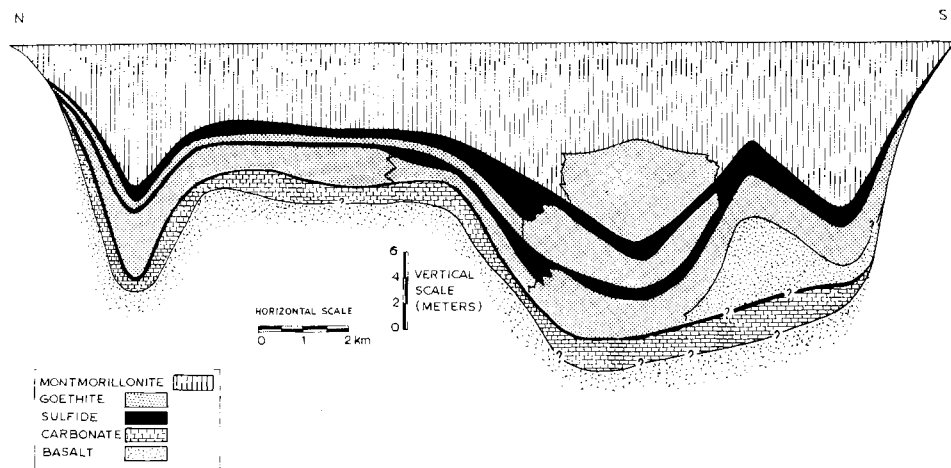

Fig. 99. Generalized cross-section of the geothermal deposits. Section depicts only major events and correlative facies. (After Hackett/Bischoff, 1973.)

Larsen/Chilingar (1967a) reproduced Teodorovich's "geochemical environments of subaqueous (mainly marine) sediments", i.e., geochemical facies. These comprise six major "zones", each subdivided into six "facies", thus totalling thirty-six facies: (a) strongly reducing, (b) reducing, (c) weakly reducing, (d) neutral, (e) weakly oxidizing, and (f) oxidizing.

Laznicka (1981a) made an excellent attempt to "typify" the platformic Pb – Zn – Ba – F (Mississippi Valley-type) ores of North America. Seventeen ore deposit types were recognized (see his figs. 9A – 9Q). If one considers merely the *gross* facies, i.e., the "carbonate hostrocks", then hardly any difference can be observed. Only by delineating the *minor* variations in facies, structures, etc., can these "types" be recognized.

Note: Eventually, in addition to the features utilized by Laznicka, detailed comparative studies of *diagenesis* will establish similarities and differences in various ores. The degree of diagenetic influences may range from intensive to nil.
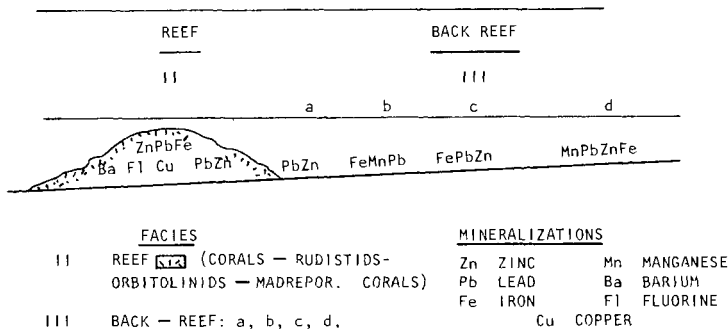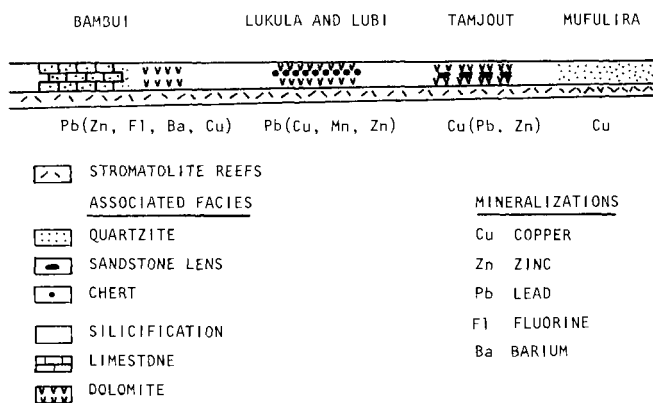

Fig. 100. Paleogeographical distribution scheme of stratified mineralizations in reef environment. (After Monseur/Pel, 1973.)

Quade (1976), like Eichler (1976), discussed the four iron facies and considered diagenesis in some detail (see his fig. 4 and table III). He also outlined the develop ment in volcano-sedimentary, sedimentary, and metasomatic hypotheses applied to the Lahn-Dill-type iron ores.

Roy (1976) summarized the facies relationships and other characteristics of the an cient manganese deposits.

Smith (1976) applied the sabkha-diagenetic and tidal-flat facies models to the stratiform copper deposits of North Texas.

Klein/Bricker (1977) and Dimroth (1979) studied the sedimentary and diagenetic en vironments of the BIF's and the diagenetic facies of iron formations, respectively.

Note: It is interesting to highlight the fact that Dimroth in several publications recorded many well-preserved syngenetic and diagenetic textures from the Precambrian deposits.

Finlow-Bates (1979/80) and Finlow-Bates/Stumpfl (1981) described the facies, cyclicity, and zoning of the Mount Isa ore deposits and hostrocks using modern geochemical data and concepts. Although most of the discussions may fall into the realm of the synsedimentation stage, diagenesis no doubt will eventually be treated in similar geochemical – geological details and each facies will have its own (overlapping?) type of diagenetic system. (See Neudert/Russell, 1981, for new interpretation of regional setting of sedimentary environments.)

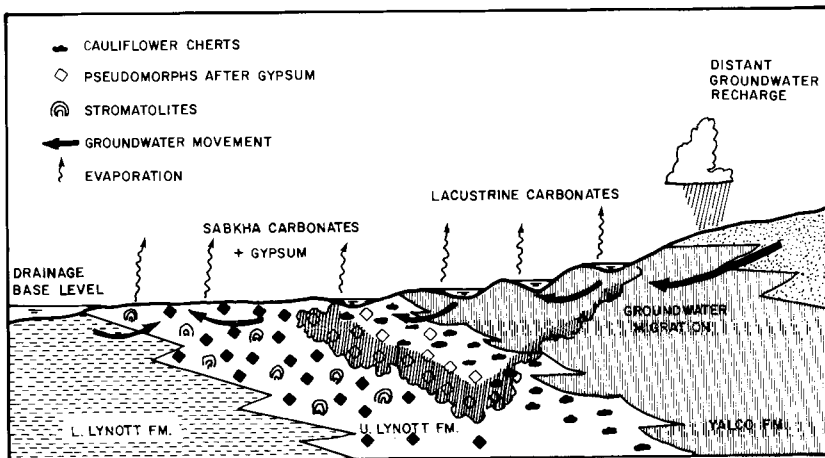Muir et al. (1980) discussed the sabkha and other nearshore sedimentary environments and facies (Fig. 101).

Fig. 101. Model for regressive development of the Yalco and contiguous formations of the McArthur Group; note proposed reflux plume (hachured) which invades the upper Lynott Formation, causing leaching with consequent silicification and dolomitization. (After Muir et al., 1980.)

Note: Such models have been applied to the hostrocks of numerous stratiform/stratabound ore deposits, so that the syngenetic and diagenetic features, for example, have become important criteria: among them are stromatolites, mud cracks, desiccation features, gypsum/halite casts, teepee structures, polygons, nodules, various types of breccias, colorations, dolomitizations, etc.

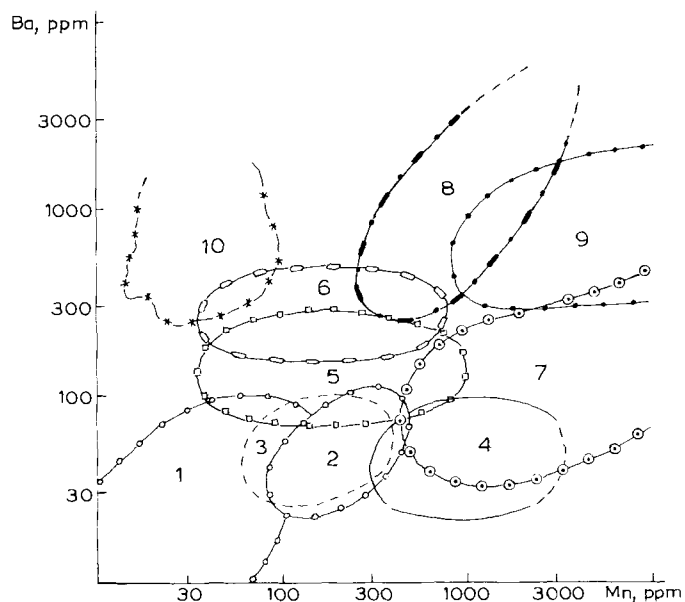Bergman/Savinova (1980) and Bergman et al. (1980) presented data on the

Fig. 102. Genetic diagram in Mn – Ba coordinates (after Yudovich/Puchkov, 1980). The numbers are genetic fields. *Field 1* is occupied by pure limestones of the arid formations. These contain very little manganese and little barium, since there is little terrigenous material, which is the barium carrier. *Field 2* is occupied by the humid limestones, which are richer in manganese and somewhat richer in barium on account of the usually higher clay content. *Field 3* corresponds to sedimentation – diagenetic dolomites (the predominant type in this region), which are somewhat richer in Mn than the associated limestone, which has a crystallochemical explanation (see original publication). *Field 4* is occupied by the limestones (somewhat dolomitized) in the Yelets depression facies, which usually contain siliceous, clayey, or silty material. The Mn levels are quite high, and it may be that the degree of enrichment is correlated with the depth of the depression. *Fields 5 and 6* correspond to sandy-silt and clayey rocks in the Yelets formation, in which Mn and Ba levels are usually at the background levels for the corresponding rocks. The Mn is usually closely correlated with the carbonate content and attains its maximum in the sandstones with abundant carbonate cement, not in the clays, whereas the clay-rich rocks almost always have more barium. *Field 7* corresponds to carbonate nodules, which are usually enriched in Mn. *Fields 8 and 9* characterize the deep-water Lemva associations, terrigenous and siliceous in field 8 and carbonate in field 9. With their high Mn contents they are comparable only with the depression carbonates of the Yelets facies, but the barium levels have no analog in such rocks. The barium levels in the siliceous-clay shales are particularly high, but the carbonates also have barium levels as high as 500 – 1000 ppm. The tentatively indicated *field 10* corresponds to local epigenetic anomalies in barium in the carbonates of the Yelets formations and sometimes in the terrigenous rocks. These anomalies are not accompanied by accumulation of Mn. (After Yudovich/Puchkov, 1980.)

geochemical facies of Precambrian iron formations by using P/B and Li/Mg ratios. Many more studies of BIF's have been performed, but more are required despite the inherent difficulties in distinguishing syngenetic, diagenetic, catagenetic and metamorphic metal concentrations and remobilizations.

Yudovich/Puchkov (1980) provided geochemical diagnostics for deep-water sediments (= geochemical Mn — Ba facies; see their genetic diagnostic diagram, Fig. 102); Devdariani/Volkov (1980) described diagenesis along a trans-Pacific geochemical facies profile (good on correlation graphs depicting element-interrelations — see their figures); and Usui (1983/4) studied the regional variation of Mn-nodule facies by using morphological, chemical and mineralogical criteria.

Golubovski et al. (1981) discussed the order of abundance of chemical elements in numerous types of facies (see their table 5), the sources of both sedimentary and elemental components, the correlation/association of trace elements and their mobility (see their fig. 4), etc.

Van Andel (1981) considered the incompleteness of the geological record. Non-preservation, non-deposition, penecontemporaneous and periodic ancient and recent erosion, etc., that have been considered by sedimentologists are also to be applied in the investigation of diagenesis; diagenesis too has an incomplete record.

Fontboté/Amstutz (1981) studied synsedimentary Zn — Pb deposits on both sides of a basin; they are localized in intertidal, dolomitic facies of a shallow-shelf carbonate platform. A complex diagenetic evolution resulted in rhythmites, crystallization differentiation, and a distinct paragenesis. (See Paragenesis.)

Brown (1981) discussed the timing of mineralization in stratiform copper deposits and the available criteria to recognize timing. Several ore districts are cited in which the ore transgresses the lithologies, and in which replacement features are obvious. Thus, the mineralization is apparently post-syngenetic or post-sedimentary in origin (e.g., as at the copper deposit of White Pine, Michigan). All the features of an epigenetic mechanism are present, and it may seem that *early* diagenesis had no influence. However, the evidence suggests that syndiagenetically formed biogenic pyrite was later replaced by copper sulfide. This copper may have been supplied by *late* diagenetic compaction fluids. Thus, the deposit appears to be diplogenetic in origin (see earlier section, and Wolf, 1981, vol. 10, p. 485, Index). (Note that in many investigations the obliteration of early diagenetic features by later epigenetic — diagenetic processes cannot be fully evaluated.)

Neudert/Russell (1981) reinterpreted the previously postulated "Red Sea-type submarine exhalative mineralization model" for the Mount Isa ore formation to have been a shallow-water system, as evidenced by numerous sedimentary features, such as stromatolites, evaporite-indicating fabrics, and depositional structures.

Boulton et al. (1982) and Turner/Hughes (1982) discussed, respectively, an isostatic-

glacio-facies model and amino acid stratigraphy, and the distribution and tectonic implication of a sedimentary – volcanic facies (see the flow-chart model on age vs. proximity of facies). Usually, the relationship between tectonism and diagenesis is ignored.

Zakrzewski (1982) provided a geochemical facies model of ore deposits as based on Eh-zonation (Fig. 103), and Frietsch (1982a) modeled the depositional environment and different Fe-ore types (Fig. 104).

Brockamp (1982, 1984) used clay minerals in facies analysis, and Schneider et al. (1984) suggested that mineralogy and diagenetic patterns are useful for lithostratigraphic (facies) subdivisions. Berner/Raiswell (1984) employed the C/S-method to distinguish between freshwater and marine sedimentary rocks.

Krashenninikov (1982, 1983), Druzhinin (1983), R.N. Walker et al. (1983), and Goncharova (1981), among many others, studied facies, genetic types thereof, methodological problems, and other aspects, such as cyclical facies in paleogeographic studies of stratabound/stratiform ores, carbonate – terrigenous rock transitions (rate of sedimentation, subsidence, tectonism), and volcanic rock facies. Are lithologic transitional facies accompanied by diagenetic facies? Not necessarily as many secondary conditions may be very different from primary ones.

Strelyanov (1983) discussed the types of exodiagenetic ore-controlling zones (Fig. 105) (i.e., the frontal, lateral and focal inter-/intra-facies). In Tables 59 and 60 he
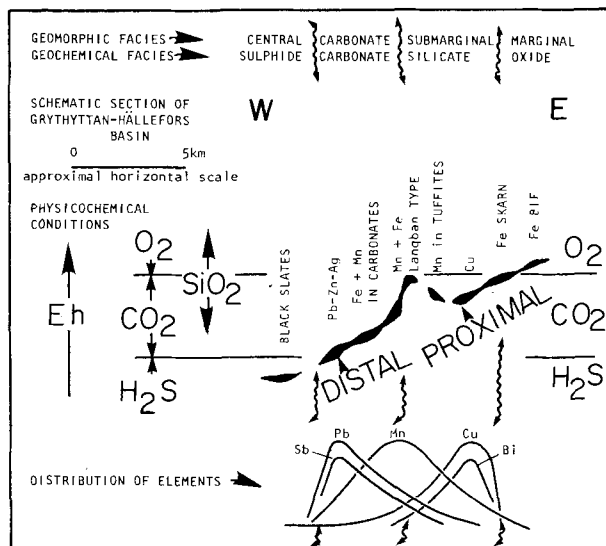

Fig. 103. Reconstruction of the geochemical facies and element distribution in the Grythyttan – Hällefors basin. (After Zakrzewski, 1982.)

summarized the lithogenetic supergenic/sedimentary, diagenetic, catagenetic/epigenetic, etc., stages as correlated with zonation/facies, U-deposits, geochemical barriers, etc.

Goudie/Pye (1983) offered much data on chemical sediments and paleogeomorphology, and thus on weathering-type residual concentrations. This book is excellent on continental to nearshore facies (including diagenetic facies).

Scheps/Friedrich (1983) and Sugisaki et al. (1982) are merely two groups of numerous researchers of facies as exemplified by their work on cherts and shales – carbonates.

Keller et al. (1983) studied multiple microtektite horizons in Eocene marine sediments: e.g., the carbonate was dissolved which resulted in a residue of microtektites and perhaps iridium enrichment. This hypothesis could be wrong if
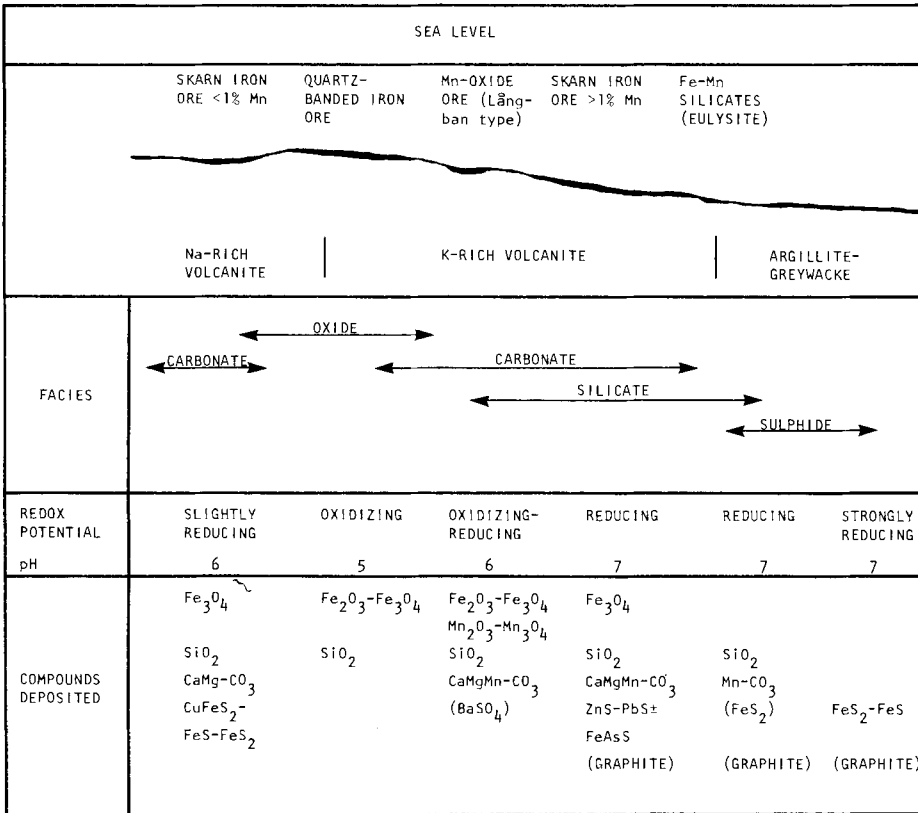

Fig. 104. Diagram showing the relation between environment of deposition and chemical composition for the different types of iron ore, manganese ore and sulfide ore in central Sweden. (After Frietsch, 1982a.)

diagenesis is ignored. Is it a "lag accumulation"? Brooks et al. (1984) similarly described iridium and other siderophile elemental anomalies along the Cretaceous – Tertiary boundary of probable extraterrestrial source, which may have led to biological extinction of certain species. (Certain objections to this concept have been raised, however.)

Sutherland et al. (1984) and Rossignol-Strick et al. (1982) investigated the Mediterranean stagnation and sapropel sedimentary facies. (See Reducing.)

Müller et al. (1985) described the distribution of metal-bearing sediments as controlled by the contemporary spreading of the East Pacific Rise (ridge): the model depicts parameters changing with distance from the spreading center, including those of biogenesis, diagenesis, hydrothermalism, and mixing in the region of metalliferous sediments. In contrast, Zhengyong et al. (1985) correlated the chemostratigraphy of Proterozoic basin sediments, including the diagenetic facies.

– See also Climate, Environments, Multi-factorial, Zoning (e.g., Fleischer et al., 1976; Jung/Knitzschke, 1976), and specific lithologies and types of ore deposits.

FJORD ENVIRONMENTS

Skei (1983a) discussed the sedimentologist's reasons for being interested in fjords: the latter offer specific anoxic environments in which metal concentrations can be investigated. Similar geochemical and geological settings are known in the ancient stratigraphic record.

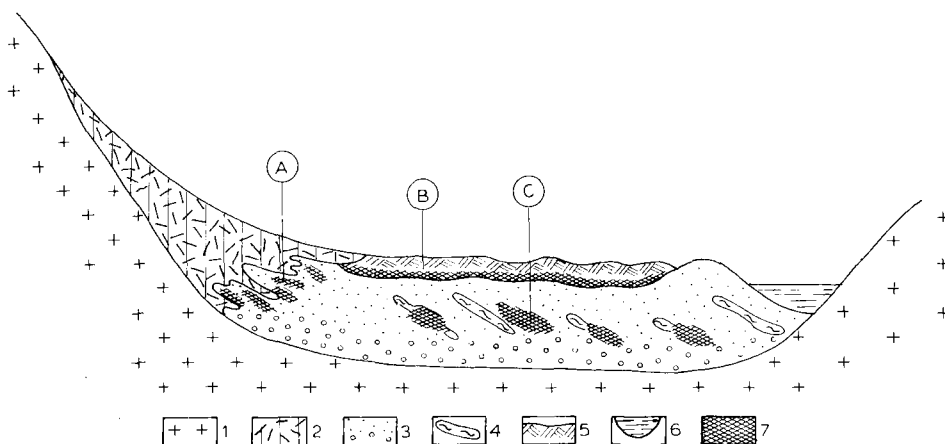Fig. 105. Some types of exodiagenetic ore-controlling zonation (during period of its formation). A = Interfacies frontal; B = interfacies lateral; C = intrafacies focal. (After Strelyanov, 1983.) 1 = Crystalline basement rocks; 2 = primary oxidized diluvial – proluvial sediments; $3 - 5$ = primary reduced channel (3), floodpain (4), and paludal (5) sediments; 6 = river channel; 7 = orebodies.

202

TABLE 59

Phases of lithogenesis, zonation of sedimentary formations, and types of uranium deposits in sedimentary rocks (Strelyanov, 1983)

Phase of lithogenesis	Zonation (class and variety)	Uranium deposit, controlled by zonation of given type
Supergenesis	Zonation of weathering products of rocks and ores: 1. Zonation of weathering crusts	Supergene: 1. Uranium-bearing weathering crusts. Eluvial placers of uraniferous accessory minerals
	2. Zonation of surface oxidation of uranium deposits and rocks enriched in uranium	2. Zones of oxidation of deposits of uranium and uraniferous rocks with redeposited mineralization
Sedimentogenesis	Zonation of geologic facies (environments and products), or facies zonation	Littoral – marine, alluvial and diluvial – proluvial placers, modern and buried
Diagenesis	Zonation of geochemical facies of early diagenesis (geochemical environments and products), superimposed on sediments 1. Facies geochemical, in basinal and continental sediments 2. Diagenetic geochemical, in basinal sediments 3. Exodiagenetic geochemical, in continental sediments	Diagenetic and exodiagenetic, formed respectively in basinal and continental sediments
Catagenesis	Zonation of geochemical facies of categenesis, superimposed on sedimentary rocks, or epigenetic geochemical zonation 1. Zonation of surface oxidation of sedimentary rocks, formed by non-pressurized groundwater 2. Zonation of stratal oxidation and gleization, formed by pressurized waters in areas of supply to artesian basins 3. Zonation of fault-fissure type, formed by pressurized waters in areas of discharge of artesian basins	Epigenetic infiltrational (1 and 2) and anagenic (3), formed in sedimentary rocks
A few phases of lithogenesis	Combination of two or several zonations of different classes	Polyphase, the formation of which begins during diagenesis and ends under conditions of catagenesis or supergenesis

Sedimentogenesis and diagenesis and syn-chronous volcanism and hydrothermal process	Zonation of interaction between products of volcanism and hydrother-mal ore solutions, and near-bottom waters and sediments of basins or con-tinental sediments (zonation of polygenic deposits)	Polygenic (volcanogenic – sedimentary)

Piper (1971) outlined the distribution of at least seven metals in an anoxic fjord.

Presley et al. (1972) and Nissenbaum et al. (1972) offered data on the early diagenesis of a reducing fjord, its trace-element distribution in interstitial water and sediment as well as isotropic changes.

Krom (1976) studied the chemical speciation and diagenesis at the sediment/water interface in a fjord.

Emerson et al. (1979) discussed the redox species in a reducing fjord and considered the equilibrium and kinetic conditions.

FLUIDS (SOLUTIONS)

Stumm/Morgan (1970), Fyfe et al. (1981), and Morel (1983), for example, sum-marized the information and concepts of aquatic chemistry. Below only a very small selection of the vast literature on fluids in geological systems is provided.

Lisitsyn (1975), Pavlov (1975), Popov (1980) and Nedra Press (1980) offered in Rus-sian books data on exogenic chloride waters and ore genesis, hydrochemistry of ore formation, geologic conditions of exogenic hydrothermal ore genesis, and on the laws governing the formation and distribution of metalliferous brines. Should these books be translated?

Parks (1967) and Gilbert et al. (1976) described aqueous surface and sediment/water interface processes considering oxide and complex oxide minerals and heavy metals.

Naumov/Naumov (1980) studied mineralizing fluids and physicochemical laws of their evolution as controlled by T, P, Eh, pH, space, time, density, state of aggrega-tion, composition, concentration, etc.

Sisson et al. (1981) studied the CO_2-brine immiscibility at high temperature as evidenced from the information of calcareous metasedimentary rocks. Can this be extrapolated to the diagenetic – catagenetic stages? Can we determine the fluid evolution ranging from syngenesis/diagenesis to higher temperature/pressure condi-tions? See for example Spear/Selverstone (1983) for water exsolution from quartz

TABLE 60

Morphologic types of ore-controlling zonations in exogenic uranium depostis (Strelyanov, 1983)

Deposits (genetic class)	Ore-controlling zonations				Geochemical barrier	Orebody (form)
	Genetic	Relationships with facies zonation	Morphology of zones			
			In plan	In section		
Sedimentational	Facies	–	–	–	–	Layered Lensoid
Diagenetic	Diagenetic geo-chemical	Monofacies	Lateral (areal)	Conformable	Sorptive, reducing hydrogen-sulfide, alkaline	Layered Lensoid
		Intra- and polyfacies	Lateral Linear	Conformable Gently discordant		Layered Banded Lensoid
			Focal	Focal		Nodular Irregular
Exodiagenetic	Exodiagenetic geo-chemical	Interfacies	Linear	Frontal	Sorptive, reducing hydrogen-sulfide and gley	Lensoid Banded Lensoid
		Intra- and polyfacies	Lateral Linear	Conformable Discordant		Layered Banded
			Focal	Focal		Nodular Irregular

Epigenetic	Epigenetic geo-chemical: layered type	Non-facies	Linear	Frontal Discordant	Reducing hydrogen-sulfide and gley	Rolled Banded
			Lateral	Conformable		Layered Lensoid
	near-surface type		Lateral	Unconformable		Mantle-like Lensoid
	fault-fissure		Linear	Unconformable		Fissure-vein
Supergene	Supergene: of weathering crusts and zones of oxidation of deposits	Non-facies	Lateral	Unconformable		Mantle-like
			Linear	Unconformable		Fissure-vein

that is significant in the generation of retrograde metamorphic fluids; Suchecki/Land (1983) for isotopic geochemistry of burial – metamorphosed volcanic sediments and on fluid evolution; and Bruce (1984) for smectite dehydration (on H_2O-evolution during clay diagenesis that varies in different basins).

Law et al. (1983) deliberated on the geologic implications of coal dewatering. Could these fluids supply organic-rich reducing fluids?

Balistrieri/Murray (1982), Hester/Boyle (1982), and Friedman et al. (1982) studied the surface chemistry of MnO_2 and major ion seawater geochemistry; the water chemistry controlling the Cd-content in foraminifera; and the economic implication of deuterium anomalies in brine and salts in a lake.

Toole et al. (1984) discussed the sampling artefact affecting the U-content of deep-sea porewaters.

Frape et al. (1984) studied groundwater – rock interaction chemistry in the Precambrian Shield.

Anderson et al. (1983) described the origin of fluids and metals in epithermal and porphyry mineral deposits – fluids that must be distinguished from all other types, e.g., basinal brines, compaction fluids, etc. See Meinel (1983) who has studied the geochemical relation between epithermal veins and evaporites (see also Evaporite): the MgO_4-rich brines or formation fluids and the $CaSO_4$-bearing fluids gave rise to two different types of dolomite and anhydrite veins. Mako/Shanks (1984) believed that exhalations of basinal brines formed stratiform sulfide and barite – fluorite ores.

Sheppard/Langley (1984) investigated the saline formation waters by using stable isotopes and concluded that most are meteoric in origin, with some also comprising fossil meteoric waters. Interesting is the observation that several generations of fluids/solutions during basin development must have been present, thus explaining several geologic features such as those produced by flushing, and the occurrence of polyphase ores and their parageneses.

Baturin/Savenko (1984) discussed briefly the Mn in sediments and porefluids of contemporary oceans.

Passaglia/Vezzalini (1985) distinguished the crystal chemistry of diagenetic zeolites in volcanoclastites, i.e., they discriminated between hydrothermal, sedimentary, and intermediate diagenetic – low-grade burial metamorphic types. They also considered open and closed geochemical systems.

Hearn/Sutter (1985) interpreted the authigenic origin of K-feldspar in carbonates as a product of brine diagenesis. What was the precise composition and the

geochemical conditions leading to precipitation? Can such fluids also carry metals? What data is available that indicate barren in contrast to potential ore-forming solutions as deduced from the information of country/hostrock alterations?

— See also Compaction, Fluid inclusions, Hydrology, Hydrothermalism, Interstitial fluids, and Water.

FLUID INCLUSIONS

Roedder (1976, 1979, and many other publications) offered general reviews on the application of fluid inclusions, including in diagenetic or sedimentary ore petrology.

Hollister/Crawford (1981) summarized in a book the application of fluid inclusions to petrologic problems.

Wilkins/McLaren (1981) studied syngenetic fluid inclusions formed in crystals by examining etch pits and the chemical reaction of crystals.

Sawkins/Scherkenbach (1981), Behr/Horn (1982), Samson/Russell (1983), and Burruss et al. (1983), respectively, gave data on the Cu-content in fluid inclusions in quartz and their ore genesis implications; fluid inclusion systems in metaplaya deposits as related to mineralization and tectonics (i.e., the source and evolution of solutions; see their model); fluid inclusions from base metal — barite deposits; and fluid inclusion — petrography and tectonic — burial history indicating the timing of diagenesis and oil migration. Theoretically, there is no limit (?) as to the application of fluid inclusion studies to ore genesis.

Yinging (1984) contrasted the fluid inclusions of three types of ore deposits, including those of M.V.- and porphyry — Cu(Mo)-type ores, as based on temperature and pH environments. Meteoric and magmatic fluids were considered.

— See also Salinity, and Temperature.

FLUORITE

Möller et al. (1980) undertook a general review of fluorite genesis in sedimentary basins. They offered interesting information on three different textural types of fluorite, described five fluorite mineralization types in a comparative table, and presented a geochemical model of brines.

Ziehr et al. (1980) described stratiform fluorite in a dolostone sequence.

Bellanca et al. (1981) treated the RRE and minor element distribution and petrography of fluorite in limestone. See their Tb/Ca — Tb/La variation diagram

depicting types of fluorites. They also discussed "hydrothermal" (i.e., hot basinal formation fluids), syngenetic and diagenetic/epigenetic solutions and fluorite types. Five different colours were observed in fluorites. [See also Götzinger/Weinke (1984) for a similar approach.]

Froelich et al. (1983) described porewater fluorite derived from seawater.

Kesler et al. (1983) compared different types of fluorite by using Sr-isotopes. The intra-limestone and igneous sources of Sr and F are contrasted.

Sheppard/Mumpton (1984) studied sedimentary fluorite in a lacustrine zeolite tuff, including the diagenesis of fluorite oolites in volcanic settings.

FRACTURING

Currie/Nwachukwu (1974) studied the geological characteristics associated with fractured reservoirs — at least five interrelated phases were involved. Similar investigations are to be carried out on the incipient to *well-developed* networks of veins that originate during diagenesis, catagenesis, and metamorphism.

See Wolf (1976, 1981, 1985, 1986; Indexes in vols. 4, 7, 10, and 14) for many references to fractures, veins, etc. See also Spry (1969).

— See also Textures, Structures, and Veins.

GASES (VOLATILES)

Velde (1968) pointed out that H_2-rich gases are released during diagenesis – metamorphism of organic matter and that these gases change the valence of iron, for example. Al is readjusted from an alumino-silicate phase to mica and possibly to kaolinite.

MacDonald (1983) discussed the many origins of natural gases and Schoell (1983) treated their genetic characterization, including those of the diagenetic gases. More studies are needed on the relationship between volatiles and diagenesis; e.g., correlating environment, processes, and types of gases with the styles of secondary mineralogical changes.

Martens/Berner (1974), Tietze et al. (1980), Sansone/Martens (1981), and Oremland et al. (1982) studied the genesis of methane from a lake, from interstitial waters of sulfide-depleted marine sediments, from acetate collected from an anoxic coastal sediment, and from anoxic salt-marsh sediment that occurred simultaneously with sulfate reduction. Reeburgh (1969) observed gases formed in bay sediments. How does methane and other gases control the origin of sulfide minerals?

Podosek et al. (1980) reported on sedimentary noble gases trapped in various shales. These gases are involved in a number of processes affecting clay minerals.

Tietze et al. (1980) examined and modeled the methane genesis in a rift lake (Fig. 106). More work is needed on the influence of *various types* of volatiles during diagenesis as related to ore formation. (See also Lake.)
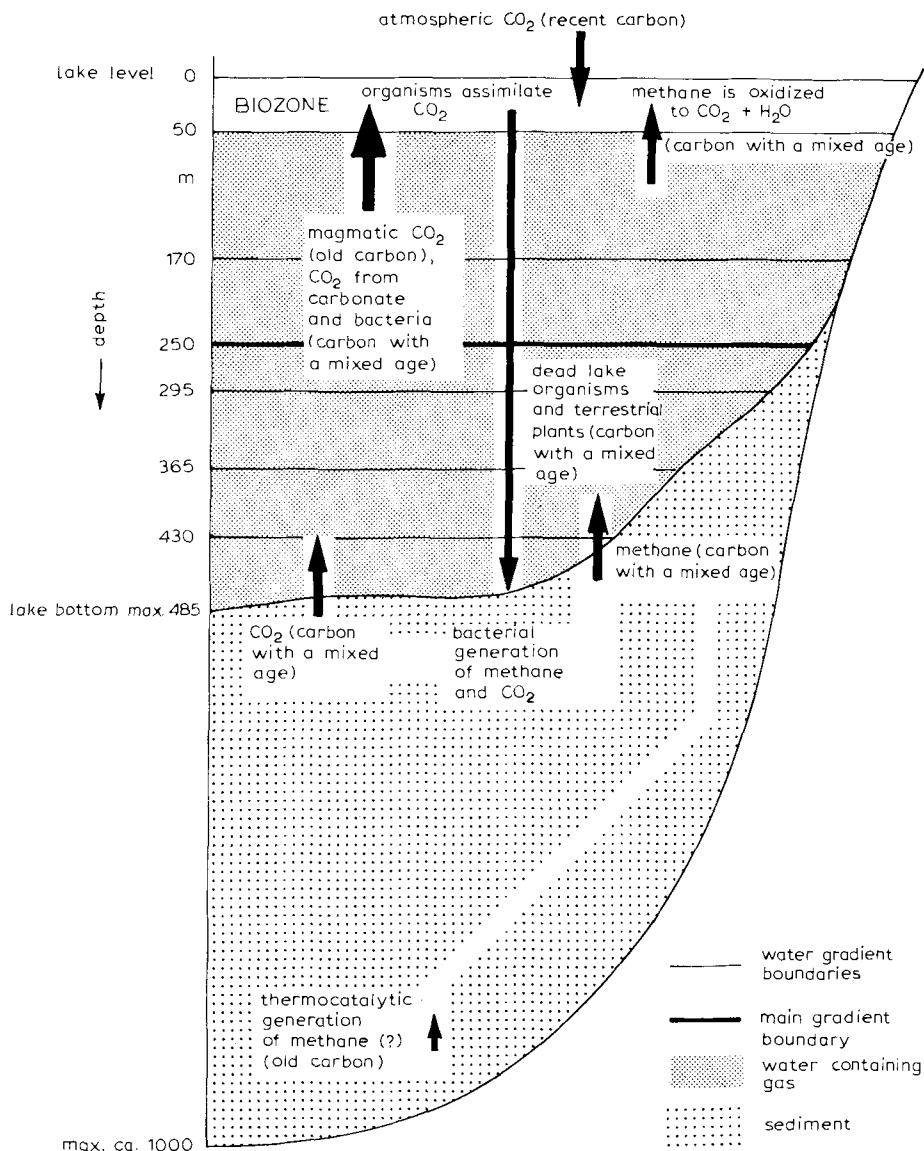

Fig. 106. Model for methane generation in Lake Kivu. (After Tietze et al., 1980.)

Varekamp/Buseck (1981) studied Hg-emissions from Mount St. Helens. What is the Hg-content of the pyroclastics and the lake sediments, for example? What is the diagenetic mobility of Hg?

Sugisaki (1981) studied deep-seated gas emissions induced by earth tides (earthquakes). Similar "pumping" mechanisms may also induce fluid movements.

Norman/Palin (1982) discussed volatiles in phyllosilicate minerals, which are present also in hydrothermal ores. Are volatiles useful geochemical guides in genetic reconstructions?

Valitov (1983) pointed to a relationship between H_2S-bearing gas fields and sulfur mineralization zones.

Abbott/Lyle (1984) discussed oceanic plate subduction and volatile recycling, i.e., gases either in or from sediments.

GENERAL (TOPICS, REFERENCES)

Engelhardt (1977), Dimroth (1980), Basan/Curtis (1981), and Cant (1983), for example, offered data on the origin of sedimentary rocks in general, discussed new developments in Precambrian sedimentology/volcanology and applied aspects in exploration and exploitation, and described subsurface sedimentology – all of which comprise some diagenesis.

Maynard (1983) summarized the geochemistry of sedimentary ores; Krauskopf (1967a) offered his well-known introduction to geochemistry and Strakhov (1976) his geochemistry of Recent oceanic lithogenesis; whereas Fortescue (1980) utilized a holistic approach for environmental geochemistry. All these authors presented data applicable in diagenetic studies. See Eitel (1964) for an earlier book on silicate science.

Perel'man's (1980) ideas on paleogeochemical landscape mapping should eventually be utilized in the reconstruction of all secondary alterations, including diagenetic modifications.

Curtis (1984) presented a chemical approach to clastic sediment diagenesis, whereas Parker/Selwood (1983/84) discussed sediment diagenesis in general (including textures/fabrics, regional diagenetic response prediction and facies trends). Morrow (1982) and McIlraith (1982) offered brief overviews, the former with seven models applicable to ore hostrocks and gangue mineral studies. Kholodov (1982a, b) presented new ideas on catagenesis (including infiltration-type processes, hydrology, evolution of gaseous solutions, etc.); Golterman (1977), on the interactions between sediments and freshwater; Price (1973), on chemical diagenesis; and Levitan/Logvinenko (1982), on problems of rock genesis in oceans (i.e., post-

depositional changes). Cabo (1980), in a proceeding on diagenesis of sediment/sedimentary rocks, covered the wole spectrum including metal and hostrock diagenesis.

Krauskopf (1955, 1956) summarized the sedimentary deposits of rare metals and factors controlling their distribution; Adamchuck et al. (1979) discussed the behaviour of some rare elements in sedimentation; Schroll (1979) commented on the progress in "indicator elementology"; Förstner (1977c), on metals in freshwater sediments and the background/cultural effects (see Pollution); and Hallberg (1982/83) discussed diagenetic, etc., heavy metal distribution in sediments. Cabri et al. (1985) offered microprobe analysis data of trace elements of massive sulfide deposits; this information ought to be extended to diagenetic ores.

Buttner (1972) deliberated on systems analysis and model-building in a book on Quantitative Geology. Such methods also apply to diagenetic investigations – as indeed do all statistical/quantitative/numerical procedures. See Sutherland-Brown (1980) for metallogeny by numbers (trace elements of all sediments in tectonic and depositional environments must be known to permit comparison); Schuiling (1980) for lithophile, etc., elements as to quantifying methods; Jones (1981) in regard to mass balance and geological constraints on migration processes; Rozen (1982) regarding calculations to quantify petrochemistry of sedimentary rocks; Ronov (1982) for quantitative patterns in the Earth's sedimentary shell, and evolution of the compositions, among others; and Sahu (1982) for stochastic modeling of mineral deposits.

Wauschkuhn et al. (1984) delivered a symposium on syngenesis/epigenesis related to ore genesis, which of course comprises also diagenesis – an excellent starting point to work your way back into the older literature, especially European. A few supplements: Institute of Mining and Metallurgy (1983) on certain problems of base metals in sediments; Chukhrov (1981) on convergence of certain supergene/hypogene processes (note that syngenesis/diagenesis/catagenesis also converge); Trudinger/Cloud (1981) on sedimentary sulfides; Müller et al. (1984) gave a classification of metal sulfides which could be adopted by ore petrologists; and Krebs (1981) outlined three types of sedimentary ores: syngenetic, diagenetic and epigenetic, which is somewhat simplistic in the light of recent information.

Deeney (1981) outlined a metallogenic model for the Irish Carboniferous ores – syndiagenetic and epigenetic theories were contrasted.

Neudert (1984) discussed the Mt. Isa Pb – Zn ores as to whether they are really syngenetic. He concluded that the hostrock diagenesis must be fully understood to unravel the origin of the ore.

Roberts/Hudson (1983) described the new type of Olympic Dam Cu – U – Au deposit, which comprises an unusual metal concentration/association that includes

also RRE. The origin is as yet not fully understood (no model is available) but a probable syngenetic/syndiagenetic – exhalative process is proposed.

A GFF symposium (1980) on ore geology included numerous aspects, including discussion on syngenesis – diagenesis – epigenesis, volcanic processes, sandstone-hosted Pb – Zn ore formed from Na – Ca – Cl brine comparable to those associated with oil in sedimentary rocks, ores as nuclei for structures, resedimentation, source of metals, etc.

Smirnov (1984) discussed some theoretical aspects of ore deposits in the USSR.

The Journal of Geological Society (1984) presented 12 articles on Precambrian metallogenesis with some topics related to secondary (including diagenetic) processes.

Dutton/Land (1985) established three stages of diagenesis that have successively affected one sedimentary sequence: marine, meteoric, and saline epigenetic (the latter due to Na-rich fluids derived from overlying evaporites). They reconstructed a phase-by-phase diagenetic paragenesis; especially the "meteoric burial diagenesis" was prominent.

Officer/Drake (1985) continued the study of the Cretaceous extinction of certain animal groups. This terminal environmental event is marked by an above-normal iridium concentration in shales, for example. It was proposed that this anomalous concentration was caused by a *single-stage* asteroid impact resulting in the extinction of the animals. Officer/Drake, however, suggested that a *series* of intense volcanic eruptions over 10,000 – 100,000 years is more likely to have occurred. How was iridium affected diagenetically in the numerous depositional environments? Was it preserved only in shales?

– See also Environments, and Multi-factorial.

GLAUCONITE

Odin/Matter (1981) and Logvinenko (1982), among many others, studied the origin of glauconite, whereas Buckley et al. (1984) discussed the compositional variations of glauconite (indicating variable conditions of formation). This mineral is generally not regarded as "ore", but its origin and secondary alterations can provide important clues related to the diagenesis and burial metamorphism of phosphates/phosphorites. Also, many hostrocks contain glauconites; the presence of the latter indicates a specific depositional marine milieu.

Birch (1979) studied a glauconite/apatite association; Srebrodol'skiy (1980) examined amber present in a glauconitic sediment (their origin is related); Laskowski et al. (1980) investigated the Rb – Sr systematics; McCouchie/Lewis (1980) discussed the

varieties of glauconite, presented a new classification, and commented on the alteration, internal textures and on a new use of radiometric age determination of glauconites; Valeton et al. (1982) outlined the mineralogy/geochemistry of glauconite pellets; Shutov et al. (1983) considered a model of globular glauconites in flysch deposits and compared their possible diagenetic/syngenetic with a hydrothermal origin; and Bergner et al. (1983) suggested that sedimentary condensation formed both phosphate and glauconite accumulations.

Odin/Morton (1987) reviewed the genesis of "green grains" (glauconites, etc.) in marine environments and demonstrated the influence of geologic time on mineralogic evolution, which resulted in several types of grains (as revealed by X-ray characteristics).

— See also Phosphates.

GOLD

Boyle (1980) described the geological and geochemical behaviour of Au and the environments of formation of Au-deposits. See his references for certain aspects related to diagenesis.

Evans (1981) treated laterization (see Weathering) as a possible contribution to gold placers. Many placer deposits have been reinterpreted as of non-detrital/non-clastic origin, so that the more we know of the placer processes *and* chemical remobilization of gold, the better we can discriminate between the numerous types of gold-concentration mechanisms. For example, see Reimer (1984) for an alternative model for the derivation of gold in a conglomerate-hosted deposit (i.e., Witwatersrand); and Mossman/Harron (1983) for the distribution of Au in a paleoplacer for which they proposed a diagenetic and a metamorphic-modification model.

Vilor (1983) described (1) gold in black shales; (2) coagulation/adsorption of Au on clays, organic matter and sulfide; and (3) diagenetic and metamorphic remobilization as well as hydrothermal Au-bearing solutions in a miogeosyncline. In this respect, one should consult Valliant et al. (1983) on Al-silicate-bearing rocks and their relation to gold mineralization (compare with Stanton's ideas on hydrothermal – diagenetic alterations); and Mangan et al. (1984) who used the Red Sea model to explain submarine-exhalative Au-mineralization.

The Engineering Mining Journal (1982, 1983) offered ideas on gold geochemistry and basics of gold geology. Some concepts are related to diagenesis.

Wilson (1984) examined the origin of quartz-free gold nuggets and supergene Au in laterites and soils.

GOSSANS

Nickel/Daniels (1985) reviewed the origin of gossans and their use in exploration of metalliferous deposits.

— See also Iron.
— See also Weathering.

HEAT

Ellis (1967), Ellis/Mahon (1977) and Goulevitch (1980) opined that divitrification of ignimbrites to quartz and feldspar is an exothermic process, providing sufficient heat to form high-temperature waters in some geothermal areas.

Note: More attention must be paid in the future to the differentiation of exothermic and endothermic diagenetic, catagenetic and metamorphic processes in order to determine the various mechanisms by which non-igneous processes can form "hydrothermal" (hot water) solutions.

Routhier (1980) mentioned two sources of heat and chemicals in geothermal waters. The heat affects the flow patterns of groundwaters in sedimentary basins (Figs. 107 and 108), which in turn determine diagenesis, catagenesis, and "epigenesis" as well as ore genesis. (See also Sources.)
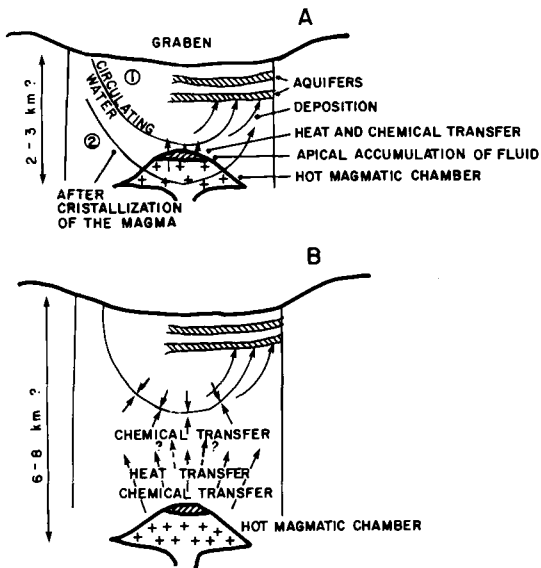

Fig. 107. Two simple alternative models for the source of heat and chemicals in geothermal waters. (After Routhier, 1980, fig. 88, p. 343; modified from Ellis, 1966.) In case A, a variation has been added where circulations (arrow 2) travel through a magmatic body after its cooling and crystallization.
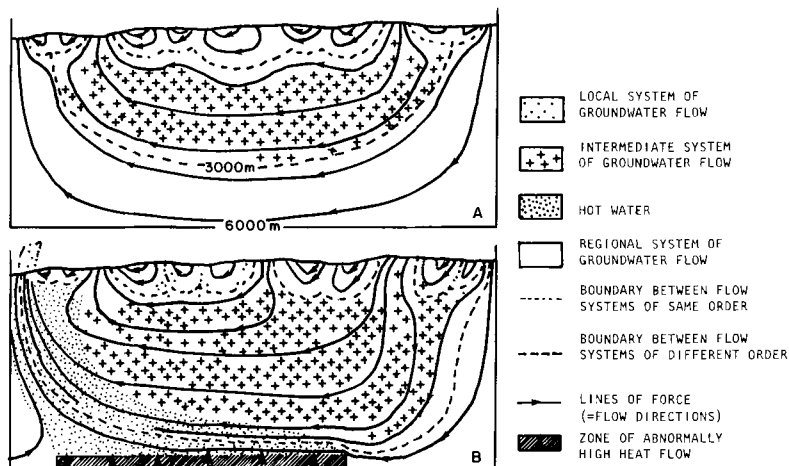
Fig. 108. Two-dimensional theoretical flow patterns of groundwater into a drainage basin underlain by homogeneous rocks; (A) under normal conditions, (B) with abnormally high heat flow beneath part of basin. (After Routhier, 1980, fig. 89, p. 345.)

Pamatmat (1982) discussed the heat productivity by sediments and the ecological implications thereof. A geochemist must consider the diagenetic significance of such heat productivity. Why not prepare a list of all known exothermic and endothermic reactions important to diageneticists?

Andrews et al. (1981) studied the flushing of geothermal heat from moderately permeable sediments. How does this heat control diagenesis in tight (impermeable) sediments where flushing is absent?

– See also Energy, Multi-factorial, Temperature, and Thermodynamics.

HISTORICAL DEVELOPMENT

Van Hinte (1978) employed the "geohistorical analysis", comprising quantitative stratigraphic techniques, to unravel the development of depositional environments in terms of water depth and other parameters, including the rates of sedimentation, subsidence, and uplift. Such exacting basin analyses are required to reconstruct the genesis of ores in sediments. Quantitative non-paleontological methods are needed where fossils are absent.

– See also Evolution, Multi-factorial, Multi-stage, and Time.

HYDROLOGY (FLUID DYNAMICS)

Ludwig (1962b) studied the hydrodynamic syngenetic − diagenetic differentiation in a sedimentological homogeneous facies. This differentiation resulted in Zn-, Pb-, and Cu-rich units.

Ostroff (1967) compared several formation-water classification schemes and systems.
   Note: Insofar as those working in oil exploration and in general hydrology may require classifications to suit their own needs, a geochemist studying special problems of diagenesis in general, and diagenesis of ores in particular, may eventually have to contrive his own classifications of natural surface and subsurface fluids. The same applies to the hydrothermal solutions (see Wolf, 1981, table XXXVIII, p. 87).

Runnels (1969) considered the mixing of natural waters in diagenesis. A classification of the waters is given in Table 21.
   Note: Such classifications ought to be supplemented by or correlated with detailed chemical classifications of all natural primary and secondary, cold and hot, surface and subsurface solutions in order to be able to delineate the range of diagenetic processes.

Hardie/Eugster (1970) and Eugster (1970): The former publication offered an overview of the evolution of closed-basin brines; the latter discussed the chemistry and origin of the brines in one such basin, i.e., Lake Magadi, Kenya.
   Note: (a) Such studies are of direct application in the reconstruction of the geological evolution of many fossil marine and non-marine basins that were exposed to evaporative conditions, including those containing ore deposits, e.g., BIF, Pb − Zn − Cu − Ba − F, and U − V, as well as associated cherts, etc. (b) The diagenetic aspects of such environments have only begun to be investigated. (c) Comparisons between closed marine and non-marine basins are required as well as a comparison with open basins. (d) What are the differences and similarities between the saline solutions formed at the surface in closed basins versus the saline subsurface fluids formed during sedimentary basin maturation? (e) Lake Kivu, East Africa, is in fluenced by "volcanic" hydrothermal exhalations debouching into the lake water resulting in precipitation of ore minerals (Degens et al., 1972). A comparative/contrastive-type study of such hydrothermally influenced saline lakes with those that are not may be advisable in establishing criteria to be used in recognizing fossil deposits.

Sato (1972) presented a model of the interaction of hydrothermal brines with seawater. When the brines are exhaled unto the seafloor, there are three basic types of interactions and mixing: Type 1 − solutions are denser than seawater, resulting in the settling of the solutions in topographic depressions with stable density layering; Type 2a − solutions are denser than seawater, so that mixing causes increase in density and sinking of the mixture beneath undiluted solutions, which rise and are continually mixing and sinking; Type 2b − solutions are lighter than seawater;

hence, mixing causes increase in density and settling occurs as in cases 1 and 2a; and Type 3 — solutions are lighter than seawater and remain so despite mixing; thus, dispersion is accompanied by infinite dilution (see diagrammatic model in original publication).

Note: (a) In all three cases outlined above, the solutions originate in a typical *volcanic* milieu and exhale, move across, interact with, and cause precipitation in a strictly *sedimentary* environment. Therefore, at one extreme is the volcanic — hydrothermal — exhalative setting (possibly causing seafloor metasomatic alteration), whereas at the other extreme lies the unaffected "normal" seafloor milieu (where marine diagenesis occurs), with numerous transitional settings in between. (b) The hydrothermal fluids may precipitate ore deposits close to the volcanic vent (or dome surrounding the vent), and form uneconomic cherts and jasper, magnetite, pyrite/pyrrhotite, and/or iron oxides and their equivalents (possibly manganese and others) up to several kilometers beyond the vent. These widespread deposits are excellent exploration guides (note that Au may accompany BIF deposits). Diagenesis varies regionally according to these facies. (c) The just-mentioned hydrothermal — exhalative chemical deposits must be distinguished from similar-appearing "sedimentary diagenetic" deposits not associated with ores, because the purely sedimentary accumulations are not guides to potential exhalative mineralizations. (d) For the effects of changes in temperature, solubilities, pH, etc., see for example Finlow-Bates (1980). (See also Solubility.)

Toth (1972), Kreitler (1979) and Galloway (1979), among many others, outlined the multiple flow systems that can occur in basins ranging from local through intermediate to regional groundwater systems (Fig. 109) comprising fluids of varying
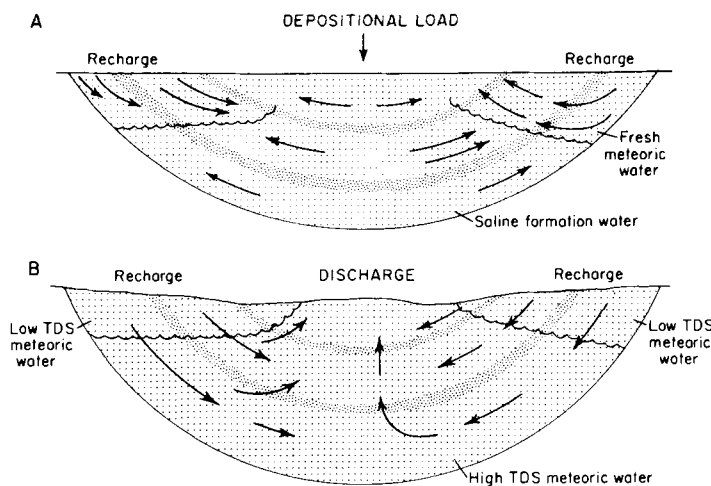

Fig. 109. (A) Hydrology of compacting sedimentary basin. Note two separate water masses. (B) Hydrology of mature compacted basin where nearly the entire basin is in hydrologic unity. (After Kreitler, 1979.)

ages and histories, origins, compositions and destinations. One type of hydrologic system is that of a compaction basin (immature to mature compaction basin) ranging from syndiagenetic to burial metamorphic (Fig. 110).

Note: Hydrology as applied to ore genesis is only in its infancy, although plenty of very generalized data is already available. The oil industry has done more studies in this regard, e.g., see Sharp/Domenico (1976), Sharp (1978) and Magara (1976a) on the energy transfer in compacting basins.

Rieke/Chilingarian (1974) reviewed briefly the hydrology of basins, including the cycles (Fig. 111). The work by Cousteau et al. (1975) and Tissot/Welte (1978) (Fig. 112) is also significant.

Note: The *dynamic* in contrast to, or to supplement, *static* hydrological systems must eventually be considered in unravelling diagenetic – metamorphic systems.

Magara (1976a) studied the volumes and directions of movement of compaction fluids, and changes in time and space. He proposed three models controlled by lithologies: vertical, horizontal, and combined models.

Note: If it is agreed that basin fluids control and form ore deposits, then such studies as done by oil companies must be undertaken also by metal explorationists.
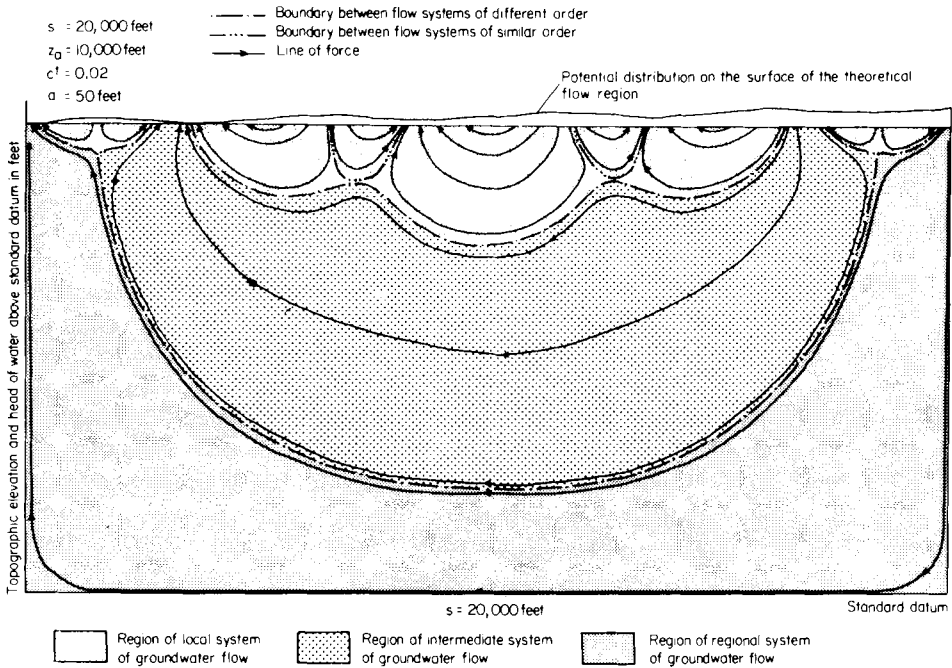

Fig. 110. Multiple flow systems can occur in the basin. The smaller the system, the more rapid the turnover of groundwater. The smaller systems may pirate water from the larger, deeper flow systems and further retard flow rates in the larger system. (After Kreitler, 1979). s = horizontal scale, z_a = vertical scale, c^f and a = model parameters.
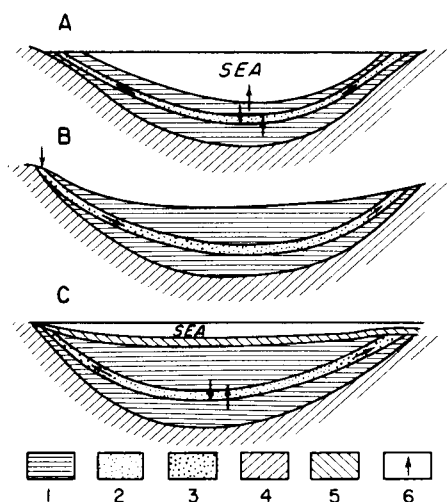
Fig. 111. Hydrologic cycle from Kartsev et al. (1969). (After Rieke/Chilingarian, 1974, fig. 153.) (A) First sedimentation stage; (B) infiltration stage; (C) second (subsequent) sedimentation stage. 1 = Muds and clays formed during sedimentation stage A and containing syngenetic waters; 2 = coarse-grained rocks containing syngenetic waters; 3 = reservoir rocks containing epigenetic waters (infiltrated atmospheric waters); 4 = bottom of depositional basin; 5 = muds and clays formed during stage C; and 6 = direction of water movement.
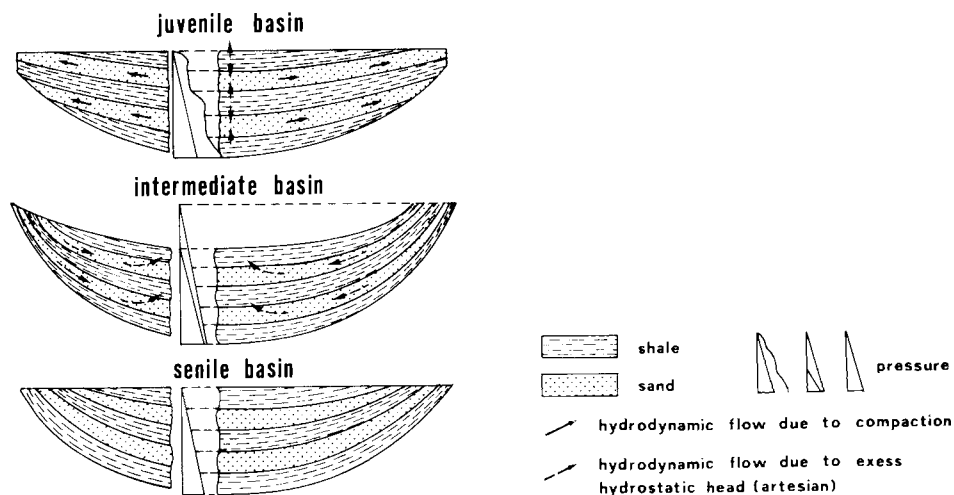

Fig. 112. Three main types of sedimentary basins classified according to hydrodynamic conditions: juvenile basins, i.e., before invasion by meteoric waters; intermediate basins during invasion by meteoric waters; senile basins, after invasion by meteoric waters. (After Tissot/Welte, 1978, p. 306; from Cousteau et al., 1975.)

Magara (1976b) investigated (a) subsurface-temperature increase upon occurrence of incipient fracturing; (b) paleotemperature and paleothermal gradients; (c) depth of burial and thickness of rocks removed by erosion; and (d) paleopore pressures. Such data ought to be applied in the future for regional diagenetic facies studies.

Norris/Henley (1976) offered information on hydraulic fracturing which causes progressive fluid release from a sedimentary pile, giving rise to the formation of veins. They also discussed metasomatism (see also Fyfe et al., 1978). Certain late diagenetic (i.e., post-lithification) veins can originate by hydraulic fracturing.

Dunsmore/Shearman (1977): Instead of two separate fluids that upon mixing gave rise to the precipitation of Pb – Zn to form a Mississippi Valley-type deposit, they proposed a one-brine hypothesis. (See Oil – ore relationships.)

Magara (1977) presented a theory on the direction and volume of horizontal and vertical compaction-water movements. The required information includes isopach maps, geological sections, sand-percentage maps, density – or porosity – depth plots, and average permeability of sands and clays.

Note: If basin fluids supplied metals, H_2S, etc., there must be a certain *maximum* amount of mineralization one can expect in specific basins. Such calculations, as offered by Magara in his numerous publications, will assist in determining this maximum.

Tissot/Welte (1978) reviewed the work by Cousteau et al. (1975), Sharp and Domenico (1976), Magara (1976a), and Kartsev et al. (1969; see Rieke/Chilingarian, 1974). Models have been developed for the *general* movement of formation waters in sedimentary basins, based on type and rate of sedimentation, porosity, pore-fluid pressure, compaction, and temperature. The basins were classified into three main types according to hydrodynamic patterns: (a) Juvenile basins – not necessarily young, with compaction-induced centrifugal, lateral water movement. Petroleum potential is very high. (b) Intermediate basins – with centrifugal water movement, artesian properties and freshwater invasion. Petroleum potential varies from very strong to moderate. (c) Senile basins with hydrostatic conditions and generally invaded by meteoric waters. Petroleum potential is negligible (see Figs. 111 and 112).

Note: The unidirectional hydrologic evolution in basins as well as the cyclic nature of such basins, has to be studied to understand fully the origin of both the oil and metalliferous potentials. Regional (diagenetic) secondary alteration patterns could assist in the reconstruction of the basin history and its cycles and in establishing deviations from the unidirectional evolution pattern. The criteria to be utilized are yet to be comprehensively identified, comparatively summarized, and then tested.

Fyfe et al. (1978) studied the following: (a) "Late diagenetic" to metamorphic fluid release, fluid/solution movements, and chemical transport processes; (b) release of fluids by various minerals (see their fluid-release curves), with fluid quantities depending on the geothermal gradients and metamorphic grades (e.g., release of 48.5% water by volume during gypsum-to-anhydrite reaction); (c) relationships be-

tween depth of burial and porosity; (d) hydraulic fracturing facilitating upward migration of connate waters and dewatering of sediments; (e) non-magmatic "hydrothermal" hot fluids forming both vein and stratabound/stratiform deposits, meso- and epithermal types; (f) trapping mechanisms of solutions, e.g., "ponding"; (g) "tectonic pumping", "fault pumping": surface expulsion of about 10^7 m^3 of warm $Na - Ca - Cl$ brine (CO_2-saturated) as "dilatancy fluid-diffusion model" for diagenetic to epigenetic hydrothermal solution migration concept; (h) lateral versus upward flow of fluids in basins forming the Pine Point $Pb - Zn$ deposit, and the amount of connate water required to form this deposit; (g) loss of connate and chemically bonded fluids due to compaction and dehydration. Many other aspects are discussed in this unusual book.

Note: Many processes referred to as "metamorphic" may also apply to late diagenetic and catagenetic (epigenetic) situations.

Sharp (1978) proposed models of energy and momentum transport supporting the lateral-secretion hypothesis for ore deposition. Hot, excess-pressured fluids, released in discrete pulses after faulting of the geopressured section, formed $Pb - Zn$ ore deposits. Sharp also discussed geothermal gradients, factors controlling temperature in basins, total-sediment accumulation, fluid velocity, amount of fluids moved, and late diagenetic compaction.

Annels (1979) and Garlick (1979) argued over the origin of the Zambian/Rhodesian sandstone-hosted Cu-deposits. Many different aspects were discussed, including fluid-movement patterns, precipitation from waters, surface versus subsurface brines, zoning, importance of compaction, detrital organic matter versus secondary-introduced hydrocarbons (i.e., syngenetic versus epigenetic organic matter) influencing ore genesis, and differences in stratigraphic and environmental reconstructions.

Note: This discussion has interesting "philosophical" implications: e.g., importance of restudying data (including fresh cores); mega- and macroscopic work to be supported by detailed microscopic studies, and field by laboratory studies, especially in making fine distinctions as to syngenetic versus early diagenetic precipitation; control by lithology and permeability; origin and influence of organic matter; open-space versus authigenic-mineral replacement mineralization; influence of compaction and other pre-ore diagenetic influences on localization; and diagenetic "cap" versus "reservoir" rock controls.

Hanor (1979) reviewed, in addition to igneous-activity-associated mechanisms, the sedimentary genesis of hydrothermal ore-forming fluids, covering diagenesis, sources of waters, properties of aqueous solutions, flow of subsurface brines, and sites of ore deposition. (See also Solutions.)

Beales et al. (1980) proposed that basinal metal-carrying brines mixed with formational sulfur-carrying solutions in the formation of the Pine Point (Mississippi Valley-type) ore deposits (see Fig. 113). (cf. his and co-workers' numerous earlier publications.) (See also Figs. 114 and 115 and contrast them to Fig. 116.)
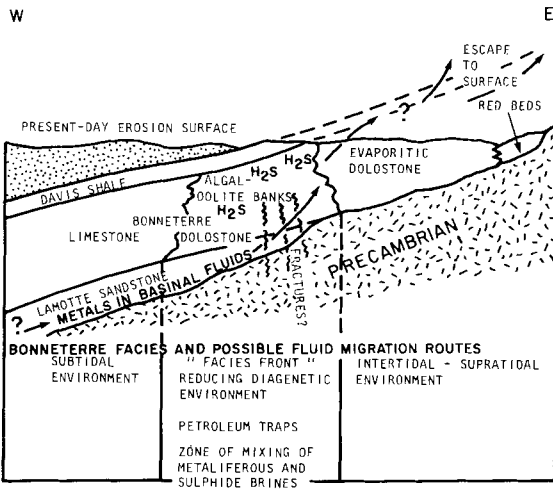
Fig. 113. The Bonneterre facies pattern and possible fluid migration routes. Ore precipitation probably took place where basinal brines carrying the metals mixed with formational fluids carrying reduced sulphur. H₂S is considered to have formed from the reduction of sulphate by petroleum which was trapped in the porosity generated in the vicinity of the "Facies Front", i.e., the complex zone marking the edge of the former shallow marine platform to the east where it abuts on the deeper water area to the west. The relatively narrow, sub-linear, now heavily mineralized, north-trending zone is about 70 km long and is referred to as the "Viburnum Trend". (After Beales et al., 1980.)
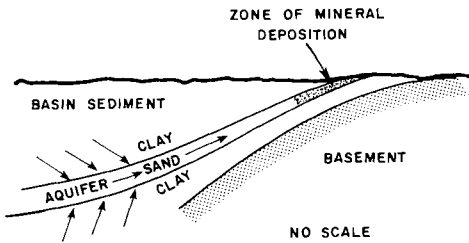

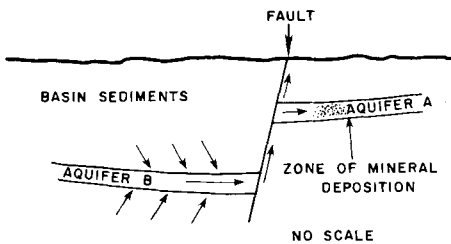Fig. 114. Diagram of lateral secretion hypothesis. (After Dozy, 1970.)

Fig. 115. Diagram of fault-controlled fluid release. (After Dozy, 1970.)

Crick et al. (1980) reviewed several genetic models ranging from syngenesis, through diagenesis, remobilization and hydrothermalism to epigenesis – weathering/weathering *per se*/supergenesis/hypogenesis enrichment. They preferred the volcanic rocks as the most likely source of the uranium, carried by descending, rather than by ascending, waters, with deposition in suitable chemical – structural traps. Crick et al. (1980) also suggested that major climatic changes can rejuvenate or expand the groundwater regime and, thus, influence leaching of the uranium.

Note: Whatever the original (primary) origin of the U may be in the sediments/volcanics, the low-grade material may have to be secondarily remobilized and reconcentrated into higher-grade economic deposits. Many other syngenetic – diagenetic metal deposits require upgrading by secondary geochemical mechanisms.

Goleva (1980) described methods of hydrogeochemical exploration for ores. The concepts developed can also apply in the study of sedimentary basinal ores, e.g., in the investigation of aqueous (water) and salt-dispersion aureoles.

Hähne et al. (1980) discussed development and aims of paleohydrology, e.g., the reconstruction of water movements as part of the interpretation of basin evolution and the origin of ore deposits (e.g., see his figs. 2, 3 and 6) of the basinal hydrothermal- and Kupferschiefer-types. A comprehensive classification of the aims and methodology of hydrology was presented by Hähne. In Fig. 117, the grey, light and deep-red coloration fronts indicate water flow directions. The present writers believe that more such Soviet papers on hydrology ought to be translated.

Hoeve et al. (1980) and Hoeve/Sibbald (1978) compared three groups of genetic
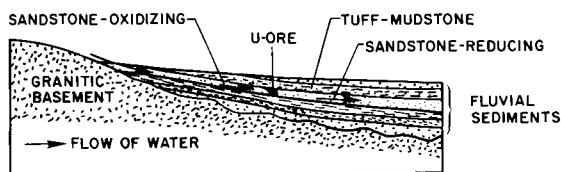
Fig. 116. A schematic diagram of the geologic environment present during the formation of sandstone-type uranium deposits. (After Barnes et al., 1981.)
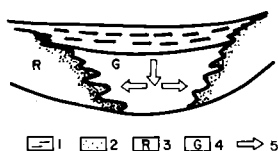
Fig. 117. Schematic diagram of the paleohydrologic system during the origin of the grey and red coloration of sediments in a basin. (After Hähne et al., 1980; from Grunewald/Baumann, 1976.) *1* = Unit containing deposits; *2* = spot/disseminations of red material; *3* = red-colored unit; *4* = grey-colored unit; *5* = movement of "sedimentary" fluids. (After Hähne et al., 1980.)

hypotheses proposed to explain the origin of unconformity-type uranium deposits: (a) near-surface supergene, (b) magmatic or magmatic – hydrothermal, and (c) diagenetic-hydrothermal. They concluded that the latter is the most plausible explanation, at least for the Athabasca Basin mineralization. The diagenetic – hydrothermal model has close similarities to certain epigenetic sandstone-type U-deposits (e.g., Eargle/Weeks, 1973; Goldhaber et al., 1978).

The following should be considered: (a) In each of the above-cited genetic mechanisms, the variables of the hydrologic system(s) (origin, maintenance or perpetuation, timing, circulation patterns, replenishment, possible mixing of various fluids, geological – geochemical controls, etc.) are so different, that one may think that by now stratigraphic – environmental – structural – lithological – mineralogic – geochemical criteria for each of them would have been established. (b) A distinction has been made between magmatic – and diagenetic – hydrothermal solutions, among several other types of hot-water fluids. (c) Another important distinction has been offered between near-surface, supergene or weathering-type solutions and the early to late diagenetic connate/compaction fluids. The former are characteristic of the intra-mountain Western States-type (Rackley, 1976) setting, whereas the latter nearshore or near-coastal sedimentary environment is represented in the Texas Gulf Coast area. Both environments give rise to uranium deposits that have many similarities and differences!

Hutchinson et al. (1980) presented data of the "deep-fluid penetration and ore deposition", i.e., on continental geothermal areas and seafloor hydrothermal – exhalative systems. Thermally driven fluid convection results in the introduction of high-temperature brines onto the seafloor environment.

Note: (a) Although there appear to be no direct connections between the above and diagenesis, several indirect influences exist, as for example, between the syngenetically and diagenetically controlled surface and near-surface (and somewhat deeper) basinal intraformational connate, compaction, etc., waters, on one hand, and the exhaled and subsurface hydrothermal gases and fluids. The fluids from the sedimentary environment are the *source* for the hydrothermal convective system; the exhalations mix with marine sediments and intrastratal waters and thus influence their diagenesis. Pre-hydrothermal diagenesis of any of the rocks can control the subsequent hydrothermal system in several ways, such as by influencing the trace-metal content of the sedimentary/volcanic rocks that are subsequently leached and by determining the permeability of stratigraphic units which may control the flow pattern of hydrothermally heated cells (see fig. 4 in Hutchinson et al., 1980).
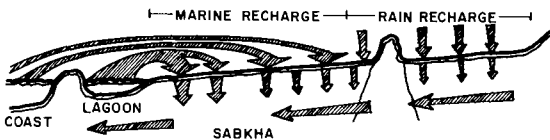

Fig. 118. Diagram of the sabkha illustrating the water movement during times of recharge, mainly in winter or spring with shamal storms. (After McKenzie et al., 1980.)

Outgassing (from vents or volcanic rocks) influences physicochemical and biological diagenetic processes in both sediments and volcanic rocks up to a fairly remote distance from the hydrothermal system because the gases (and fluids) are spread over a wide area. The hydrothermally derived chemically precipitated "sediments" (such as silica-, iron-, barite-, even gold-rich deposits) *create* their own diagenetic milieus. (See Volcanic – exhalative ores, e.g., Franklin et al., 1981; etc.)

McKenzie et al. (1980) and Muir et al. (1980), among many others, studied the hydrology of the sabkha environment and with it the diagenetic system thereof (involving silicification, dolomitization, etc.) (Figs. 118 and 119 and see Facies).

Note: The sabkha model has been evoked for numerous sedimentary hostrocks of stratiform/stratabound base-metal ore deposits, e.g., McArthur Group deposits and Zambian/Rhodesian Copper Belt.

Sears/Lucia (1980), among others, discussed the hydrologic system of reefs (Fig. 120; see also their fig. 3 for the hydrologic cycles and evolution within reefs). The following questions arise: (a) How does the hydrology affect the localization of Pb – Zn ores in carbonate reefs? (b) Is pre-ore diagenetic occlusion or permeability increase due to dolomitization, for example, controlled by the hydrologic system, which in turn influences ore localization?

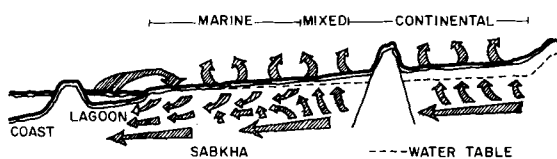Fig. 119. Diagram of the sabkha illustrating the origin of the water and the circulation pattern during times of evaporation, the situation during most of the year. (After McKenzie et al., 1980.)
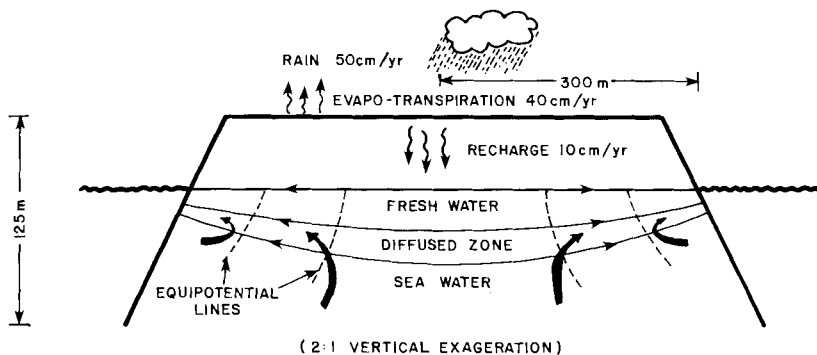

Fig. 120. Schematic diagram of hydrology of hypothetical pinnacle reef. Arrows show direction of flow. (For explanation of numbers, see original publication.) (After Sears/Lucia, 1980; see also their fig. 3 for hydrologic evolution.)

Almon (1981, see especially pp. 111 – 137) discussed the impact of diagenesis on reservoir properties related to hydrocarbons, e.g., porosity/permeability distribution. Some interesting data and discussions are presented, however, that are applicable to sediment-hosted ores, such as: (a) The study of diagenesis as based on lithofacies, depositional environments, geochemical parameters (e.g. pH), and basin-water evolution; and (b) the intensity of diagenesis, which is not controlled by the facies distribution, but by two other factors, namely (i) location within the basin (those sands underlying the true salt or evaporative basin underwent extensive diagenesis, whereas those close to mixed clastic – carbonate rocks were much less intensively altered), and (ii) the proximity to the faults showed that the fluids moved along them and spread outwards causing leaching, illitization, and kaolinitization, for example. (c) The evolution of the basinal fluids (surface water, meteoric-derived water, and salt-basin-derived water) is reflected by variation in diagenetic minerals depicting several stages of development, changing pH and salinity, and fluid evolution during early, middle, and late burial. (d) Regional "diagenetic potential" maps established low and moderate to high potentials of diagenetic influence.

Note: (a) Similar regional studies can be applied to the sandstone-hosted U- and Cu-deposits, for example. The influence of faults as conduits must be determined. (See Almon, pp. 162 – 172, for diagenesis of volcanic sandstones.) (b) The above-cited book offers many more interesting data.

Barnes et al. (1981) offered a brief summary of diagenetic to metamorphic processes in U-, Pb + Zn- and Cu-ore genesis, including discussions on fluid movements, maturation of basins, and pH – Eh controls.

Bjørlykke/Sangster (1981) compared the hydrothermal (basin brine) model with the
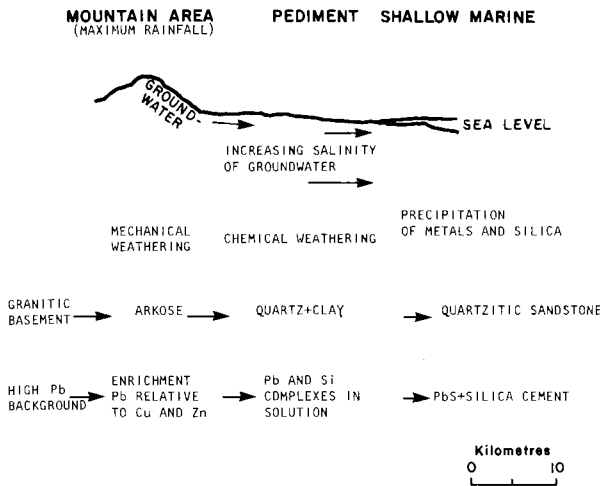

Fig. 121. Schematic representation of the main features in the preferred groundwater transport genetic model for sandstone-type lead deposits. (After Bjørlykke/Sangster, 1981, p. 606.)

groundwater transport model used to explain the origin of the sandstone-hosted Pb deposits (see Fig. 121).

Ferguson/Burne (1981) advocated *terrestrial* (continental red-bed) groundwaters of suitable pH, Eh, and salinity for the transport of Cu, Pb, and Zn in high concentrations, which may be generated in semi-arid climates. These groundwaters are capable of mobilizing large quantities of metals held in Fe-oxide grain coatings. The groundwaters then moved to coastal carbonate complexes and, in the absence of organic matter, the metals are possibly removed from solution by adsorption onto marine carbonates, or by oxidation and precipitation (by fluid mixing) as oxides or hydroxides.

Gustafson/Williams (1981) discussed the nature of mineralizing fluids for the Pb – Zn and Cu ores in carbonate and sandstone rocks, respectively, as well as the source – transport – trap chain of events. They also presented the schematic model of the relationship between several types of ore deposits, source of metal-carrying fluids and the dominant fluid pathway (Fig. 122).

Note: (a) The three solutions derived from intrabasinal sources during maturation (?) of the sedimentary pile gave rise to the marine and non-marine stratiform Cu – (Pb – Zn), the sandstone-hosted Pb – Zn, and the M.V.-type ores, respectively. In contrast, seafloor volcanism resulted in "hydrothermal" fluids that are believed to have formed a whole spectrum of discordant and stratiform deposits, which may be genetically related to the volcanogenic massive sulfides. In some instances, sedimentary basinal fluids may also have contributed to the discordant/stratiform group of ores. Through convection, they may have produced or become mixed with volcanically heated hydrothermal solutions. (b) Where is the boundary between diagenesis, catagenesis and burial metamorphism, volcanic and other types of hydrothermalism, and metasomatism? There are gradational/transitional possibilities between all of them.

Russell et al. (1981) described the origin of sediment-hosted exhalative Zn + Pb deposits formed by subsurface convective circulation of modified highly saline seawater debouching onto the seafloor. Diagenesis was probably involved during downward and upward movements of the fluids, and within the deposits on the seafloor. Little information, however, is available. Pre- and post-ore syngenetic – diagenetic enrichments of metals was proposed. (See Fig. 123 of the convection cell.)

Barton (1981), based on the types of hydrologic systems, divided the types of ore into nine categories (see his fig. 22.2).

Gromov et al. (1981) treated the dynamics of the origin of mineral deposits, e.g., they discussed hydrology, mass transport, etc.; Bubela (1981a, b) offered a model for sulfide banding under epigenesis as based on simulated sedimentary systems (by comparing dynamic vs. stationary fluids); and Wood/Hewett (1982) studied fluid convection and mass transfer in porous sandstones, e.g., contrasted diagenesis with hydrothermalism and transitional mechanisms.

SOURCE OF MINERALIZING
FLUIDS

DOMINANT FLUID MIGRATION
PATH

EXAMPLES OF DEPOSIT
TYPES

Increasing temperature (± depth) in sedimentary basin

SEDIMENTARY BASIN

Cool, SO_4^{2-} rich brine, evaporite redbed source

Warm brine richer in Fe, Ba, and reduced S

↑ Heat

Intrusive magma

SEA FLOOR VOLCANISM

Up dip

Up dip and/or cross faults

Large faults ± some dip up

dense brine flow on sea floor

Convective marine groundwater

STRATIFORM Cu-(Pb-Zn)

Marine	Non-marine
Zambian Cu belt	Corocoro
Creta	Nacimiento
Udokan	
Kupferschiefer	
Dzhezkazgan	

SANDSTONE-HOSTED Pb-Zn

Largentière
Laisvall

MISSISSIPPI VALLEY TYPE

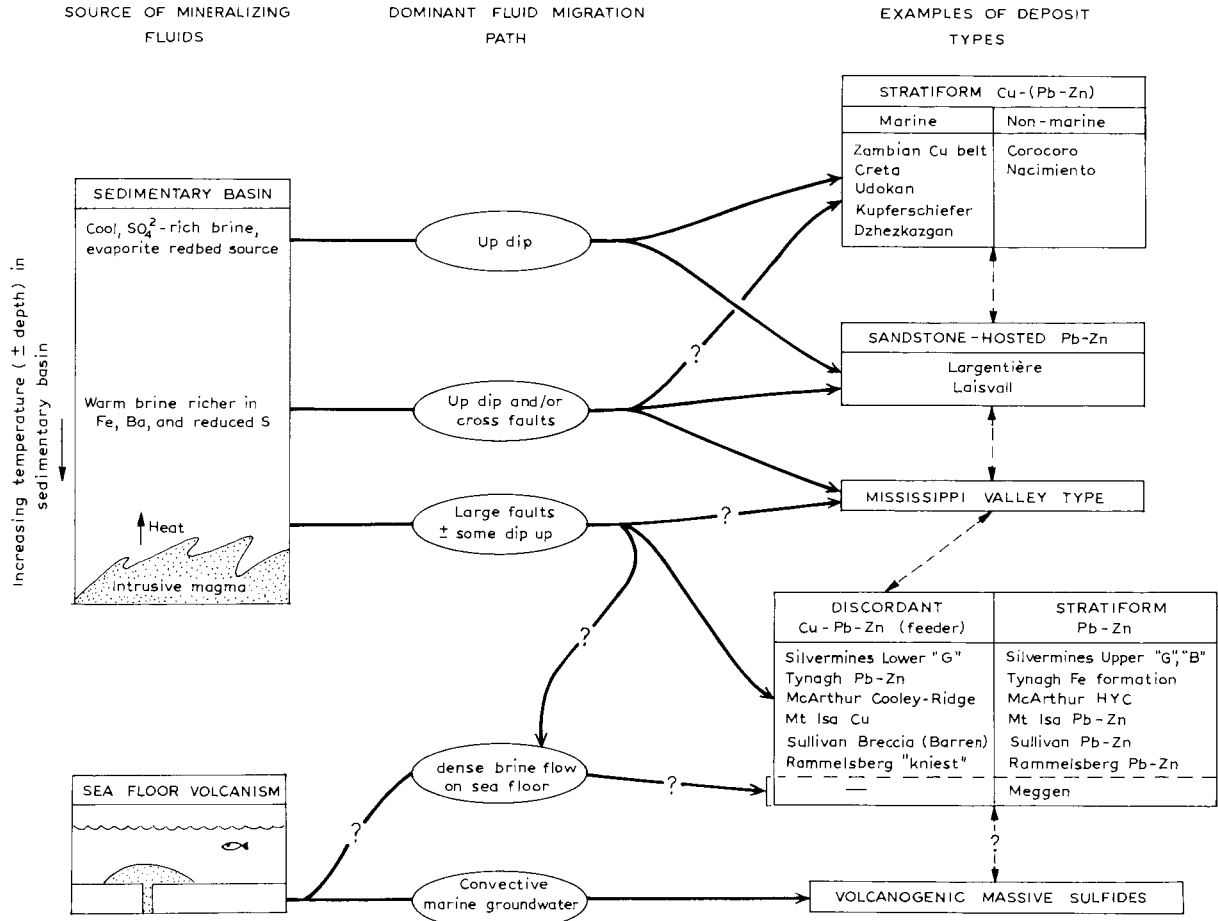| DISCORDANT Cu-Pb-Zn (feeder)	STRATIFORM Pb-Zn
Silvermines Lower "G"	Silvermines Upper "G","B"
Tynagh Pb-Zn	Tynagh Fe formation
McArthur Cooley-Ridge	McArthur HYC
Mt Isa Cu	Mt Isa Pb-Zn
Sullivan Breccia (Barren)	Sullivan Pb-Zn
Rammelsberg "kniest"	Rammelsberg Pb-Zn
—	Meggen

VOLCANOGENIC MASSIVE SULFIDES

Fig. 122. Schematic relationships are shown between types of deposits, source of mineralizing fluids, and dominant fluid pathway. Volcanic massive sulfide and Mississippi Valley-type deposits are also shown for comparison. (After Gustafson/Williams, 1981, p. 168.)
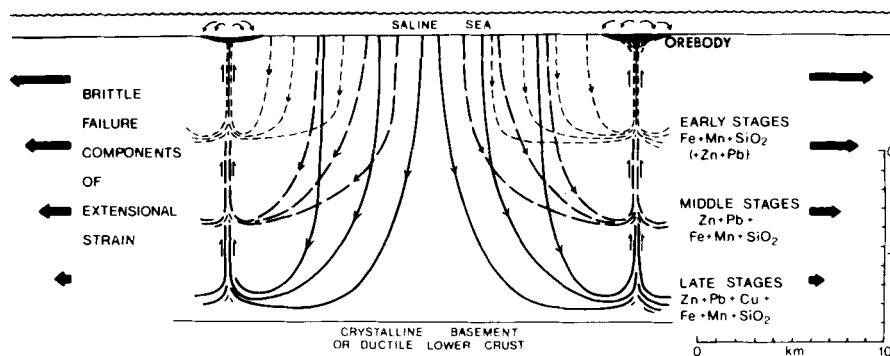
Fig. 123. Generalized model for downward penetrating convection cells. (After Russell et al., 1981.)

Moore/Druckman (1981) reconstructed the burial diagenesis, porosity evolution, paleohydrology, and resulting secondary mineral suites, all in the context of hydrocarbon migration. The stages are: early precompaction, shallow burial-compaction, early moderate burial-initial brine invasion, moderate burial-brine dominance, and moderate burial-hydrocarbon migration. Three regional zones were recognized: meteoric water, mixed meteoric – marine, and marine water environments; each being characterized by specific minerals, textures, and lithologies (see the schematic diagrammatic model in their fig. 13), as exemplified by calcite and dolomite cementation, dissolution; anhydrite, sulfate, pyrite replacement; among others.

Castang's (1981) ideas on the hydrology of deep aquifers, Winograd/Robertson's (1982) on deep oxygenated groundwaters, Stegena's (1982) on water migration influencing geothermics of basins (e.g., on compaction fluids' hydrology), Plummer et al.'s (1983) reaction models for groundwater systems, and Neuzil/Pollock's (1983) regarding erosional unloading and fluid pressures in hydrologically tight rocks, among others, all contributed data of hydrologic concepts applicable to the investigation of diagenetic (late) – burial catagenesis/metamorphism.

Behr/Horn (1982) unraveled the source and *evolution* of fluids by investigating the *development* of fluid inclusions. Four stages were recognized: graben/geosynclinal, folding/metamorphic, nappe/thrusting, and final stages. Each stage was characterized by the origin of specific solutions which precipitated specific minerals containing fluid inclusions (see model in their fig. 4) – indeed offering a neat case history.

De Wit et al. (1982) described the various structures associated with mineralized hydrothermal vent systems (see model in their fig. 9), including fluid circulation patterns based on field data: e.g., ironstone pods and mud-pool structures are indicative of fluids movements. Also, the interference of convection cells may have caused large-scale gravity sliding and overthrusting. Solomon (1980) outlined ideas

on hotwater plumes on the seafloor as clues to submarine ore genesis. In the future we have to find criteria that would allow us to discriminate between the various styles of surface and subsurface cold- and hot-water hydrologic systems. (See also Hydrothermalism.)

Ferguson et al. (1983a) modeled the hydrologic pattern of a supratidal/peritidal zone that formed iron mineralization within a carbonate sequence: the continental groundwater supplied the iron (Fig. 124).

Gregory (1983) edited a book on the Background to Paleohydrology; presenting a fundamental review for diageneticists, among others.

Garven/Freeze (1984), Sanford (1982) and Haynes/Mostaghel (1982) advanced concepts related to groundwater, e.g., a mathematical/numerical model of groundwater flow in the genesis of stratabound ores; a model of regional paleogroundwater flow in the origin of uranium deposition; and one depicting the present-day Pb – Zn precipitation from groundwater, respectively.

Hughes et al. (1984) provided Pb-isotope data of some Precambrian stratabound ores, proposing that the ore-forming fluids were supplied by basin dewatering rather than being of syngenetic origin. Thus, the dewatering-type fluid, if hot, is another variety of hydrothermal solution produced by compaction(?) during the late diagenetic – catagenic phase. They also discussed the M.V.-type and Copperbelt-type ores.

Paul et al. (1984) described sulfide-rich hypersaline water seeping out at near-ambient temperature onto the seafloor close to an escarpment. This resembles a hydrothermal vent system. The senior author (KHW) strongly believes that non-igneous basinal compaction waters, for example, can reach the surface and exhale onto the seafloor to cause various environmental changes. (Remember that a few kilometers off the island of Bahrain freshwater is "exhaled" into the ocean, thus
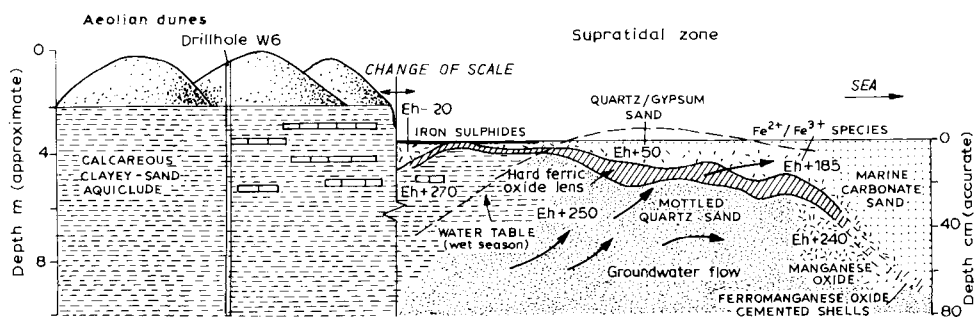

Fig. 124. Schematic cross-section of iron-mineralized area showing the relationships of the iron lens to the incoming groundwaters and to the underlying Pleistocene and overlying marine carbonates. (After Ferguson et al., 1983a. See also their other figures for details.)

creating a local diagenetic environment particularly conducive to the development of the world's best (?) oyster pearls. In the historic past, sailors used this potable water derived from rain water on the island.)

How do we differentiate between truly igneous hydrothermal and other types of exhaling hot solutions? These *exhalative*-type fluids must also be distinguished from purely *surface* phenomenon, e.g., McDougall (1984) outlined convective processes caused by dense hot saline brines moving into submarine (topographic) depressions from above and/or adjacent environments.

Campbell et al. (1984) offered models of surface-water fluid dynamics which can influence the deposition of ores, e.g., massive sulfides.

Olade/Morton (1985), using fluid-inclusion and trace-element information, among others, determined that a Pb – Zn deposit in Nigeria formed by rapid cooling due to wallrock reaction and/or mixing with meteoric or descending water of low salinity. A high geothermal gradient mobilized the connate brines.

Fritz/Eady (1985) discussed hyper-filtration which caused the precipitation of calcite cement. Numerous other diagenetic implications resulting from, for example, compaction-driven hyper-filtration, ought to be examined, some related to metalliferous concentrations in sedimentary rocks.

Domenico/Robbins (1985) commented on the displacement of connate fluids from aquifers.

Holcombe (1985) modeled the paleoflow/paleohydrology of sedimentary ore bodies. One of the major problems, of course, will be to develop techniques to determine the presence of fossil waters in the present subsurface fluids as they will modify the earlier diagenetic systems. Issar (1985) and Rozanski (1985) used deuterium and ^{18}O-data to recognize fossil water and, in the latter study, to link the groundwater composition to atmospheric circulation in the past.

King's (1985) papers are concerned chiefly with earthquake prediction utilizing concepts from hydrology and geochemistry. However, very little (if anything) is known about the process – response sequence starting with an earthquake that may trigger mechanisms controlling (enhancing, changing, destroying) diagenetic systems. For example the sequence "earthquake → compaction/particle settling/thixotropic changes → fluid release/remobilization → fluid/solution mixing → chemical precipitation" is a natural possibility. Earthquakes will also form vein/fracture systems in both unconsolidated (but having some coherence) and well-lithified rocks, i.e. of diagenetic and of epigenetic origin, that then act as conduits.

Gold/Soter (1985) discussed the ascent of fluids through the solid lithosphere and its connection to earthquakes. How do "earth shocks" control the hydrodynamic systems in sedimentary basins? Can diagenetic systems "in progress" be influenced by sudden shocks? Static diagenetic systems can become dynamic, resulting in the mobilization of material.

– See also Fluids, and Hydrothermal.

HYDROTHERMAL

Hutchinson (1983) covered the old and new concepts of hydrothermalism. He too must have been impressed by the several hundred publications available treating the whole spectrum of ancient and contemporary hydrothermal deposits. Only a few, however, have dealt with diagenesis per se and one has "to read between the lines" of the descriptions and discussions to discern the aspects of interest to those studying sedimentary and volcanic – exhalative – diagenetic mechanisms. There is a whole continuum of related processes to be examined carefully: at one end is the *subsurface* hydrothermalism (purely "epigenetic") and at the other extreme the *surface* phenomena comprising several inter-related and/or transitional/gradational processes, such as exhalative hot hydrothermalism near vents (see below) through exhalative – diagenetic cold(er) hydrothermalism to sedimentary syngenetic/ diagenetic processes. A number of natural laboratories are known (Red Sea, oceanic ridges, Yellowstone Park, etc.: see below) where the mixing of hydrothermal solutions and marine or continental water permits the investigation of processes and products that have commonly been considered by earth scientists as separate, unintegrated entities.

Bischoff/Sayles (1972) delineated diagenetic and hydrothermal processes by geochemical studies of sediments and pore fluids, including heavy metal muds. Meylan et al. (1981) and Degens/Ross (1976) reviewed the metalliferous deep-sea sediments and the stratabound metalliferous deposits near or in active rifts.

Monin et al. (1981), Butuzova et al. (1983) and Pantot et al. (1984) treated the visually recorded Red Sea brines, authigenic layer silicates in metal-rich sediments of the Red Sea (comparing clays and ore) and a large brine deep in this rift.

Boström/Widenfalk (1984) described the Fe-rich muds near a Greek island outlining the transition from hydrothermal to "normal" water environments; the sediments are enriched in Mn, Cu, Zn, Ni, and Ba.

Spiess et al. (1980), Hekinian et al. (1980) and Bischoff (1980) provided some general and specific data on mid-oceanic hydrothermal systems (e.g., on hot springs, sulfide deposits, geothermal fluids, adiabatic expansion, and on geophysics).

Schrader et al. (1980), Barrett/Friedricksen (1982), Easton et al. (1982), and Moorby/Cronan (1983) provided information on the hydrothermalism along oceanic spreading ridges with special reference to mineralogy, geochemistry, and alteration of pelagic sediments. See also Shearme et al. (1983) dealing with sediment geochemistry of the TAG hydrothermal field.

The Geological Society of London (1980a) issued a six-part symposium on the metallogenesis of oceanic spreading centers that, among others, deals with hydrothermalism of associated volcanics and sediments.

Edmond (1981) and Goldie/Bottrill (1981) offered a general review of seafloor/mid-oceanic ridge-type hydrothermalism. Haymon/Kastner (1981) and Schilling et al. (1982) described the East Pacific Rise and Galapagos system, respectively, including the distribution of mounds/chimneys in relation to sediments – see their models. Hekinian/Fouquet's (1985) work on the metallogeny of axial/off-axial oceanic rises (e.g., East Pacific Rise) demonstrated six main genetic stages of which at least two involve intermixing of hydrothermal and oceanic waters, the last stage involving seafloor processes. Baker et al. (1985) and Knüttel et al. (1985) studied, respectively, the hydrothermal particle-plumes over an oceanic ridge (Juan de Fuca) (thus outlining the transportation pathway of hydrothermal components over the seafloor) and the downslope movements of metal-bearing sediments along a similar ridge (East Pacific Rise) in the geologic past. (See also Rona, 1984.)

Schmitz et al. (1982) studied the hydrothermal serpentine in a sediment core. To what degree is that similar to the talc (and sulfide) hydrothermal coprecipitation in a seafloor brine pool as advocated by Costa et al. (1983) for a Precambrian $Zn - Cu$ sulfide deposit? What were the precursor(s) of the serpentine and talc: sediments and/or pyroclastics and volcanics? See below for clays in association with hydrothermal systems.

Mottle (1983) described metabasalts associated with axial hot springs and hydrothermal systems and Seyfried/Mottle (1982) discussed the hydrothermal alteration of basalts. Can we compare the exhalative – diagenetic alteration of submarine basalts with those of associated sediments that merely underwent halmyrolysis? Dymond et al. (1983) studied ^{226}Ra- and ^{222}Rn-contents of rift hydrothermal fluids in relation to low-temperature interactions with crustal rocks, including reactions with sediments. The Rn/Ra were plotted vs. the vent temperature. See also Bischoff et al. (1981b) and Rosenbauer et al. (1983) for graywacke and basalt hydrothermal alteration.

Zierenberg et al. (1984), like the following references, dealt with sulfide deposits of oceanic ridges by describing the mixing of hydrothermal fluids with seawater, resulting in cooling and precipitation of sphalerite plus pyrite due to $fO_2 - fS_2$ increase. Seawater is the source of S (not the hydrothermal fluids) for anhydrite and barite, for example. Koski et al. (1984) provided a model of the sequential origin of sulfide layering, paragenesis according to temperature decrease, etc. Bäcker et al. (1985) described the surface sedimentary geochemistry vs. distance from a rise crest and the $Fe + Mn$ concentrations in sediments vs. depth and distance from the crest. The transitions/overlaps from the hydrothermal to the nonhydrothermal sedimentary diagenesis ought to be established in such settings.

Karato/Becker (1983) examined the porosity and hydraulic properties of sediments and their relation to hydrothermal circulation in the ocean crust. The degree of diagenesis would affect permeability, for example.

Haymon (1983) dealt with the growth history of hydrothermal chimneys, including their chemical gradients.

Wood/Walther (1983) discussed the hydrothermal reaction rates. Kiyosu/Kurahashi (1983), Campbell/Gieskes (1984), and Michard et al. (1984) studied the waters of hydrothermal centers. For example, hydrothermal venting provides clouds of fine suspended matter of Mn, SiO_2, etc. The chemistry of the solutions (e.g., acid sulfate – chloride) and the S-species were described. (See also Zhabina/Sokolov, 1982, for S-compounds in Red Sea sediments.)

Stoffers et al. (1985) deliberated on "fossil" hydrothermal accumulations in the South Pacific, describing a hiatus of sedimentary/hydrothermal activity controlled by pH/Eh variations.

McMurty (1981) described hydrothermal clay-mineral genesis; Murname/Clague (1983) studied nontronite from an oceanic ridge and modeled the low-temperature vs. the high-temperature hydrothermal system; whereas Cole (1985) investigated the composition, O-isotope and origin of smectite in metalliferous sediments in the Pacific Bauer Deep, and discussed regional factors controlling the smectite genesis. Wilkinson et al. (1985) modeled (see their fig. 13) submarine "hydrothermal weathering" (= hydrothermal halmyrolysis?), which could be considered as an exemplar of the triad of hydrothermalism, diagenesis and subaqueous weathering.
   Let us compare this with data obtained from ancient deposits: Stanton (1984) dealt with the derivation of cordierite from a clay – chlorite precursor and proposed the involvement of hydrothermal fluids in the diagenesis of hostrocks that generated a wide variety of clay – chlorite – zeolite, etc., minerals of both primary and chemical alteration origins. These minerals were later overprinted by metamorphism, similar to the Kuroko-type rocks. Stanton also concluded that the phyllosilicates of some Paleozoic stratiform sulfide deposits are of hydrothermal – exhalative/diagenetic origin.

Marchig et al. (1982, 1984) proposed some geochemical indicators to discriminate between diagenetic and hydrothermal sediments. To what extent are fluid inclusion studies of both sulfide and gangue minerals useful in this regard (Le Bel/Oudin, 1982)? Certain concepts developed for the study of ancient rocks ought to be applied to contemporary hydrothermal deposits (e.g., see Beeson, 1980a, for recognition of hydrothermal origin of U- and Th-enriched tuffs through trace-element geochemistry).

Zierenberg/Shanks (1983) outlined the epigenetic features in metalliferous sediments of the Red Sea. Note that "epigenesis" need not be a late-stage phenomenon as they can occur very early while the host-sediment is still unconsolidated/uncemented and, consequently, is of the diagenetic – epigenetic variety.

Toth (1980) described Mn + Fe submarine crusts and offered a model, discriminatory data between hydrothermal and other types of deposits; Halbach et al. (1983) dealt with Co-fluxes and ferromanganese growth rates of diagenetic vs. hydrothermal nodules; and Moorby et al. (1984) examined hydrothermal Mn-oxides deposits. All their concepts can be applied to ancient deposits as done, for instance, by Crerar et al. (1982) to Mn-rich cherts, and by Kaeding et al. (1983) to Mn-deposits. The latter discussed also Fe-oxides, pyrite, associated clays, mixed Fe – Al gels, mixing of marine water and degassing, Eh/pH, etc.

Des Marais et al. (1981) studied the molecular C-isotopic evidence for the origin of geothermal hydrocarbons; Mackenzie (1982) investigated a hydrothermal plume that remobilized sedimentary organic matter; Baross et al. (1982b) examined the CH_4, H_2 and CO_2 vented from submarine hydrothermal systems which could have been produced by thermopilic bacteria (?) (see also below and the Bacteria section); Lilley et al. (1982) similarly dealt with CH_2, H_2, CO and N_2O in submarine hydrothermal vent fluids; and Jedwab/Boulègne (1984) described graphite crystals in hydrothermal vents. To what degree is the carbon and carbonaceous matter in hydrothermal systems influential in diagenesis? Nakashima et al. (1984) studied the mechanism of uranium fixation and reduction by sedimentary organic matter under both diagenetic and hydrothermal conditions, which can serve as a demonstration that the *derivation* and behaviour of organic matter is of fundamental importance (see also Organic matter).

Rona et al. (1983) summarized the hydrothermal processes at seafloor spreading centers with some contributions touching diagenesis, including the biology of hydrothermal vents; Enright et al. (1981) and Grassle (1985) examined the animal communities associated with deep-ocean hydrothermal vents; and Fry et al. (1983) tested the S-isotope composition of hydrothermal vent animals. Both Bernhardt et al. (1984) and the Canadian American Seamount Expedition (1985) studied the high-temperature control on bacteria of oceanic ridges and the Black Smokers; e.g., sulphate-reducing bacteria are active in the hot vent water. As to similar organism-associated hydrothermal systems, see Haymon et al. (1984) for vent worms from Cretaceous hydrothermal sulfide ores, and Banks (1985) for worms in the hydrothermal Tynagh Pb – Zn deposits.

Bargar/Beeson (1981), among others, studied the hydrothermal alteration in a drillhole of the Yellowstone field. How do these alterations compare with those of the New Zealand field? One aspect needs to be examined in the future: how can one discriminate such "epigenetic" hydrothermal modifications (especially if very low-grade) from earlier diagenetic – catagenetic burial and regional metamorphism? (How many publications can you cite that make such comparisons?!)

McKibben/Elders (1985) described the intracontinental geothermal system of the Imperial Valley, California, containing Fe – Zn – Cu – Pb mineralization. The influence of diagenesis is illustrated by earlier-formed pyrite which was replaced by Cu – Pb – Zn sulfides. The fine-grained diagenetic Fe-sulfide was overgrown by

coarser pyrite upon burial and heating; at still greater depth the latter pyrite was then replaced by the $Cu - Pb - Zn$ sulfides.

Haack et al. (1984) deliberated the loss of metals from pelites during regional metamorphism which resulted in "hydrothermal" ore deposits in a low-grade environment and in remobilized metamorphic-type hydrothermal fluids that can carry Ba, Pb, Bi, Zn, Cu, Hg, Cd, etc. See also Stendal (1982), among many others, in regard to the problem of hydrothermalism in conjunction with syngenetic – diagenetic metals that were subsequently remobilized.

Studemeister (1985) reviewed numerous processes operative in the genesis of hydrothermal ores, including the influence of seawater, and meteoric and metamorphic fluids/brines of the Red Sea – Salton Sea – Cheleken Peninsula-type systems. Again, it is obvious that syngenetic/diagenetic, surface/subsurface metasomatic and exhalative hydrothermal mechanisms are transitional, overlapping and contemporaneous.

Lagerblad/Gorbatschev (1985) investigated hydrothermal alteration; see model in their fig. 11 depicting syngenetic – diagenetic and epigenetic processes, including infiltration of elements from seawater, surface/subsurface leaching and other mechanisms as part of diagenetic metasomatism and exhalative hydrothermalism.

Karl et al. (1980) described the deep-sea primary production of S, CO_2, bacteria, and others at a Recent oceanic hydrothermal vent; and Lupton/Craig (1981) examined a major He^3 source. Are the products of He, Mn, S, CO_2, etc., plumes reflected in surrounding sediments?

Carne/Cathro (1982) investigated a sedimentary – exhalative $Zn - Pb - Ag$ deposit and modeled the behaviour of geothermal brines in seawater (after Sato, 1972, and others; see their fig. 5). At least three depositional systems are possible with their own temperature – salinity and metal zonation characteristics. All these processes are surface phenomena – hence, diagenesis must play an active role.

Maris/Bender (1982) studied "upwelling" of hydrothermal fluids through oceanic ridge-flank sediments as shown by pore-water profiles (cf. Upwelling, and Interstitial fluids).

Boyce et al. (1983b) investigated the genesis of fossil hydrothermal chimneys and mounds (see model in their fig. 5): the ore accumulated in brine pools on the irregular paleotopographic seafloor from the precipitation of metal-rich exhalants which reacted with sedimentary interstitial seawater, reducing bacteria, and organic matter. This offers a good analogue of hydrothermal-to-sedimentary diagenetic transitional mechanisms.

Kalogeropoulos et al. (1983) modeled the stages of barite ore development of Kuroko-type deposits as a consequence of mixing of ascending hydrothermal fluid
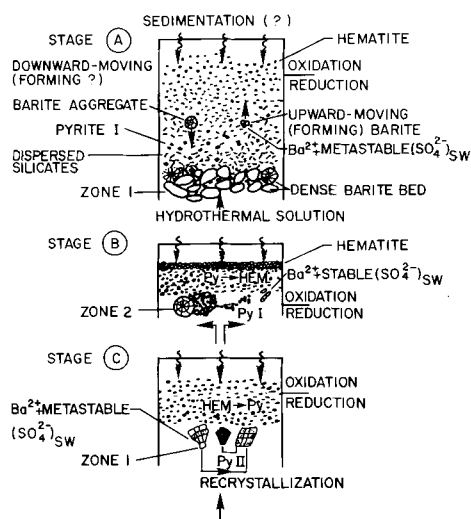
Fig. 125. Stepwise development of the barite ore zone of Kuroko-type ore deposits (not to scale) produced by mixing of an ascending hydrothermal fluid and cold seawater in a fluctuating hydrothermal system. (After Kalogeropoulos, 1983.)
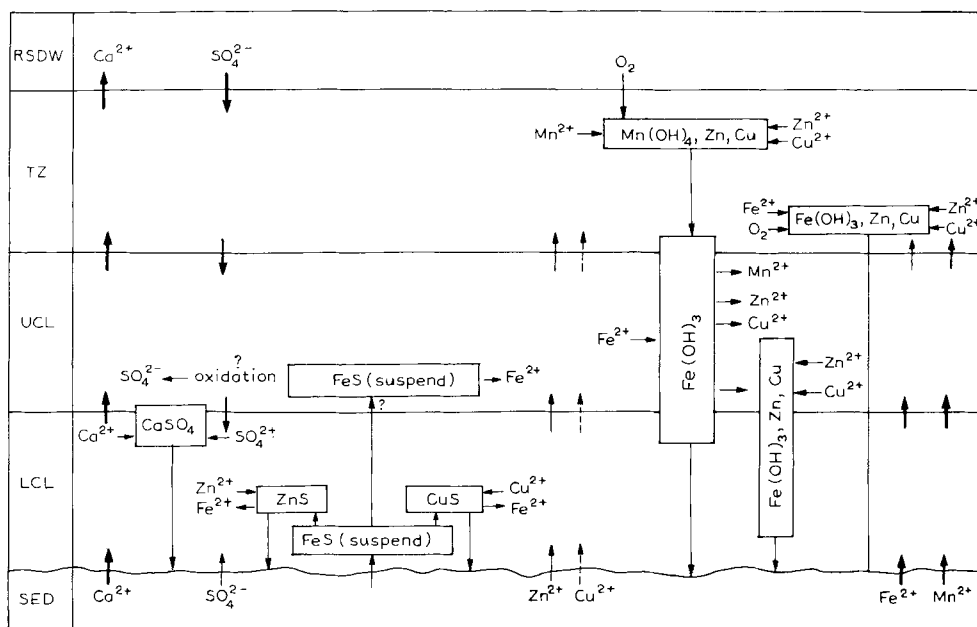

Fig. 126. Scheme of mixing and precipitation/dissolution processes throughout the whole depth profile between discharging hydrothermal brine and RSDW (involving Ca, SO_4, sulfides, oxygen, and metals). In boxes: solid components forming from solution or other solid components by reactions within the brine sections covered by the boxes. Vertical arrows indicate the addition of the respective components from the hydrothermal vents and/or RSDW and their transport through the brine interfaces. (After Hartmann, 1985.) $RSDW$ = Red Sea deep water; TZ = transition zone; UCL = upper convection layer; LCL = lower convection layer; SED = sediment. See also Figs. 231 and 232.

and cold seawater in a fluctuating hydrothermal system (Fig. 125). The processes involved are gradational into purely sedimentary types.

Kadko (1985) studied the sedimentation and metal deposition in the North Pacific during the Late Cenozoic and discussed hydrothermal vs. sedimentary/diagenetic processes. Piepgras/Wasserburg (1985) used Sr- and neodymium-isotope data from hot-spring accumulations to conclude that interaction with metalliferous sediments must have occurred (e.g., the metals were derived from the sediments).

Hartmann (1985) modeled a number of interconnected syngenetic – diagenetic processes of the Atlantis-II Deep geothermal brine system: i.e., the chemical processes between hydrothermal brines and the Red Sea water (Figs. 126 and 127).

Skripchenko (1984) offered a model of the accumulation/differentiation of ore-rich muds, Atlantis-II Deep, and the Red Sea (see Fig. 128), illustrating beyond doubt that the combination of hydrothermalism and sedimentogenic diagenesis (both biological and physicochemical; plus mechanical?) is transitional and constitutes two end-members along a spectrum.

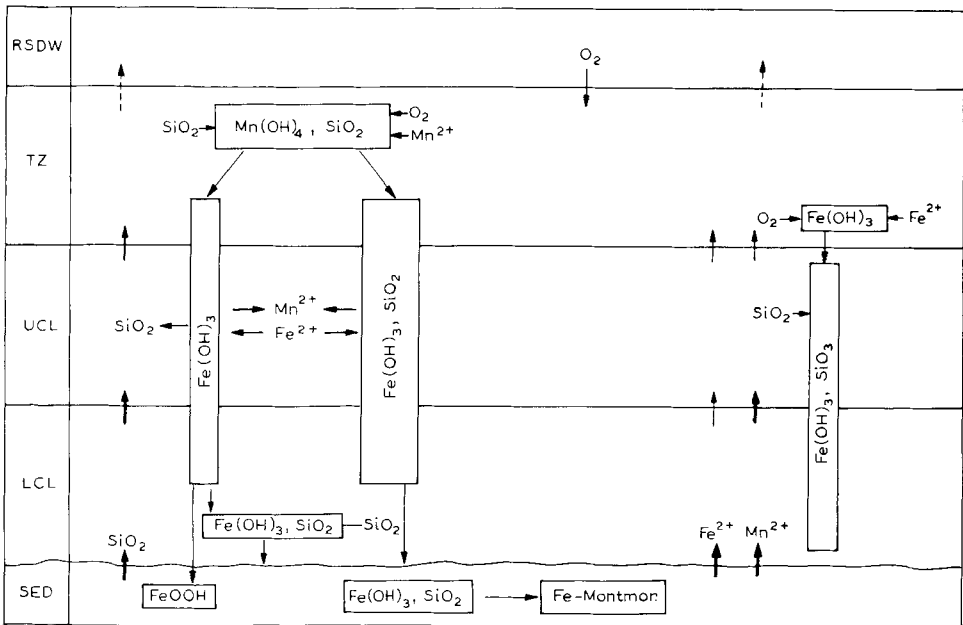Jannasch/Mottle (1985) reviewed the geomicrobiology of deep-sea hydrothermal vents (Fig. 129).

Fig. 127. Scheme of mixing and precipitation/solubilization processes involving silica, metals and oxygen, (After Hartmann, 1985.)
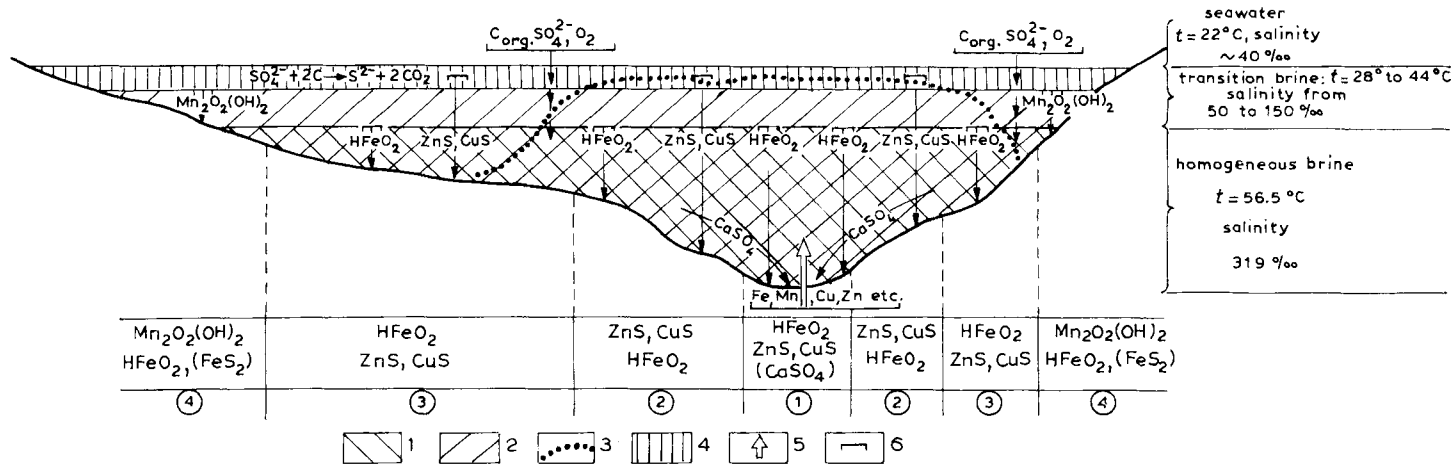
Fig. 128. Schematic diagram for the deposition of ore muds in the Atlantis II Deep: (1 – 2) zone of maximum: 1 = iron (over 87 ppm), 2 = manganese (over 77 ppm), 3 = boundary of brine with zinc concentration over 7 ppm, 4 = zone of biogenic sulfate reduction, 5 = point of emergence of the brine in the trench part of the deep, 6 = zones of formation of zinc and copper sulfides and of iron and manganese oxides; (1 – 4) distribution of the types of ore accumulation on the floor of the deep: 1 = iron – copper – zinc, 2 = rich copper – zinc, 3 = lean copper – zinc, 4 = iron – manganese – pyrite and anhydrite are shown in parentheses. (After Skripchenko, 1984.)

On mixing

$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$

$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$

$FeS, Mn^{2+} + O_2 \rightarrow FeO(OH), MnO_2$

Plume
Pillow lava
Sheet lava
Seawater

$6° - 23°C$

$350°C$

Sedimentation

Permeation

$20° - 100°C$

Shallow
(10 - 200 m)

Deep
(1 - 3 km)

En route
precipitation
FeS, FeS$_2$
CuFeS$_2$

$350°C$
contour

Hydrothermal
fluid

$SO_4^{2-} \rightarrow S^{2-}$ | $HCO_3^- \rightarrow CO_2, CH_4$ | $Mg^{2+} \gtrless Mn^{2+}$ | Ca^{2+} | Fe^{2+} | Cu^{2+} | H^+
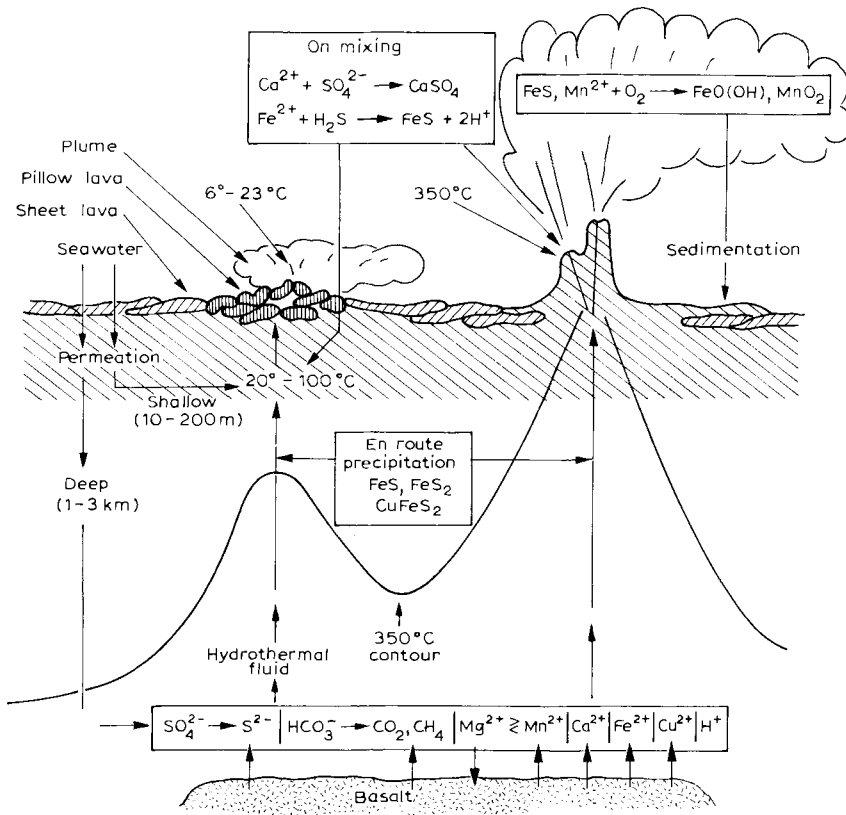
Basalt

Fig. 129. Schematic diagram showing inorganic chemical processes occurring at warm- and hot-water vent sites. Deeply circulating seawater is heated to 350° − 400°C and reacts with crustal basalts, leaching various species into solution. The hot water rises, reaching the seafloor directly in some places and mixing first with cold, downwelling seawater in others. On mixing, iron − copper − zinc sulfide minerals and anhydrite precipitate. (After Jannasch/Mottle, 1985.)

Hutchinson et al. (1982) reviewed comprehensively Precambrian sulfide deposits, many of which are believed to be of syngenetic or early post-depositional (rather than late-stage epigenetic) origin formed from hot ascending waters or as chemical − exhalative precipitates on the seafloor. In particular in the latter situation numerous diagenetic reactions took place. Consequently, at least three groups of deposits were recognized, namely, exhalative − volcanic, exhalative − sedimentary, and miscellaneous ore types. The precursors of the hydrothermal solutions were believed to be meteoric and/or marine waters − not solutions produced by magmatic differentiation.

La Tour et al. (1984) described hydrothermal alteration and dynamic recrystalliza- tion of feldspar in an iron formation as the result of convergence of volcanic, sedimentary and hydrothermal processes; a complex interplay of several processes which must be understood to identify "primary" from "secondary" products.

Robinson (1984) studied tuffaceous silicate exhalite facies of an iron formation and the stratabound alteration formed by "sedimentary – hydrothermal mixing", and thus illustrated the convergence of syngenetic (sedimentary) and diagenetic (exhalative-type) processes.

Susak/Crerar (1985) examined the spectra and coordination changes in transition metals in "hydrothermal" solutions and their implication in ore genesis; see model in their fig. 8 depicting M.V.-, Kuroko-, Cyprus-, Rhodesian Copperbelt-, unconformity-related U – Ni – C-, and vein-type deposits.

Plimer (1985) pushed the concepts of hydrothermal diagenesis back into the Precambrian by considering the Broken Hill Pb – Zn – Ag deposits as the product of mantle metasomatism and by including in his model (see his figure) fluid exhalations of Si, Zn, Mn, Fe, and Bi.

Andrew/Ashton (1985) provided another ancient example of integrated/combined hydrothermalism-cum-diagenesis as applied to both hostrocks and ore concentrations (see their discussions of textures).

Goodwin et al. (1985) described the chemostratigraphy and origin of an Archean siderite/pyrite-rich iron formation, and considered diagenesis, hydrothermalism, pH/Eh controls, cyclicity, and others. See their models.

Fulp/Renshaw (1985) reconstructed the volcanic – exhalative (= syngenetic) origin of a subsequently metamorphosed Proterozoic tungsten deposit and discussed the exploration implications. The finer details of a possible diagenetic modification were, of course, obliterated during metamorphism.

– See also Fluids, Hydrology, Volcanic – exhalative, and Temperature.

INTERSTITIAL (PORE) FLUIDS

Emerson (1976) examined the chemical equilibria in interstitial waters in context with early diagenesis in anaerobic lake sediments, whereas Lerman (1977) reviewed in a book on The Sea the migrational and chemical reactions in interstitial fluids. These were followed by many publications, including one by Bubela (1980) on interstitial water movements (also on algae); by Davidson et al. (1982) on the handling and measurement techniques for anoxic interstitial waters as he warned of "in vitro diagenetic changes"; by Musgrave/Reeburgh (1982) on density-driven interstitial water motion; and by Bender (1983) on pore-water chemistry of a hydrothermal field of a Recent oceanic spreading center.

Brooks et al. (1968) studied the trace elements in interstitial fluids of marine sediments, as have others done before and since. Emerson et al. (1980) dealt with early diagenesis in sediments, considering the pore water nutrients, carbonate and

metals; Pushkina et al. (1981) investigated ten metals in interstitial fluids from metalliferous Red Sea sediments; whereas El Ghobary (1982) reported on four metals. Stoffyn-Egli (1982), Schnier et al. (1981) and Tebo et al. (1984) examined, respectively, Al, Mn and Co in interstitial fluids. The literature on Mn-nodule genesis, especially, offers many more data on interstitial fluid diagenesis.
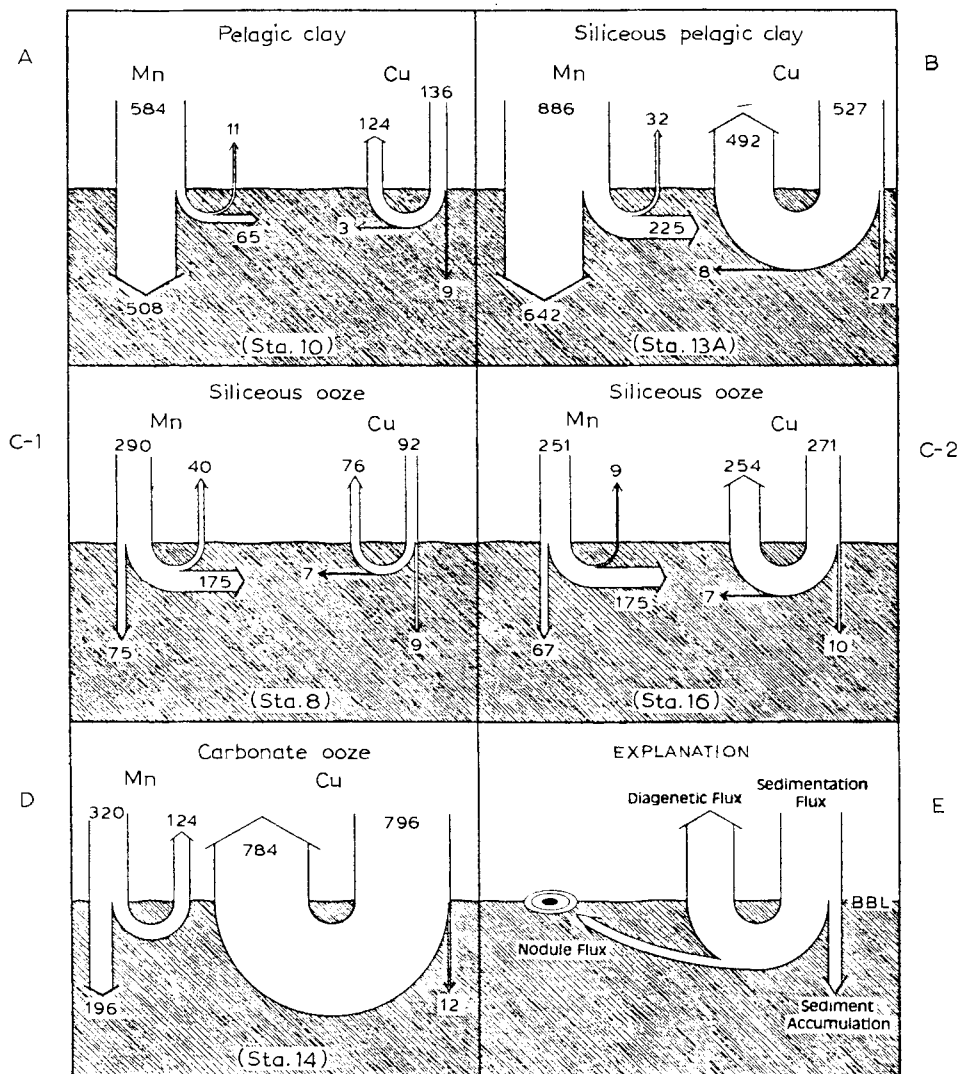

Fig. 130. Fluxes of Mn and Cu in the northeast equatorial Pacific Ocean: (A) pelagic clay (sta. 10); (B) siliceous pelagic clay (sta. 13A); (C) siliceous ooze (sta. 8 and 16); (D) carbonate ooze (sta. 14); (E) schematic representation of flux diagram. All fluxes are expressed in $\mu g\ cm^{-2}\ 10^{-3}$ yrs; BBL = bottom biogenic layer. (After Callender/Bowser, 1980.)

Krom/Sholkovitz (1977), Saliot et al. (1980), Suess (1981), and Jahnke et al. (1982) dealt with organic matter, nutrients and P regenerated from organic debris from interstitial fluids. Jahnke et al. offered a model of the processes involved, including diffusion (see Diffusion).

Callender/Bowser (1980) modeled the fluxes of Mn and Cu in interstitial fluids related to the origin of nodule-rich pelagic sediments (Fig. 130).

Irwin (1980) modeled the pore fluid/interstitial solution-type migration related to early diagenetic carbonate precipitation. The Fe-flux has been considered also (Figs. 131 and 132). Similar models may apply equally to other metals in the origin of ore deposits.

Elderfield/Gieskes (1982) studied the Sr-isotopes in interstitial fluids and provided data on diagenesis of volcanics, on hydrothermal signals, etc.; whereas Kusakabe/
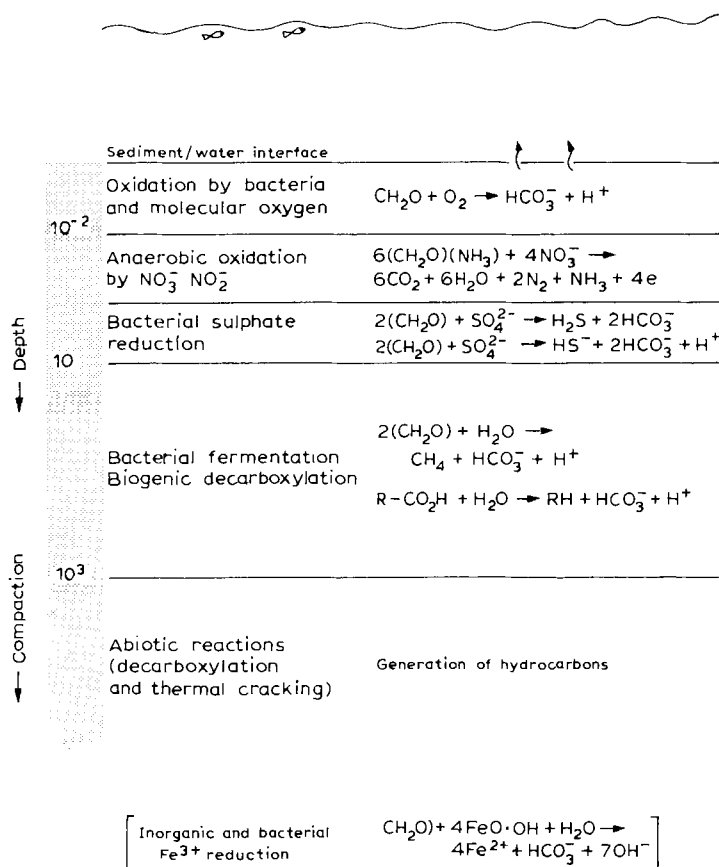
Depth / Compaction		Reaction zone	Reaction
		Sediment/water interface	
	10^{-2}	Oxidation by bacteria and molecular oxygen	$CH_2O + O_2 \rightarrow HCO_3^- + H^+$
		Anaerobic oxidation by NO_3^- NO_2^-	$6(CH_2O)(NH_3) + 4NO_3^- \rightarrow$ $6CO_2 + 6H_2O + 2N_2 + NH_3 + 4e$
	10	Bacterial sulphate reduction	$2(CH_2O) + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$ $2(CH_2O) + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+$
		Bacterial fermentation Biogenic decarboxylation	$2(CH_2O) + H_2O \rightarrow$ $CH_4 + HCO_3^- + H^+$ $R-CO_2H + H_2O \rightarrow RH + HCO_3^- + H^+$
	10^3	Abiotic reactions (decarboxylation and thermal cracking)	Generation of hydrocarbons
		Inorganic and bacterial Fe^{3+} reduction	$\left[\begin{array}{c} CH_2O + 4FeO \cdot OH + H_2O \rightarrow \\ 4Fe^{2+} + HCO_3^- + 7OH^- \end{array} \right]$

Fig. 131. Depth-related reaction zones involving breakdown of organic matter. (After Irwin, 1980.)

244

Ku (1984) examined the incorporation of Be-isotopes and other trace metals into Fe – Mn deposits.

Burdige/Gieskes (1983) modeled the diagenetic pore water – solid phase system for Mn and eliberated advection, diffusion, Eh-reactions, micro-zoning, etc., as related to interstitial fluids (Fig. 133).

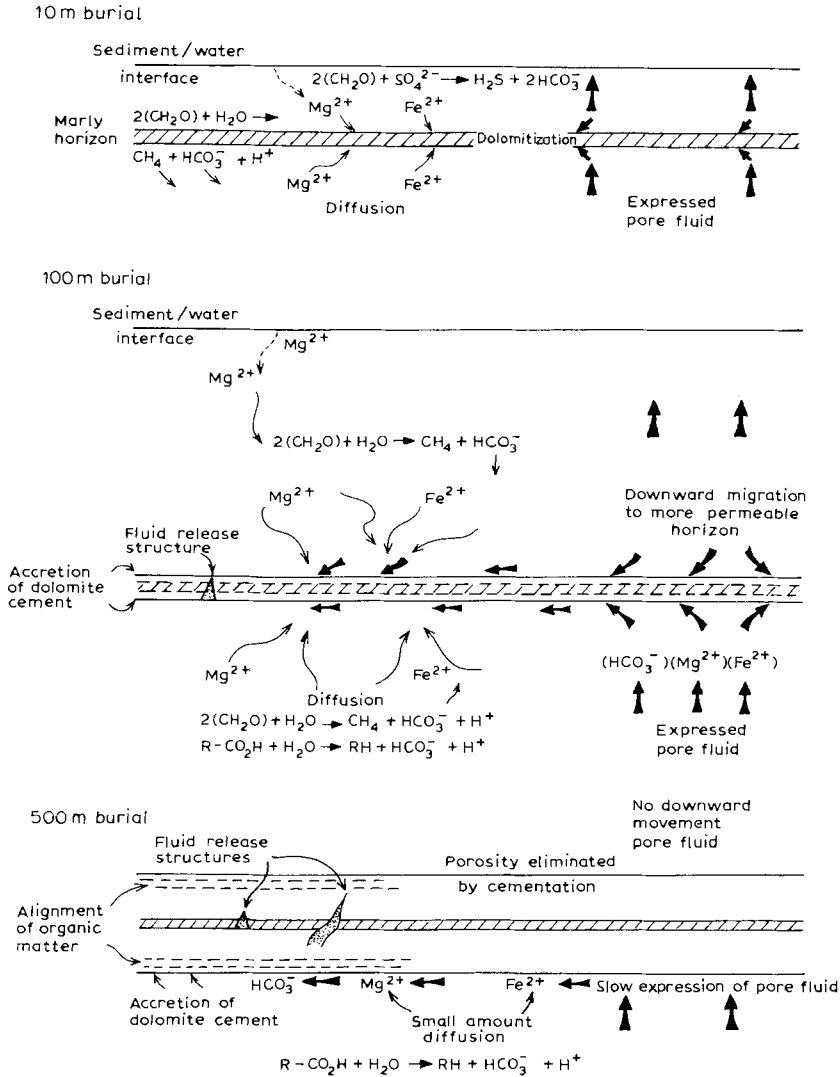– See also Diffusion, Fluids, Solutions, and Water.

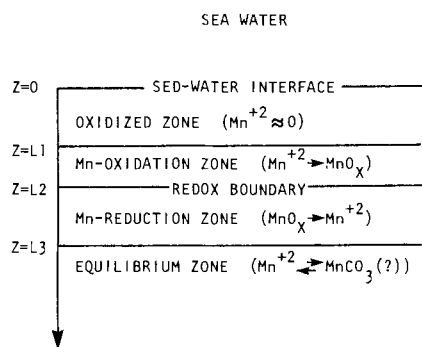Fig. 132. Pore fluid migration and induration of the Yellow Ledge, Kimmeridge Clay. (After Irwin, 1980.)

SEA WATER

```
Z=0  ┌────────── SED-WATER INTERFACE ─────────
     │
     │   OXIDIZED ZONE   (Mn⁺²≈0)
Z=L1 ├─────────────────────────────────────────
     │   Mn-OXIDATION ZONE   (Mn⁺²➤MnOₓ)
Z=L2 ├──────────────REDOX BOUNDARY─────────────
     │   Mn-REDUCTION ZONE   (MnOₓ➤Mn⁺²)
Z=L3 ├─────────────────────────────────────────
     │
     │   EQUILIBRIUM ZONE   (Mn⁺²⇌MnCO₃(?))
     │
     │
     ▼
```

Fig. 133. Schematic illustration of the zonation of marine sediments with regard to manganese geochemistry. (After Burdige/Gieskes, 1983.)

ION-EXCHANGE

Devine et al. (1973) pointed out that in studying the mechanisms of diagenesis in Recent sediments certain "interstitial solution extractions do not distinguish between inner and outer solution around clay minerals . . ." Thus, the older data on ion exchange, cation-selectivity, etc., may be unreliable.

Hanshaw/Coplen (1973) mentioned that clays and shales act as semi-permeable membranes (= reverse osmosis, ultrafiltration) due to ion-exchange capacity of the clays. As a result, concentration of elements, and formation of subsurface brines, and diagenetic-to-epigenetic ore deposition takes place.

Van Olphen (1963a, b), Yariv/Cross (1979) and Eitel (1975), among others, provided basic data on ion-, base-, etc., exchange mechanisms.

Jenny/Elgabaly (1943) reported on the cation and anion interchange with Zn-montmorillonite clays; Ramamoorthy/Rust (1978) studied the heavy metal exchanges in sediment – water systems; Rashid (1969) and Hunt (1981) studied the cation-exchange capacity of humic or organic matters; Balistrieri/Murray (1981) examined the surface chemistry of goethite in major ion-containing seawater; and Gurskii/Levshenko (1981) dealt with the types of cation-exchange as related to "metamorphism" of interstitial fluids.

Rieke/Chilingarian (1974) discussed in detail the subject of fluid filtration through clays (semi-permeable membranes, etc.). Note that extensive data on ion exchange has been developed by drilling fluid experts (see Chilingarian/Vorabutr, 1981).

– See also Adsorption, and Organic matter.

IONIC POTENTIAL

Mason (1965, pp. 155 – 157) and Krauskopf (1979, pp. 483 – 484) deliberated on the ionic potential in sedimentary environments. The ionic potential of an element largely determines its place of deposition and explains the similar behaviour of dissimilar elements (e.g., Be, Al, Ti precipitated together in sediments and Be, Ga, Ti, Zr, Nb concentrated in bauxites). In Fig. 134, the elements are divided into three groups: soluble cations, elements of hydrolysates, and elements of soluble complex ions. Krauskopf discussed some of the limitations of the ionic potential "hypothesis" in comparison with adsorption! Just like geologists, too often the geochemists do not state clearly the limitations, assumptions, and restrictions of their interpretations (especially in the work on isotopes).
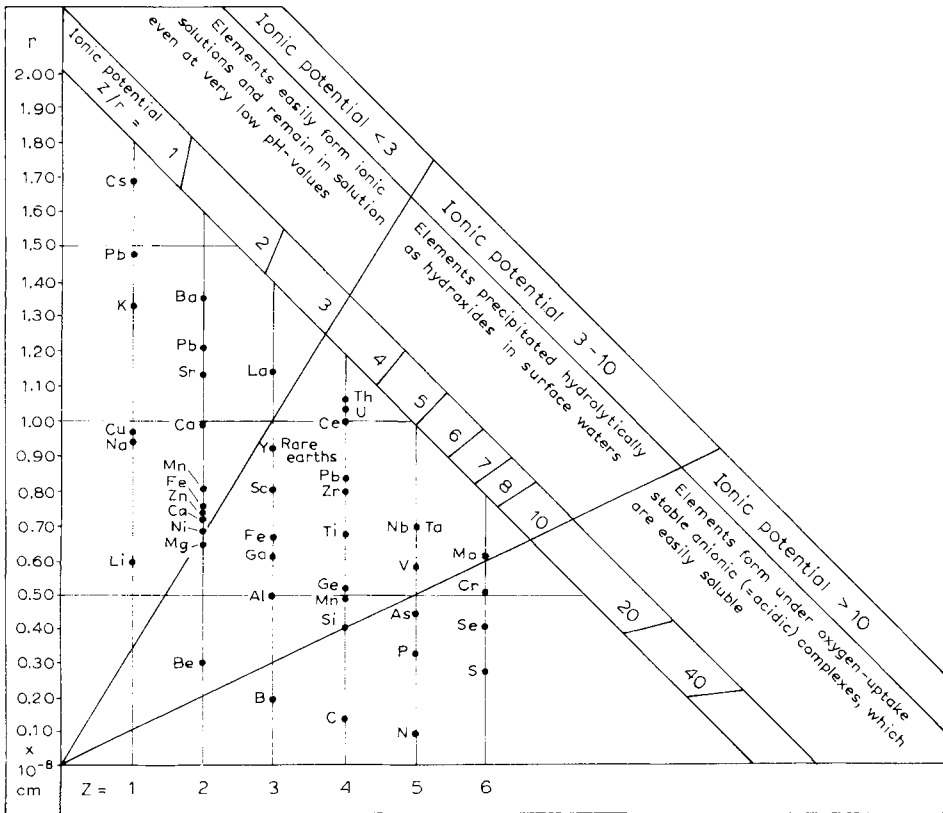

Fig. 134. Triangular diagram of the ionic potential of the most important elements present in rocks and ore deposits, divided into three groups according to their characteristic chemical behaviour. r = ionic radius; z = valence. (After Wolf, 1981, fig. 68, p. 193.)

Fyfe (1964), Mason (1965), Garrels/Christ (1965), Berner (1971), Rösler/Lange (1972), and Krauskopf (1979) presented an introduction to ionic potential and related topics.

Jung/Knitzschke (1976) discussed the metal concentrations at various redox potentials (ion radius, ion potential, solubility product, Eh) in regard to the genesis of the Kupferschiefer deposit.

Millero/Schreiber (1982) studied the ion-pairing model to estimate activity coefficients of the ion components of natural waters.

IRON

Trendall/Morris (1983) reviewed comprehensively the iron formations; Beukes (1980) suggested a useful classification and nomenclature for these formations; whereas Morris (1985) dealt with one variety of iron ores, i.e., supergene and supergene – metamorphic ores (with some comments on diagenesis). Eichler (1976), Dimroth (1976) and Quade (1976) covered the geology (including diagenesis) of the Precambrian BIF's, cherty IFs, and the Lahn-Dill-type of deposits, respectively.

Beukes (1980a) provided a detailed description of the lithofacies and stratigraphy of one Fe-formation complex, including its cyclicity, but a meticulous diagenetic – paleogeochemical reconstruction is needed. Rai et al. (1980) obliged us with primary and diagenetic features of a BIF. Gole/Klein (1981) described the BIF through Precambrian time, and Gole (1981) the Archean BIF of Western Australia, followed by Ewers/Morris (1981) who concentrated on one member of the latter. Morris/Horwitz (1983) continued studying the BIF of a platform. See also Erikkson (1983) for a general environmental reconstruction of an iron deposit.

Brown (1982) deliberated the Fe-formation and the associated stratiform Zn-ores; a rather interesting association. Phillips et al. (1984) treated BIF-hosted gold deposits of epigenetic affiliation, thus describing an important new type. Some additional general publications: Lougheed (1983), Mücke/Golestanch (1982; with model and comparison of orthomagmatic and volcanic – sedimentary origins); Beukes (1984; on Eh/pH, textures, diagenesis, including chert); and Cisne (1984; on geochemical, sedimentation dynamics, loading, oxide vs. carbonate facies, water depth, cyclicity, etc.).

Teyssen (1984) should be mentioned as one of innummerable researchers who have examined the oolitic Minette ironstones. This complex formed in a subtidal environment, but diagenetic studies are relatively scarce. (See also Kimberley, 1981.)

Leggett/Smith (1980) and Appel (1980) in studying Ordovician and Precambrian iron deposits, respectively, compared them with the recent deposits of active oceanic ridges, e.g., they provided a model of processes including diagenesis, and outlined the submarine – exhalative origin of brines, for example.

Loberg/Horndahl (1983) and Channell et al. (1982) dealt with the ferride geochemistry (e.g., trace elements distinguish magmatic, exhalative and sedimentary Fe-ores; a V vs. temperature diagram was given) and with the timing of diagenetic hematite in red pelagic limestones (magmatite-to-hematite diagenesis affected various magnetization components; see Magnetization). (V = vanadium.)

Perry/Ahmad (1981) studied the O- and C-isotope geochemistry of an iron formation; Youzheng (1982) the paleohydrology; Braterman et al. (1983) examined the photo-oxidation of hydrated Fe^{2+} in BIF genesis; and Towe (1983) investigated the Precambrian atmosphere oxygen in BIF origin (see Evolution).

Aschan (1932) discussed the role of water humus in the formation of marine iron ore; to mention merely one haphazardly chosen 50-year old study, which was succeeded by hundreds of others. Berner (1964) handled the stability fields of Fe minerals in anaerobic marine sediments; Aston/Chester (1973) treated the influence of suspended particles on Fe-precipitation and Gordon et al. (1982) the Fe in Pacific waters; Studemeister (1983) examined the redox state of Fe as an indicator of hydrothermalism (see Eh, and pH); Rozanov/Morozov (1983) the diagenetic
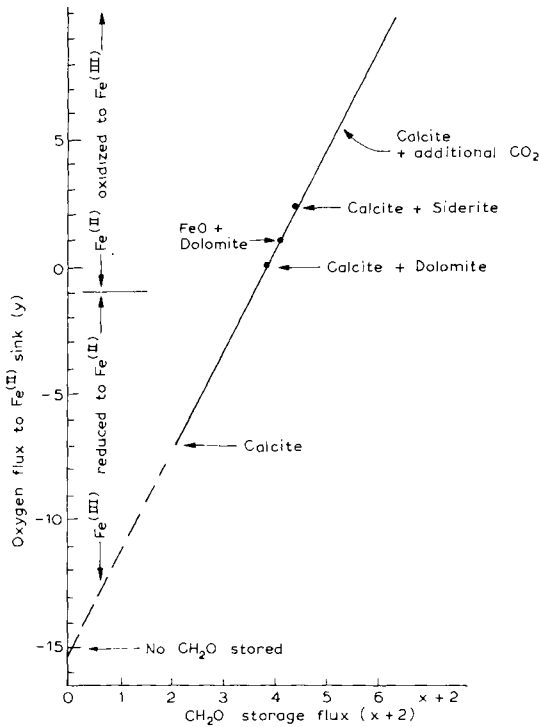

Fig. 135. Relationship between the flux of oxygen to the $Fe^{(II)}$ sink (stoichiometric coefficient y) and the storage flux of organic carbon in sediments $(x + 2)$. (After Lerman, 1982, in Holland/Schidlowski, 1982.)

sulfides of Fe in sediments (e.g., diagenetic vs. hydrothermal minerals); Laxen/Chandler (1983) investigated the size distribution of Fe + Mn species in freshwater; and Nishri/Stiller (1984) studied the iron in the Red Sea (e.g., the rate of oxidation of Fe^{2+} in interstitial fluid, Fe-flux).

Gross (1980) offered a classification based on depositional environments, which ought to be matched by diagenetic/geochemical/textural facies concepts.

Lerman (1982, in Holland/Schidlowski, 1982) opined on the Phanerozoic sedimentary cycle and, among others, on the relationship between O_2-flux to the Fe^{2+} sink and the storage flux of organic C in sediments (e.g., influencing Fe^{2+} vs. Fe^{3+}) that controls the carbonate mineralogy (i.e., calcite, dolomite, siderite) (Figs. 135 and 136).

Drever (1974; see also in Maynard, 1983, p. 37; and in Holland/Schidlowski, 1982) modeled the mineral facies of BIFs as based on diagenetic mechanisms and upwelling. The facies changes from deep-water hematite + siderite through hematite + greenalite and hematite + magnetite to nearshore, shallow-water hematite indicates that the carbon content is greatest in the deeper-water setting. See also Borchert (1965) for similar zoning in oceans as reflected by Eh/pH, etc. If upwelling (and diagenesis) is responsible for some types of phosphorites *and* iron-rich deposits, what are the differences between the two systems because they usually occur separately?

Simonson (1985) summarized the sedimentological (including diagenetic) constraints on the Precambrian iron formations (see his six comparative models).
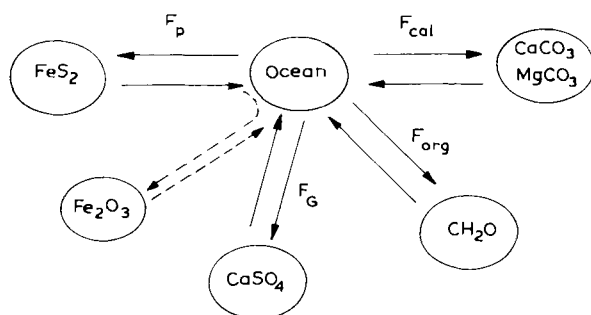
– See also Gossans.

Fig. 136. Model of the sedimentary cycle in the Phanerozoic. The sedimentary reservoirs shown are reduced sulfur and iron (FeS_2), sulfate ($CaSO_4$), oxidized iron (Fe_2O_3), reduced carbon (organic matter, CH_2O), and carbonates ($CaCO_3$, $MgCO_3$). (After Lerman, 1982, in Holland/Schidlowski, 1982.)
F_p = fluxes of pyrite; F_{cal} = fluxes of carbonate; F_G = fluxes of gypsum or sulfate; F_{org} = fluxes of organic carbon.

ISOTOPES

Hudson/Friedman (1976) deliberated on the C- and O-isotopes of early and late calcite, pre- and post-compaction concretions (Fig. 137). Similar comparative work ought to be carried out on sulfide-containing concretions, sulfide veins, and various cements in Mississippi Valley-type ore and gangue minerals to unravel paragenetic sequences.

Irwin et al. (1977) studied the C-isotopic evidence of the alteration of organic matter by several processes during burial and basin maturation. The isotopic values are preserved in diagenetic carbonates (calcite, dolomite, and ankerite) as cements, bands, and nodules, that originated at specific depths and temperatures (see Figs. 138 and 139). Such studies are to be done on sediment-hosted ores: e.g., on diagenetic versus hydrothermal gangue minerals, dolomite types, significance of C-isotopic variations, and importance of types of organic matter in ore genesis.

Coleman (1977) replaced the idea that one particular ore-forming mechanism was responsible for a large number of deposits by the notion that no two deposits are alike, at least in regard to the origin of sulfur. He concluded that the large range of isotopic values observed in nature allows only limited success in the determination of sulfur-derivation: there are numerous sources of sulfur and various mechanisms to alter the isotopic value. Both diagenetic *and* burial metamorphic
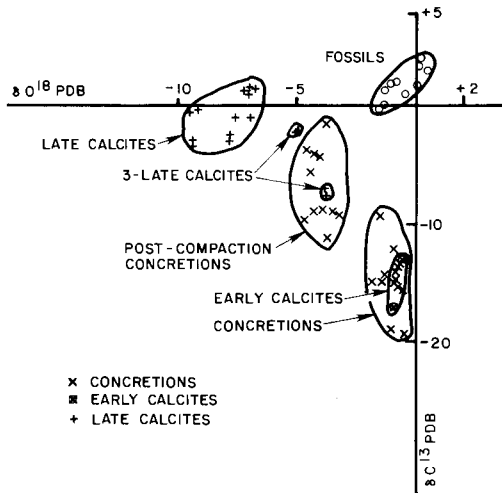

Fig. 137. Distribution of carbon and oxygen isotopes in fossils and concretions from the Oxford Clay, central England, summary plot. *Fossils* = bivalve (aragonite and primary calcite) from the Lower Oxford Clay. *Concretions* = pre-compaction septarian concretions of grey calcilutite. *Early calcites* = brown, fibrous fillings of septarian cracks. *Post-compaction concretions* = concretions that surround crushed fossils. *Late calcites* = coarse calcite crystals from septarian calcites associated with a post-brecciation phase of barite precipitation in some concretions; late fibrous calcite from clay adjacent to concretions. (After Hudson/Friedman, 1976.)

processes can alter the basic isotopic composition of sulfur and organic matter, for example.

Note: During deep-burial and compaction (e.g., late diagenetic processes), sulfur previously fixed in oil can be released as a result of thermal maturation to react with metalliferous brines formed by the same process.

Boles (1978) studied the range of O- and C-isotopes of carbonate cements (diagenetic to low-temperature "hydrothermal") (Fig. 140).

Perry et al. (1978) discussed the O-isotopic composition of a Precambrian chert and iron formation (including the sedimentary and diagenetic history which was preserved — but compare the data with that in Perry/Ahmad, 1981). Hoefs et al. (1982) correlated O-isotopic variations with the deformation history in polymetamorphosed iron ores (i.e., the processes were sedimentary – metamorphic rather than merely metamorphic).

Robinson/Ineson (1979) studied O- and S-isotopes in barite, O- and C-isotopes in calcite and limestones. The S-isotopes in galena and sphalerite indicate regional
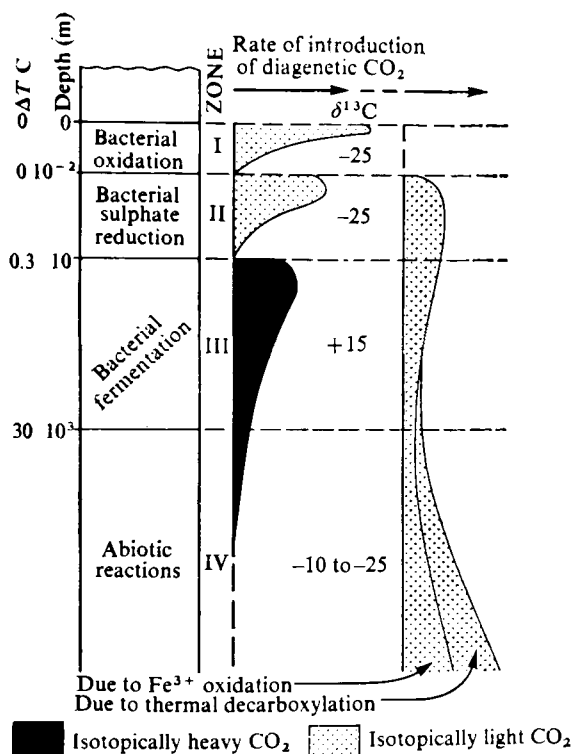

Fig. 138. Introduction of diagenetic CO_2 within different diagenetic zones. (After Irwin et al., 1977.)
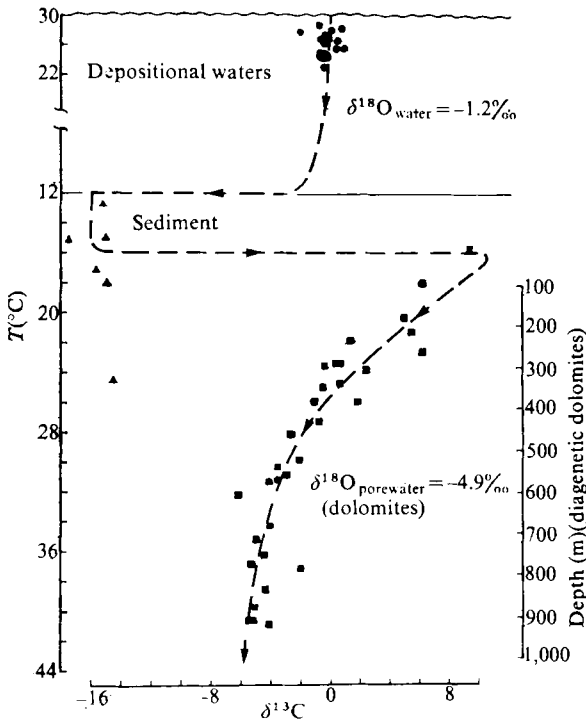
Fig. 139. Plot of calculated precipitation temperatures for Kimmeridge carbonates against carbon isotope ratio. "Primary" carbonates are shown associated with depositional waters, diagenetic carbonates with sediment porewaters. Precipitation pathway is indicated showing passage through zone II (sulphate reduction) to zone III (fermentation – heavy C) to zone IV at the base where light carbon isotopic ratios are again encountered. (For details, see original publication by Irwin et al., 1977.)
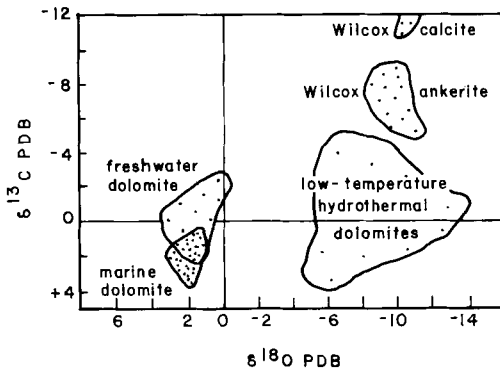

Fig. 140. Stable isotopic compositions of carbonate cements in marine-deltaic sandstones of the Wilcox Formation in the subsurface Eocene of southwest Texas. (After Leeder, 1981.)

variations in the sulfate sources, suggesting mixing of freshwater with connate seawater. The sulfur has a dual source: (a) kerogens and (b) seawater. En toto, at least four different diagenetic-to-epigenetic sources were involved in the origin of this M.V.-type ore.

Hattori/Sakai's (1980b) data on O- and C-isotopes of calcites in volcanic rocks indicate that "meteoric hydrothermal" solutions, which also caused submarine propylitic alteration, formed the calcite. Is this applicable to gangue minerals of the Kuroko-type deposits?

Sawkins (1980) related isotopic data to the evolution of meteoric fluid and seawater through rock – water interactions. Similar studies must be done on seafloor diagenesis, i.e. on halmyrolysis.

Ridge (1980a) and Gustafson/Williams (1981) discussed the numerous influences (including diagenetic controls) on changing the isotopic composition. This complexity seriously limits the direct one-to-one correlation of the isotopic composition with sources and genesis. Such limitations ought to be considered explicitly, and every paper on isotopes ought to state the *assumptions, limitations, and restrictions,* which is not done in most instances.

Robinson (1980) discussed the sources of S and their isotopic compositions of sulfide and sulfate minerals in Mississippi Valley-type ores (Fig. 141). The latter's S-isotope inhomogeneity is only exceeded by sedimentary-type ore deposits. The isotopic composition can become heavier if low-temperature equilibrium with the ore fluid and reduced S is approached. Continued bacterial reduction of a limited sulfate reservoir could also produce heavy sulfate. The H_2S can originate by several
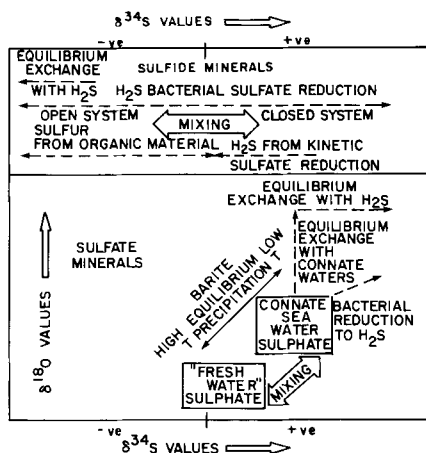

Fig. 141. The sources of sulfur and their isotopic compositions for sulfide and sulfate minerals in Mississippi Valley-type deposits. Sulfide $\delta^{14}S_{CDT}$ values range from approximately -30 to $+30‰$; sulfate: $\delta^{34}S_{CDT}$, from 0 to $30‰$ and $\delta^{18}O_{SMOW}$, from $+10$ to $+25‰$. (After Robinson, 1980.)

mechanisms from various sources (Fig. 142), each controlling the isotope composition. Mixing of the sources and the variability of the processes involved may explain the range of values often observed.

Note: The isotope data has attracted much controversy, speculation and the application of "in vogue" geochemical reconstructions. Several models have been proposed, e.g., the bacterial-reduction and equilibrium-isotope models. All diagenetic-to-metamorphic processes must be considered to explain the differences in isotopic variations.

Lambert et al. (1980) studied the isotopes of a stratabound Cu-mineralization: the data suggests that the Cu in veins was derived from the host sediments before lithification. Gulson et al. (1983) used Pb-isotopes to support their genetic reconstruction of the Mt. Isa ore bodies.

Leeder (1981) discussed the factors (including diagenesis) that influence the O-isotopic values in natural waters (see Hudson, 1977), as well as those parameters that control the C-isotopic composition (Figs. 143 and 144).

Note: Many such influences have not been considered in simplistic interpretations, not only of O- and C-isotopic data but also of S-isotopes.

Yaroshevich/Tvalchrelidze (1981) examined the distribution of S-isotopes in iron sulfides of various *endogenic* types of pyrite deposits. A similar comparative investigation ought to comprise all *exogenic* deposits.

Wetzel/Schütze (1981) provided ideas on the evolution of the earth's crust as based on an isotopic geochemical model (e.g., O-isotopic cycle, including the sedimentary cycle and environment).

Allan/Matthews (1982) provided isotopic signatures associated with early meteoric diagenesis, whereas Schidlowski (1980) offered δ ^{34}S-evidence for the Precambrian origin of sulfate respiration; and Zhukov et al. (1981) outlined the stages of isotopic/compositional changes of S during ore genesis (see Evolution).
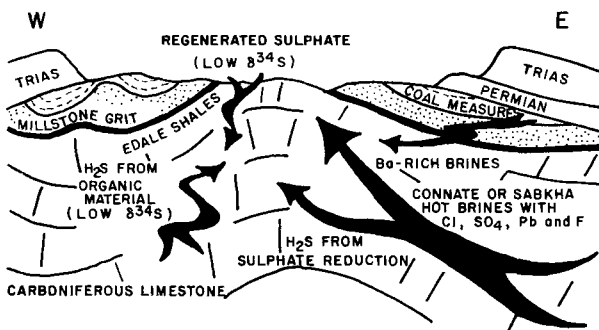

Fig. 142. Hypothetical genetic model for Derbyshire orefield. (After Robinson/Ineson, 1979.)

Shukolyukov (1980) researched the isotopes of hydrothermal mineralizations and concluded that the *geological* data must be combined with the geochemical information to permit plausible interpretations, as exemplified by deposits like the Pine Point and other M.V.-type concentrations. Hart et al. (1981) found Pb-isotopic zoning in galena as revealed by a microprobe study. Morrow/Cumming (1982) also used Pb-isotopic data to investigate the Zn – Pb ores of Western Canada; Nesbitt et al. (1984) concentrated on the O-isotopes of the Sullivan massive sulfide deposits; Carr/Gulson (1984) determined a considerable Pb-isotopic variation (increase from the foot to the hanging-wall) due to multiple sources; and Akande/Zentilli (1984) studied the stable isotopes of fluid inclusions.

Keith (1982) in his study of volcanism – stagnant oceans – petroleum – mass extinctions – stratabound ore relationships determined the long-term C- and S-isotopic changes (Fig. 145).
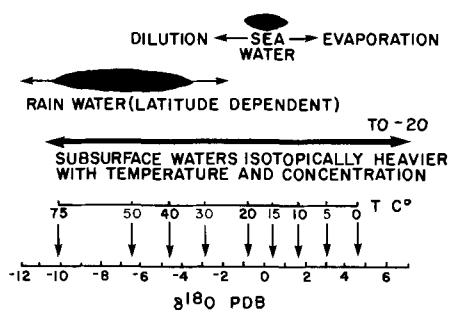

Fig. 143. Factors that control oxygen isotopic values in natural waters. The temperature scale is valid for precipitation of carbonates of $\delta^{18}O$ PDB shown on the lower scale from water of $\delta^{18}O$ SMOW = 0 (average seawater). (After Leeder, 1981.)
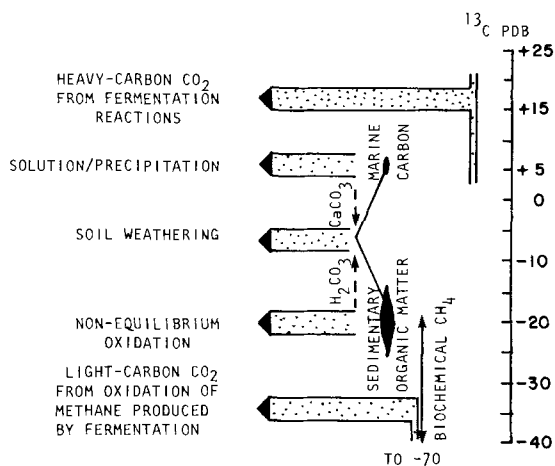

Fig. 144. Factors that control carbon isotope values in $CaCO_3$ precipitated from natural waters. (After Leeder, 1981.)
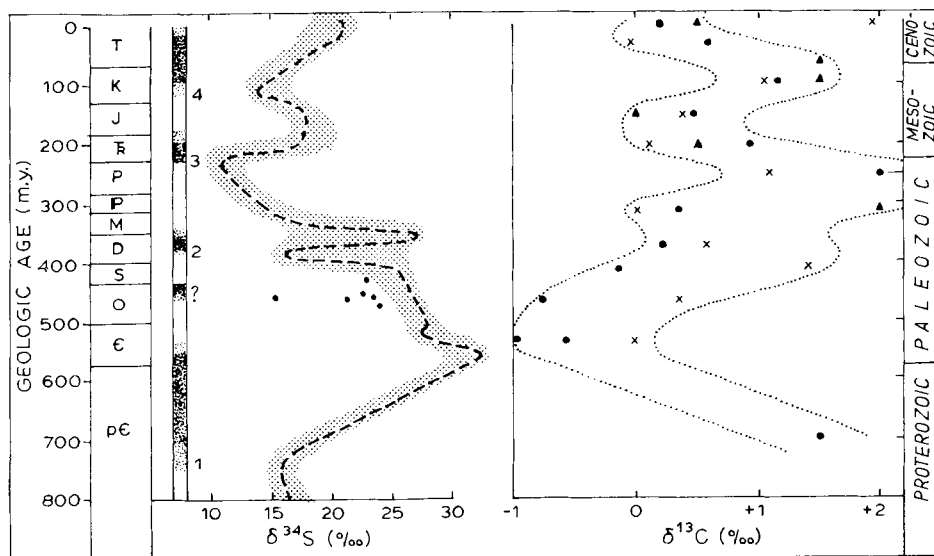
Fig. 145. Long-term isotopic changes in oceanic sulfate and carbonate. (See Keith, 1982, for details and original sources.)

Cecile et al. (1983) offered a model explaining the isotopic composition of barites.

Arthur (1983) reviewed the use of stable isotopes in sedimentary geology, including diagenetic histories.

William/Coleman (1983) investigated the S-isotopes of a Ba − Zn − Pb deposit in a metamorphic terrane and compared the data with numerous "hydrothermal" deposits (see models in their figs. 17 and 19). The isotopic temperatures of formation are contrasted with fluid-inclusion information of several deposits, and they conclude that some of the deposits must have been influenced by late diagenetic − catagenetic processes. The wide variations of the isotopic data is explained by the mixing of S derived from several sources, by geologic evolution, and other variables.

Schidlowski et al. (1984) depicted the assimilatory pathway and geochemical implications of superheavy organic C from hypersaline microbial mats: they studied C-isotopes of various organisms and marine sediments, isotope-discrimination steps (diffusion, fractionation, etc.), among others.

Chyi et al. (1984) reported on the isotope and trace-element geochemistry of an ancient hydrothermal Mn-deposit and discussed the implications for hydrothermal convection at oceanic spreading centers (O-isotopes were controlled by diagenesis not by hydrothermal alteration).

Oti/Müller (1985) examined the textural and mineralogical modifications during meteoric diagenesis (see their excellent diagrammatic conceptual models) in algal calcareous material; the diagenesis also influenced the isotopic composition. If isotopic studies are performed on calcareous hostrocks, the concepts outlined ought to be considered.

Baur et al. (1985) investigated the milli-scale isotopic variations in carbonates from a BIF, comparing both sedimentary and metamorphic mechanisms; the former was accepted.

Stiller et al. (1985) demonstrated extreme C-isotopic enrichments in evaporating brines. In relation to the alteration of isotopes during diagenesis, the question is: How can the C-isotopes of surface-derived marine and non-marine brines be differentiated from those that have a subsurface evaporite-rock precursor? What are the C-isotope differences, similarities and overlaps of gangue minerals in ore deposits, if they are the products of varitype brines?

Burchardt/Nielsen (1985) used O- and C-isotopes in limestones to demonstrate deep-burial diagenesis. A comparison of hostrock minerals with those of the associated ores (and gangue minerals) may well enable us to discriminate between a number of stages or generations of several mineral assemblages and any superimposed alterations. Very exacting sampling, however, would be a prerequisite; precise selective sampling, not just bulk collecting would be needed. Additionally, if clastic/detrital components are present (as in the case of sandstone, pyroclastics, or clastic carbonate rocks or calclithite à la Folk), the isotopic provenance might be identifiable (Heller et al., 1985).

Finlow-Bates et al. (1985) and McGoldrick et al. (1985), among others, have reconfirmed the more recent realization that isotopes do not supply the easily-obtained, unequivocally reliable panacean data many geochemists have made us believe and have refrained from admitting. For example, as early as 1973, Thom analyzed critically the "credibility gap" (or degree of reliability or accuracy) of radiometric ages, among other aspects, as exemplified by ^{14}C- and U-series-dating methods and O-isotopic temperature determinations. Older data, consequently, are suspect.

Finlow-Bates et al. (1985) concluded that the hydrothermal system that formed the Mt. Isa deposits were more complex than earlier isotopic and other information has suggested. (Maybe it is not the data that was misleading, but the interpretation/extrapolation by the researchers?) The geochemical/geologic system changed with time during the multi-stage origin of the Mt. Isa ore complex. Important to realize is that the isotopic data has to be supported or supplemented by other information to reconcile all observations. Contradictory data should not be ignored/shelved, but must be explained. McGoldrick and co-workers have admitted that isotopic data cannot distinguish certain genetic models, although they may be applicable in other instances. They referred to the common "egg-and-chicken" conundrum. Tauxe et al. (1985) demonstrated in their study of calibrating the geomagnetic reversal time

scale that paleomagnetic plus isotopic data *in combination* are better than either one alone in stratigraphic correlation; thus the combination provides an unprecedented resolution. Another example illustrating certain limitations of the isotopic information: Stein/Kish (1985) considered the timing/dating of glauconites and concluded that the M.V.-type ore fluids caused isotopic homogenization. The age, therefore, reflected "most likely" the time of ore genesis, not the time of glauconite origin in the country or hostrock.

— See also Age, and Dating.

KARST – KARSTIFICATION

Quinlan (1972), Zuffardi (1976), and others summarized the karst-related mineral deposits and the criteria for the recognition of paleokarst.
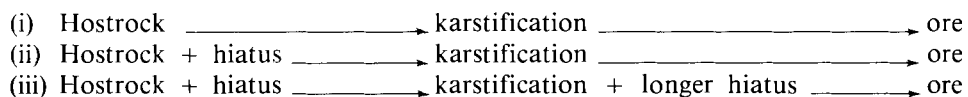
Note: Much more data is required on the processes and characteristic features related to the micro- to megascopic (local to district in size) dissolution of carbonates before one unequivocally understands the initial (embryonic or incipient) and fully developed karst systems, especially in connection with ore genesis. The following aspects are important in relation to diagenesis: (a) The *time* of dissolution or karst origin. Strictly speaking, all karst features are epigenetic, i.e., post-depositional and post-lithification. At least very slight cementation must have occurred during very early diagenesis to produce a coherent rock that does not totally crumple when it undergoes dissolution. Does that mean that all karsts are *"post-early diagenetic"*, i.e., any mineralization associated with it *cannot* be early diagenetic in origin? If the answer is in the affirmative, then the question is: *"How early* or *how late* in the *idealized time continuum* of syngenesis – early diagenesis – late diagenesis – catagenesis – metamorphism – uplift + pedogenesis? Actually, *each* of these stages can be interrupted by uplift and pedogenesis, so that the above-cited continuum may be interspersed by several periods of karstification. It may seem, therefore, that only the stage of syngenesis lacks karstification; however, certain *pseudo*-karst features may form during syngenesis.

It appears then, that the age of the dissolution-cum-karst structures in hostrocks can vary from one extreme to another; therefore, it is necessary to establish stratigraphic, paleontologic, structural, and geochemical procedures to date the paleokarsts in both relative and absolute terms.

These dating procedures are mainly related to the regional scale, i.e., correlation, sedimentological – environmental reconstructions of the origin of the unconformities or diastems with which the karsts are associated. The local textural and microstructural features that are not put into the regional context do not provide any plausible dates (only fossils might). In the case of "hydrothermal pseudo-karsts", other supplementary methods have to be employed (see below).

(b) To be able to make any progress at all, it is necessary to recognize first the observational, communicational and terminological shortcomings. Interpretation is not as simple as it may appear on superficial examination. For example, when it is believed that an ore in a karst system is of "diagenetic" origin, what precisely is

meant by "diagenetic" in relationship to (i.e., in full context with) both the hostrock *and* the karst? There are the following three genetic sequences (parageneses?):

(i)   Hostrock ───────────→ karstification ───────────────→ ore
(ii) Hostrock + hiatus ─────→ karstification ──────────────→ ore
(iii) Hostrock + hiatus ──────→ karstification + longer hiatus ───→ ore

In case (i), all three (the hostrock, karst system, and ore) are more-or-less of the same age (= penecontemporaneous), with possibly only a *minor time interval* (= hiatus) between them, so that only *minor diastems* may be expected. (ii) Between the hostrock origin and the karstification there is a *larger hiatus* during which various geologic events may have occurred (e.g., uplift and partial erosion). Consequently, an unconformity (in contrast to a diastem) should be present. The karstification processes and the ore precipitation are intimately related and occurred simultaneously (geologically speaking), so that there is no hiatus between the karstification and ore deposition. (iii) The first stage of the third setting is like case (ii), but the intimate genetic connection between the karst and the ore accumulation is absent. The karst openings merely acted as conduits. Thus, a second *longer hiatus* is to be expected, resulting in a second unconformity, namely one between the karst and the ore.

Insofar as "hiatuses" can range from a very short period (weeks to years) to a very long time interval (millions of years), the relationships described can be very complex indeed. However, the compositional, textural, structural, stratigraphic, etc., relationships between the hostrock and unconformity, on one hand, and the ore and gangue mineral deposits and unconformity, on the other, are often insufficiently known, so that these relations *may seem identical for the three cases outlined above.* Thus, when "diagenesis" is applied to the ore, does it refer to the hostrock – karstification – mineralization system *as a whole*, or only to one or two of these? When one takes into account the fact that syngenetic and diagenetic surface fluids can either ascend or descend into an older rock to precipitate ore, then the relation between hostrock, karst and mineralization becomes even more complicated (see Tables 41 and 42, and discussions in an earlier section). It seems, therefore, that independent of how meticulously the terms "diagenesis" and "epigenesis", for example, are defined, they are not or may not be applicable to multi-stage complex ore-forming systems. Consequently, a full *paragenetic stage-by-stage sequential* (may-be tabular) outline or history is necessary, accompanied by more detailed text-like descriptions.

(c) It must be emphasized that the above arguments are restricted to genuine karstification taking place at or near the earth surface and not to *"hydrothermal pseudo-karstification"*. The latter process may form features that resemble many of the karsts per se. Indeed, on a microscopic to local scale they can be indistinguishable, and only on a more regional scale will one find crucial differences.

(d) Much remains to be accomplished in regard to summarizing comparatively/contrastively the widely distributed data already available and in obtaining new information. All possible simple to complex relationships of the above-listed (i) to

(iii) situations ought to be diagrammatically modeled and depicted in flow-chart-like fashion (one preliminary attempt has been made in Table 42). Genuine karst and hydrothermal *pseudo*-karsts must be compared and criteria found to recognize and distinguish the numerous processes and products. For example, various depositional, reworking, tectonic, solution, etc., breccia types exist with which syngenetic, diagenetic, and epigenetic (catagenetic) ores are associated; however, no comprehensive comparative review is available at present. In one ore district (e.g., Callahan, 1964) there may be several breccia types, whereas in others only one variety prevails. Inasmuch as the mode of origin of the breccias and their intra- and inter-fragmental ore mineralizations can reveal much about the genesis, a more penetrating study is urgently needed. The following is one example of the state of confusion which the senior author has been pointing out since about 1957(!): The expression "intraformational" breccia is really a misnomer, because the prefix "intra-" means "within", so that intraformational breccia is one that originated *within* a formation. Contrary to this, the expression is almost exclusively applied to a breccia that formed by reworking (by waves and storms, for example) *at or near the surface* within a depositional sedimentary environment! The breccia originates within a sedimentary milieu, *not* within the formation. Consequently, the senior author has made for several years a distinction between intra-environmental breccias and intraformational breccias. The former are syngenetic-cum-diagenetic in origin, in contrast to the latter that can form much later, ranging from late diagenetic through catagenetic to metamorphic types.

Bernard (1973) described the processes of intrakarstic sedimentation and the origin of Pb – Zn – Ba deposits.

Geldsetzer (1973) utilized excellent stratigraphic control and diagenetic changes to demonstrate the temporal relationships as well as the process of Pb – Zn mineralization associated with a karst system. Karsting and concomitant brecciation especially affected the Precambrian laminated algal carbonates. Subsequent subsidence resulted in a topographically restricted marine milieu and in evaporative conditions. The earlier-formed brecciated carbonates and extensive subsurface channels provided passageways for a refluxing dolomitizing brine, which completely dolomitized the breccia and channelled hostrocks. In addition to the Mg introduced (for dolomitization), the circulating seawater brine also supplied the metal ions as chloride complexes. The metals combined with the possibly seasonal supply of sulfide ions generated by sulfate-reducing bacteria, and the Pb and Zn sulfides precipitated in fractures (disseminated type) and in channels (massive type).

 Note: Stratigraphy, structures, textures, environment, etc., all were utilized to demonstrate the syndiagenetic – epigenetic origin of the ore.

Padalino et al. (1973) summarized many ore deposits in karst formations in Sardinia. However, only the major features were considered.

Hagni (1976), Laznicka (1981a, pp. 467 – 491), and Hoagland (1976), among many others, discussed the paleokarst and paleoaquifer environment of the Tri-State and

Appalachian Pb – Zn deposits (see fig. 19 in Hoagland, 1976, and the very pertinent discussions in Laznicka, 1981). Kyle (1981) offered an excellent study of the Pine Point district in which he also considered reef-barrier karstification and dolomitization as part of diagenesis and development of the sulfide-hosting structures (see his figs. 8, 21, and 22, and the comparative table V). Diagenesis *prepared* the hostrocks for sulfide mineral concentration.

Mitchell et al. (1981) studied the leaching of uranium and SiO_2 from volcanic rock, which then percolated downward into a karst system within a generally impermeable limestone. Organic matter and pyrite in the limestone furnished the reducing conditions that precipitated the U in a hexavalent state.

Jadoul/Omenetto (1980) described the diagenetic evolution of ore-bearing *internal* sediments in karst openings. The precise time/space and genetic/paragenetic relations of both the cavities *and* the internal sediments plus cements are of utmost significance: many complex possibilities exist, which have not been fully considered or have been interpreted simplistically.

Fanning et al. (1981) studied geothermal springs related to a karst system (down to 1000 m below sealevel!) and associated dolomitization and radionuclide enrichment. Of particular interest for M.V.-type ore studies are (a) the relatively great depth of 1 km at which the karst was formed; (b) the possible geothermal springs in forming (?) the karst system or the latter's use as a conduit; and (c) the presence of the system on a continental shelf maybe offering access to normal and abnormal fluids of various derivations.

Buchbinder (1981) examined the dolomitization, porosity development, and late mineralization of a karst system.

Andrews et al. (1982) showed a connection between the thermal springs of Bath and a karst system (hydrothermal karst?).

Kutyrev/Lyakhnitskii (1982) opined on the role of karst systems in the genesis of Pb, Zn, Hg, As, fluorite deposits; and offered a good classification of cavity types, systems, structures, and ore bodies in karst cavities. Olson (1984) described the paleokarst and associated Pb – Zn sulfides in a Precambrian dolostone.

Barbieri et al. (1983) studied the yttrium, lanthum, and manganese in karst fluorite deposits, and concluded that the concentration is prevalently of hydrothermal origin. But the question remains: what type of hot fluids? Özlü (1983) utilized the trace elements of karst bauxites to unravel their origin – he too considered diagenesis.

Goudie/Pye (1983) offered a good review of chemical sediments (precipitates and residua) in the near-surface environment in general – including those in caves.

James/Choquette (1984) summarized the meteoric diagenetic limestone environment and also treated karst systems.

Dzulynski/Sass-Gustkiewicz (1985) discussed the hydrothermal karst phenomena in the genesis of M.V.-type ores.

Yusupova (1983) considered the dual, combined control of karst and organic matter within rocks in the origin of sulfide mineralization.

— See also Carbonates, Dolomitization, M.V.-type deposits, Limestones, and Multi-stage.

KUPFERSCHIEFER-TYPE DEPOSITS

Jung/Knitzschke (1976) offered a good introduction to the origin of the Kupferschiefer deposits and covered numerous diagenetic aspects.

Rentzsch/Kampe (1979) dealt with the geochemistry of the sediments; Magaritz et al. (1981) with the C-isotopic change at the base of the Zechstein sequence; Kucha (1981) studied the precious metal alloys and organic matter of the Kupferschiefer (Zechstein Cu-deposits) and examined $Au - Ag - Pt - Hg$ alloys, native Pd, Bi, native Pb and plumbian gold associated with nests of secondary (diagenetic?) calcite and admixed compounds; Kucha (1983) supplemented his earlier report on the metal-rich shale of Cu-deposits (e.g., compared sabkha with the Davidson-brine
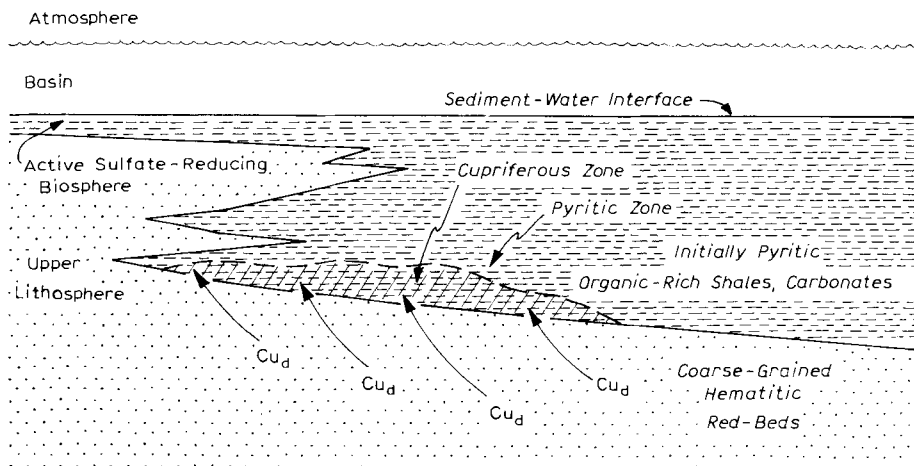

Fig. 146. Schematic model for stratiform copper mineralization showing locations of (1) syndiagenetic iron sulfide accumulations beneath an active sediment – water interface, and (2) early diagenetic copper deposition by a subsurface influx of dissolved copper (Cu_d) into the initially pyrite-bearing sediment. (After Brown/Chartrand, 1983.)

hypotheses), concluding that organic matter is important. He also contrasted epigenetic with syngenetic/diagenetic origins of the Kupferschiefer; and in 1984 Kucha investigated the palladium minerals of low-temperature phases of the Kupferschiefer.

Annels et al. (1983) opined on the genetic conditions of the Zambian Copperbelt with special reference to the role of Co. The question: What are the differences and similarities of the Kupferschiefer and the Zambian/Rhodesian belt?

Brown/Chartrand (1983), Fleischer (1984), and Annels (1984) modeled the origin of the stratiform Cu-ores controlled, for example, by syndiagenetic sulfide precipitation beneath a sediment – water interface and by subsurface influx of dissolved Cu into the initially pyrite-bearing sediments (Fig. 146). Thus, they also modeled the zonation, metal dispersion, hydrology, sources, upwelling, etc. (Figs. 146 – 150).
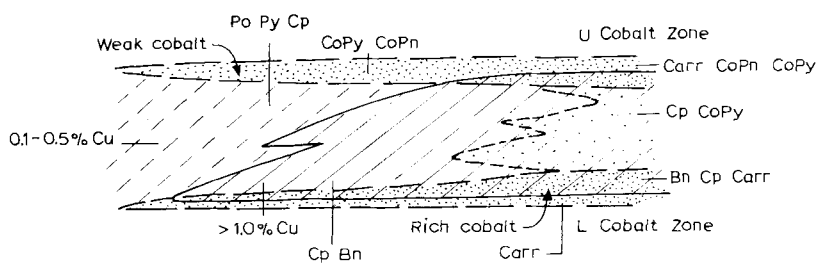
– See also Copper, Upwelling, and Zoning.

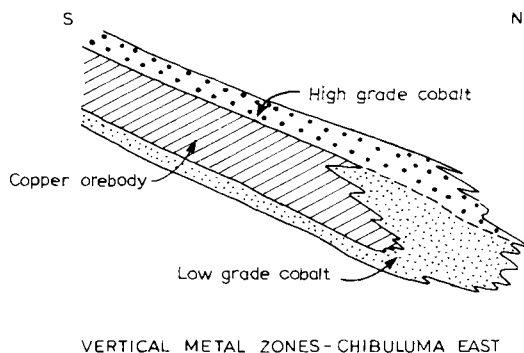Fig. 147. Metal and sulfide zones in the ore-shale of the Chambishi Basin. (After Annels, 1984.)

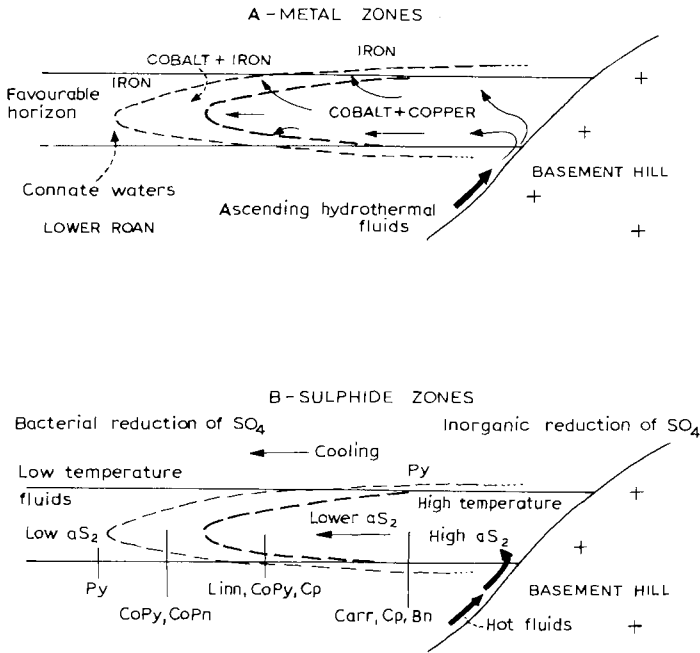Fig. 148. Vertical metal zones at Chibuluma East. (After Annels, 1984.)

A - METAL ZONES

B - SULPHIDE ZONES

Fig. 149. (A) Model for Cu − Fe − Co dispersions within an arenite host horizon; (B) generalized model for sulfide zones. (After Annels, 1984.)

KUROKO-TYPE DEPOSITS

Sawkins (1982) deliberated on the origin of the Kuroko-type deposits as viewed within the broader context of ore genesis theories. Several hundred publications on this type of ore are available now, but only a few discuss the possible influence of diagenesis.

Hattori/Muehlenbachs (1980) described the marine hydrothermal alteration of the Kuroko ore deposits, and Kusakabe (1982) concentrated on the zeolitic zoning on the basis of hydrothermal experimental data. Kumita et al. (1980) studied the sedimentology and biostratigraphy of the Kuroko complexes.

Hariya/Tsutsumi (1981) restricted their study of the H-isotopic composition of the Mn-minerals from manganese oxide and massive sulfide (Kuroko) ores.

Sugawara et al. (1982a, b) offered a rare study of the sedimentological and diagenetic features, including the diagenetic evolution of the Kuroko deposits; followed by Kajiwara/Hirayama (1983) who opined on the "diagenetic chemical differentiation" of Kuroko ores.
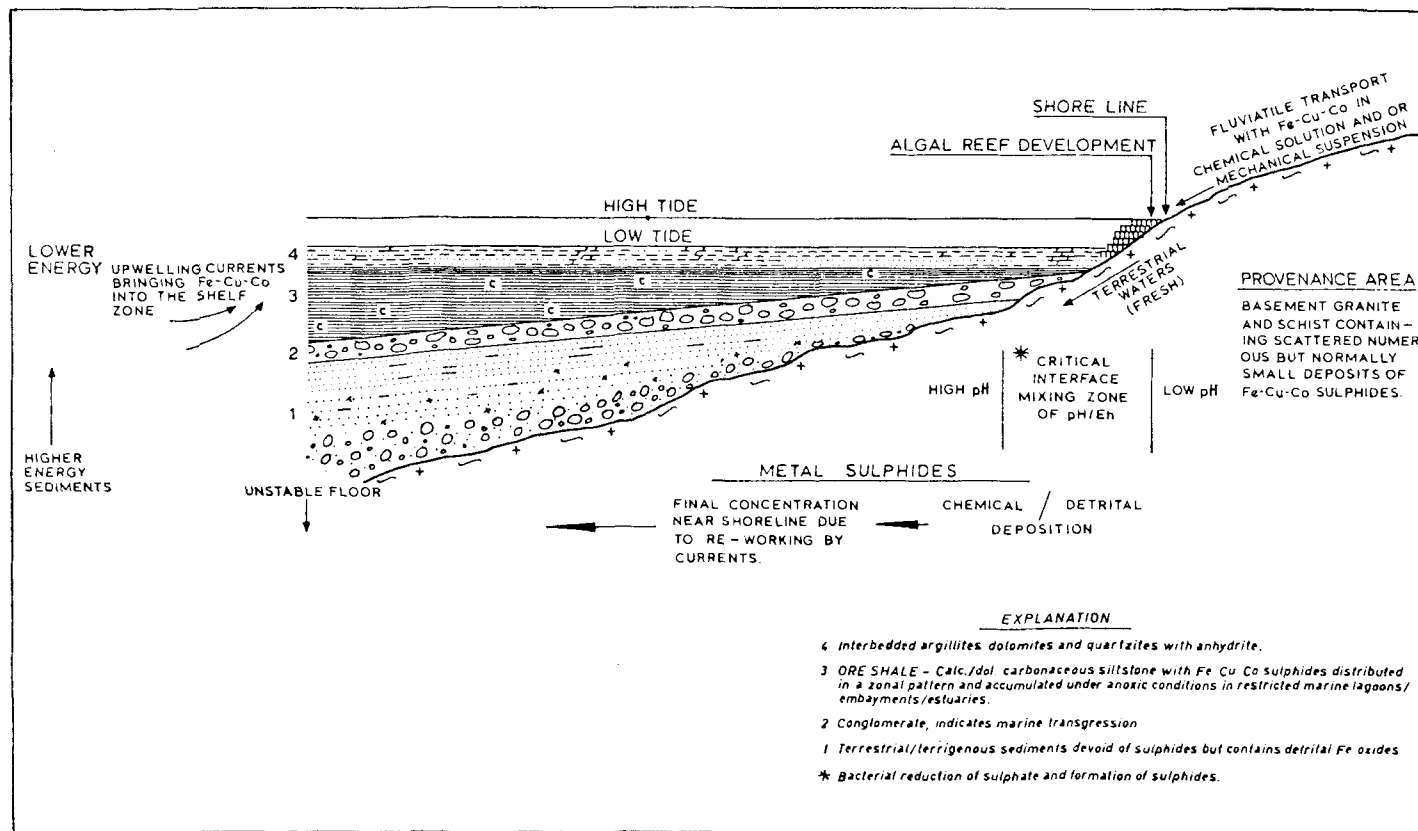
SHORE LINE

ALGAL REEF DEVELOPMENT

FLUVIATILE TRANSPORT
WITH Fe-Cu-Co IN
CHEMICAL SOLUTION AND OR
MECHANICAL SUSPENSION

HIGH TIDE

LOW TIDE

LOWER
ENERGY   UPWELLING CURRENTS   4
          BRINGING Fe-Cu-Co
          INTO THE SHELF   3
          ZONE

TERRESTRIAL
WATERS
(FRESH)

PROVENANCE AREA

BASEMENT GRANITE
AND SCHIST CONTAIN-
ING SCATTERED NUMER
OUS BUT NORMALLY
SMALL DEPOSITS OF
Fe-Cu-Co SULPHIDES.

                                    2

                                    1

HIGHER
ENERGY
SEDIMENTS

UNSTABLE FLOOR

* CRITICAL
  INTERFACE
HIGH pH MIXING ZONE   LOW pH
  OF pH/Eh

METAL SULPHIDES

FINAL CONCENTRATION   CHEMICAL / DETRITAL
NEAR SHORELINE DUE   DEPOSITION
TO RE - WORKING BY
CURRENTS.

EXPLANATION

4 Interbedded argillites dolomites and quartzites with anhydrite.

3 ORE SHALE - Calc./dol. carbonaceous siltstone with Fe Cu Co sulphides distributed
   in a zonal pattern and accumulated under anoxic conditions in restricted marine lagoons/
   embayments/estuaries.

2 Conglomerate, indicates marine transgression

1 Terrestrial/terrigenous sediments devoid of sulphides but contains detrital Fe oxides

* Bacterial reduction of sulphate and formation of sulphides.

Fig. 150. Genetic model for ore shales at Chambishi Southeast prospect. (After Fleischer, 1984.)

265

Kajiwara/Hirayama (1983) presented a genetic interpretation of the time – space distribution of the Japanese Kuroko metal concentrations.

LAKE/LACUSTRINE ENVIRONMENTS

Lerman's (1978a) and Förstner/Müller's (1974a) books, in combination with the excellent reviews by Picard/High (1972), Dole/Picard (1981), Picard/High (1981), and Dean (1981), serve as a superb introduction to lacustrine environments, including their (paleo-)geographic setting, sedimentology, biology/paleontology, geochemistry, mineralogy, diagenesis and economic aspects. Lake milieus are, together with their associated fluvial systems, another natural diagenetic (and pollutional!) laboratory. Several hundred pertinent publications are available, and a comprehensive comparative summary is needed every ten years.

Robbins (1983) studied the genesis of fossil fuels and metallic minerals in both active and ancient rift lakes, and offered models on the factors and processes, geochemical interfaces and environments, including thermal indicators and mobilization (Fig. 151). Tables 61 and 62 summarize the source (hotsprings) and the lake-sedimentary sink of chemical elements (see also Gases).

Callender/Bowser (1976) reviewed the freshwater (including lake-type) ferromanganese deposits; Davidson (1981) studied the supply of $Fe + Mn$ to an anoxic lake basin; and Moore (1981) examined the $Fe - Mn$ banding in lake nodules.
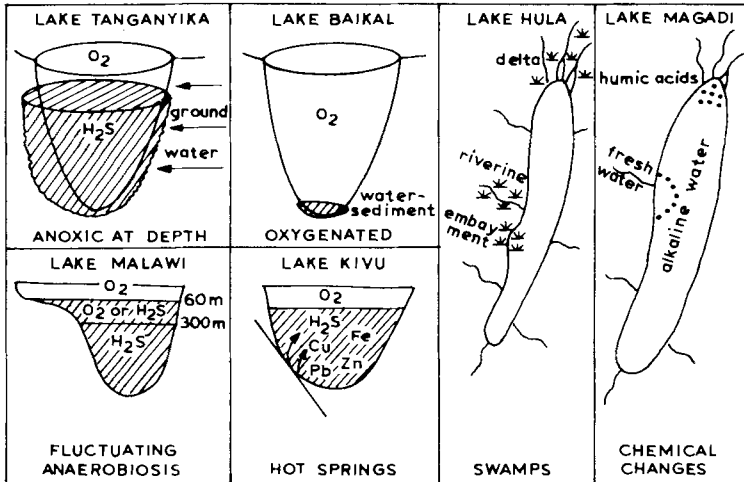

Fig. 151. Geochemical interfaces and environments in modern tectonic lakes. (O_2 = oxygenated, H_2S = anoxic waters.) (After Robbins, 1983.)

Wagner (1971) investigated FeS-concretions in a recent lake, whereas Hall/Donovan (1978) examined the origin of complex sulfide nodules during diagenesis of a Devonian lacustrine sedimentary rock.

TABLE 61

Minimum and maximum values of elements (ppm) accumulating in Lake Kivu in the East African Rift (Robbins, 1983)[1]

	Source		Sink	
	Murundu River	hot springs	water column	surface layer of anoxic sediment
Ag	–	–	–	< 2 – 3
Al	–	–	–	21,200 – 80,560
As	–	–	–	< 38 – < 50
B	–	–	–	12 – 23
Ba	–	–	–	185 – 1387
Bi	–	–	–	< 3 – 8
C org.	–	–	15 – 30	148,000 – 192,000
HCO_3-CO_3	–	–	13.15 – 7130	–
Ca	0	82.2 – 85.5	4.8 – 112.6	10,650 – 210,870
Cl	0	63 – 80	28.5 – 210	–
Co	–	–	0.01	< 10 – 37
Cr	–	–	0.02	16 – 112
Cu	–	–	0.03 – 0.2	20 – 170
F	–	–	1.79 – 2.3	–
Fe	0	–	0.045 – 45	20,970 – 252,100
Ga	–	–	–	< 5 – 23
Ge	–	–	–	< 4 – 6
K	–	56.6 – 67.4	18 – 430	–
Mg	3.9	53 – 60	82 – 820	5400 – 27,000
Mn	–	–	0.32 – 1.2	60 – 2024
Mo	–	–	0.1	8 – 138
N	0	–	7.9	12,000 – 14,500
NO_3	–	–	0.01 – 0.041	–
Na	36.8	179.6 – 226.0	120 – 487.4	–
PO_4	–	–	< 0.0001 – 0.117	2769
Ni	–	–	0.03	23 – 127
Pb	–	–	0.25	41 – 361
Sb	–	–	–	< 38 – < 50
Sc	–	–	–	< 23 – < 30
SiO_2	16	–	2 – 71	191,000 – 688,000
SO_4	15.4	16.8 – 29.0	6 – 220.0	–
Sr	–	–	–	367 – 3192
Ti	–	–	–	1800 – 16,200
V	–	–	–	79 – 265
Zn	–	–	0.13 – 7.10	34 – 410
H_2O				66.26 – 90.27%
pH	–	–	6.6 – 9.2	–

[1] Dashes indicate no data available.

TABLE 62

Metal accumulation (ppm) in shales of an ancient rift lake in the Taylorsville Basin of the Newark Rift in Virginia (Robbins, 1983)

	Source (rocks of Piedmont)			Sink (lacustrine shale)
	granite	amphibolite	gneiss	black shale
Fe	18,200	24,000	32,000	21,350 – 35,110
Ti	2800	3150	2880	83 – 3038
V	92	150	120	44 – 1250
Ni	0	53	62	80 – 1130
Zn	10	45	60	11 – 430
Cr	0	320	167	0 – 320
Cu	20	0	26	0 – 125
Pb	0	2	28	0 – 96
Co	0	0	29	7 – 88
Mo	0	12	2	0 – 80

Yuretisch/Cerling (1983) studied the hydrogeochemistry of a contemporary alkaline lake (its mass balance and mineral reactions, etc.), whereas Bailey (1980) reviewed the petrology of cryolite and other aluminofluorides formed in alkaline lake deposits.

Finley et al. (1983) were concerned with the biological participation in lacustrine Ba-chemistry; Warren (1982) described the hydrological setting and the gypsum deposits of Quaternary salt lakes (including several types of the sabkha variety); and Förstner (1977a) dealt with the mineralogy and geochemistry of arid lake sediments of Australia.

Deurer et al. (1978) investigated the selective chemical extraction (see also Coprecipitation) of carbonate-associated trace metals in recent lake sediments; followed by Schmoll/Förstner (1979) on the chemical association of heavy metals in calcareous lake sediments from different climatic zones.

Fisher/Schmincke (1984) in their book on Pyroclastic Rocks reported on lakes associated with volcanic terranes — but many more references need to be consulted to cover adequately the diagenetic aspects. Wissmar et al. (1982a, b) studied the chemical changes of lakes within the Mount St. Helens blast zones and the biological response therein (on bacteria also). To what extent are animal and plant populations destroyed, altered and/or established/reestablished due to volcanism? Since organisms can control the pH/Eh sedimentary profiles in lakes (e.g., Davis, 1974), changes in the bacterial and algal population, for example, will influence diagenesis.

Davand (1977) opined on the chemical evolution of muds in a eutrophic lake (see the symposium for additional references); Mortimer (1971) reported on the chemical

sediment – water exchanges and the mechanisms involved; Cline/Upchurch (1973) discussed the heavy-metal migration; Chan/Lum-Shue (1974) studied the labile and strongly bound metals; Baccini (1976) investigated the heavy-metal budget and Förstner (1977b) and Förstner/Müller (1974a) the metal concentrations; whereas Förstner (1978) considered the geochemical background and pollutional factors of recent lake deposits.

LEACHING

Alekseyev et al. (1982) described the interactions of sulfur acid solutions with carbonates and feldspar in U-leaching.

Dickin (1981) studied hydrothermal leaching of rhyolite glass as to implications for nuclear waste disposal. The data may be of interest to diageneticists.

Augustithis (1983) summarized the leaching and diffusion in rocks and weathering products; he also referred to leaching of metals from clays and laterites, soils in general, weathering crusts on cherty BIFs, ion exchange, etc.

– See also Remobilization, Solutions, Sources, and Uranium.

LIMESTONES

Flügel (1982) and Schneidermann/Harris (1985) offer, respectively, a superb general review of limestones and a specific treatment of cements – of value to those engaged in exacting studies of reservoir and host rocks.

– See also Carbonates, Dolomites, and M.V.-type ores.

MAGNESITE

Pohl/Siegl (1986) offered a comprehensive review of the sediment-hosted magnesite deposits covering numerous aspects related to syngenesis, diagenesis, epigenesis, and metamorphism.

Bone (1983) reconstructed late-diagenetic recrystallization origin of magnesites by using fluid-inclusion data.

MAGNETISM

Creer et al. (1983) reviewed the geomagnetism of baked clays and Recent sediments.

Gillett (1983), McCabe et al. (1983), Johnson et al. (1984), and Horton/Geissman (1984), respectively, described stylolites in limestones, including their use in petrography in combination with paleomagnetic dating; discussed diagenetic magnetite with ancient secondary remnance in Paleozoic carbonates and concluded that the geophysical properties were controlled by diagenesis; outlined the relation between paleomagnetism and diagenesis in Jurassic carbonates; and examined the paleomagnetism of a Mississippian carbonate as to its implication for the dating of sub-regional dolomitization (a method recommended for studying M.V.-type ore hostrocks).

Karlin/Levi (1983) described diagenesis of magnetic minerals in contemporary hemipelagic sediments; whereas Whitmarsh (1982) studied the variations of oceanic magnetite stripes — are they related to low-temperature hydrothermal circulation?

Frankel (1981) and Kirschvink/Chang (1984) discussed magnetotactic bacteria at the geomagnetic equator and ultra-fine magnetite in deep-sea sediments, which possibly reflect bacterial magnetofossils. How does diagenesis affect these bacteria?

Wu/Beales (1981) studied paleomagnetism to determine the age of mineralization in carbonate rocks (see model in their fig. 5). At least two stages were involved: acquisition of detrital remnant magnetism and remagnetization during mineralization when basinal (?) brines formed the ore.

Suttill et al. (1982) investigated the geochemistry of Fe in Recent tidal-flat sediments, including their magnetic properties (also considering diagenesis); Opdyke et al. (1982) examined the paleomagnetism/demagnetization of red-beds, but the question remains as to the influence of diagenesis; Özdemir/Deutsch (1984) concluded that the intensity of remnant magnetism depends on hematite percentage, but stated that the primary chemical (precipitational) magnetization and remagnetization due to recrystallization are as yet not well understood. The hematite occurred mainly as oolites with minor siderite and chamosite, with the matrix being composed of siderite and calcite. Perroud/Van der Voo (1984) examined the secondary magnetization of the Clinton-type iron ores.

Roy/Morris (1983) investigated the paleomagnetism of red-beds: at least three stages were involved in their lengthy development, namely depositional, authigenic, early diagenetic and late diagenetic cementational phases (see their model of magnetite remnant acquisition). McIntosh et al. (1985) compared authigenic and diagenetic influences on the paleomagnetism of oxide minerals in red-beds and basalts. The reliability and accuracy of paleomagnetism applied to environmental reconstructions depends on primary and secondary influences.

Kalinichenko et al. (1981) studied the genetic types of proton magnetic resonance in pyrites.

Turner/Ixer (1979) opined on the diagenetic development of unstable and stable magnetization in a sandstone; whereas Vaughan/Turner (1980) examined the magnetization of a marl-slate Kupferschiefer-equivalent deposit.

Smit/Kyte (1984) studied siderophile-rich magnetite spheroids along the Cretaceous – Tertiary boundary; such spheroids could lend magnetic properties to any type of sediment. Can secondary (diagenetic) changes modify or destroy the magnetism?

Ellwood (1984a, b) described the effect of bioturbation on the magnetic fabric in sediments, concluding that the physical/biological mechanical processes can influence the magnetic properties.

Bylund (1981) deliberated on the stability of paleomagnetism; Hall/Butler (1983) studied the potential problems in magnetostratigraphic studies of shallow-water sequences; and Verosub (1982) used paleomagnetism to determine the lower limit of original water content in deformed sediments.

Cisowski (1984) provided evidence for Tertiary remagnetization and discussed the influence of diagenesis.

Hodych et al. (1985) considered chemical remnant magnetization in deeply buried diagenetically affected oolitic hematitic ironstones (see their fine table III for a list of diagenetic effects).

Reynolds et al. (1985) examined paleomagnetic and petrologic evidence that bears on the age and origin of a uranium deposit.

MANGANESE

Glasby/Read (1976), Callender/Bowser (1976) and Roy (1976) reviewed, respectively, the deep-sea, freshwater, and ancient ferromanganese/manganese deposits; whereas Varentsov/Grasselly (1980) and Roy (1981) offered comprehensive general summaries. All cover diagenesis.

Halbach/Özkara (1980), among many others, dealt with the Ni- and Cu-rich manganese nodules of the deep oceans as products of early diagenesis. Halbach et al. (1984) studied the Pt concentration of Fe – Mn seamount crusts, and Goldstein/O'Nions (1981) the Nd – Sr isotopic relations, whereas Ku et al. (1982) examined the constancy of oceanic deposition by the ^{10}Be present in Mn-crusts. Moore et al. (1981) discussed in general terms the metal fluxes to Mn-nodules, whereas Glasby/Thijssen (1982) studied the supply of divalent transition metal ions that controlled the mineralogy and composition of marine manganese nodules.

Bischoff et al. (1981a) studied the alumino-silicates of oceanic Mn-nodules, and Halbach et al. (1981b) the geochemical variation of Fe – Mn nodules of the Pacific. Garber et al. (1981) investigated the Dead Sea-shore manganese deposition, whereas Balkhanov/Razvalyayev (1981) the Red Sea types (associated with rifting) comprising both sedimentary and vein varieties.

Volkov/Shterenberg (1981) described the main types of Fe – Mn ores in Recent basins, offered a genetic classification and models, and discussed the mobility series of elements.

Sundby et al. (1981) modeled the Mn-pathways/cycle of an open estuarine system (Fig. 152). Do other metals and non-metals have a similar or a different cycle that can control diagenesis? The scales (local, regional, worldwide) must be taken into account in unravelling geochemical cycles (see also Cycles).

Cronan et al. (1982) concentrated on submarine hydrothermal Mn-deposits of the Southwest Pacific island arc, in contrast to other publications that deal with sedimentary – diagenetic – remobilized styles of manganese nodules (see Aplin/ Cronan, 1985).

Pedersen/Price (1982) dealt with the geochemistry of a manganese carbonate concentration.

Brand (1983) studied the mineralogy and geochemistry of a Pennsylvanian deposit using Mn as an indicator of the degree of diagenetic alteration (referring also to compaction).

Szabo et al. (1981) posed some "conceptual questions" in regard to the genesis of an ancient Mn-deposit, comparing normal sedimentary shelf-type manganese precipitation with volcanic – sedimentary types in geosynclines or along deep fracture zones.

Ostwald (1981) and Varentsov (1982) investigated the major Australian manganese deposits, including their general characteristics and the evidence for a biogeochemical origin.

MASS BALANCE

Mackenzie/Garrels (1966) studied the mass balance between rivers and oceans, whereas Boyle et al. (1974) the mass balance in estuaries.

Hardie (1983) examined the origin of $CaCl_2$-brines by basalt – seawater interactions as based on some simple mass-balance calculations.

Mason (1965) and Rösler/Lange (1972) dealt briefly with mass balance and related topics.
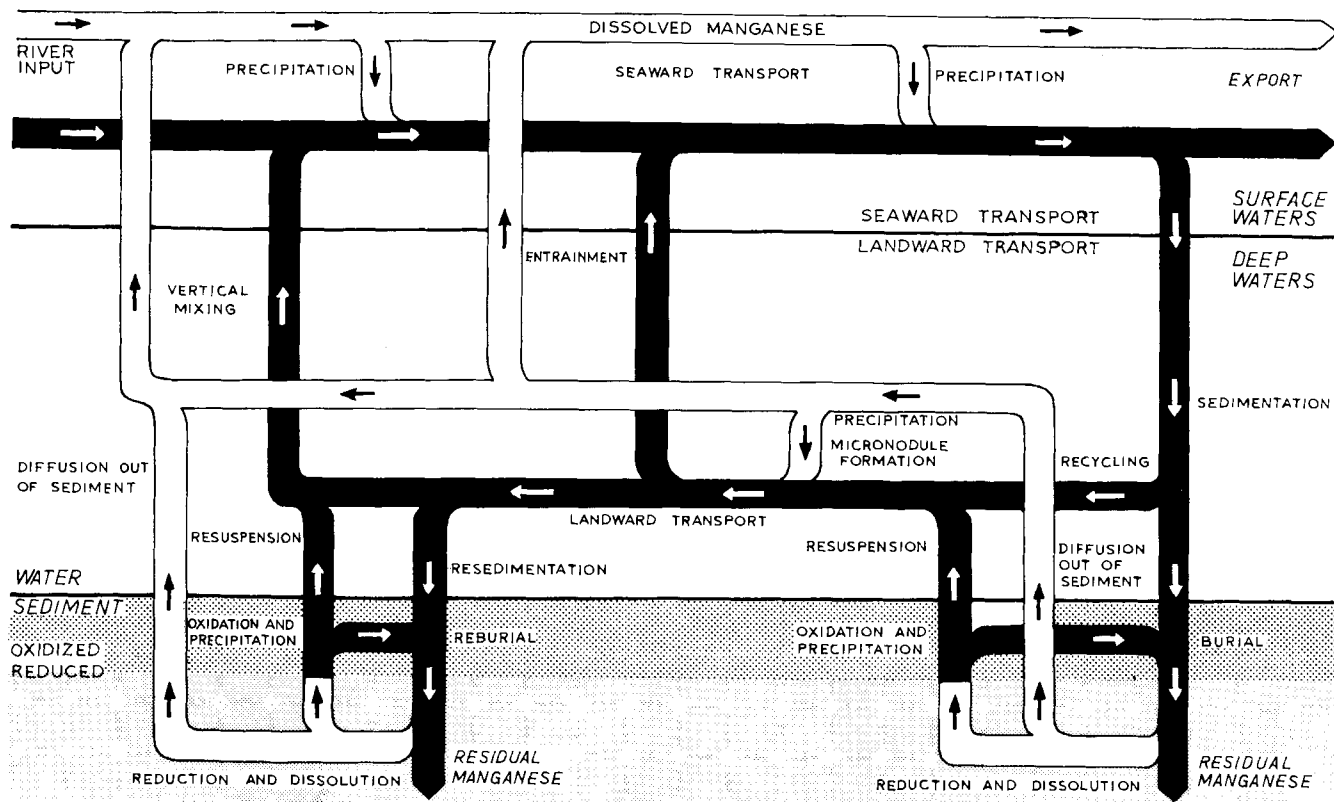
Fig. 152. Pathways of manganese in an open estuarine system. (After Sundby et al., 1981.)

MATURATION (OF SEDIMENTARY BASINS)

Jackson/Beales (1967), Beales/Jackson (1968), Mookherjee (1976), Wolf (1976), Gustafson/Williams (1981), Kisch (1983), Tissot/Welte (1984), and many others, extrapolated the concepts developed by the oil exploration geologists to the study of ores or their hostrocks, for instance. Partly based on their own ideas, they suggested that during basin evolution, the "maturation" of sedimentary lithologies and organic matter and the development of basinal fluid systems of various types are responsible for the origin of both hydrocarbons and metalliferous deposits, although they do not necessarily occur in close proximity. For example, Gustafson/Williams (1981) concluded that "the stratiform copper deposits are probably formed from cool sulfate-rich brines, derived at an early stage of basin evolution and migration updip to reducing sites of deposition. The Pb – Zn deposits are probably formed from similar but more evolved brines that have been heated and probably chemically reduced deeper within the basin. Some of the latter may have been formed by exhalation of dense basinal brines on the seafloor." By "early" they mean "early diagenetic", whereas "more evolved" means "late diagenetic". It is important to note that the "exhalation of basinal brines" need not be "volcanic – hydrothermal" exhalations, but can be hot basinal sediment-derived fluids of late diagenetic or catagenetic/burial metamorphic origin.

Barnes et al. (1981) examined "ores formed by diagenetic and metamorphic processes". According to them, extensive migration of fluids and associated solutes during diagenesis and metamorphism forms several important types of ore deposits, the most valuable of these being sandstone-type uranium deposits, Mississippi Valley-type Pb – Zn deposits, and red-bed copper deposits. Such processes also form non-metallic ores of sulfur, asbestos, talc, tremolite, kyanite, vermiculite, and the abrasives emery and garnet. The flow pattern of the solutions, as depicted for the origin of the epigenetic types of M.V. ores, is shown in Fig. 153.
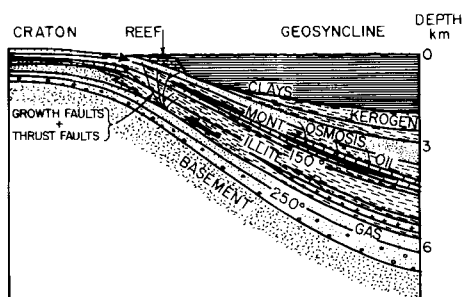

Fig. 153. Flow of solutions near the margin of a maturing geosyncline. The arrows show, respectively, the flow of freshwater down-dip along a shallow aquifer, osmotically into deeper more saline horizons, and then upward from zones of lithostatic pressure. The upward flow may debouch on the seafloor through growth and thrust faults or extend updip in the shelf sediments of the craton. (After Barnes et al., 1981.)

Wolf (1981c) indicated that the over-emphasis and wrong application of maturation data of merely a few local analyses can result in an inappropriate negative evaluation of a large sedimentary basin — the hydrocarbon potential is downgraded when in fact it may be relatively good.

— See also Metamorphism, Multi-factorial, and Multi-stage.

METAMORPHISM (e.g., burial)

Murata/Larson (1975) recognized three depth-controlled zones characterized by different forms of silica: (a) biogenic opal zone (diatoms, etc.), (b) diagenetic cristobalite zone, and (c) diagenetic quartz zone. The temperature range was $50° - 110°C$. The results of this study are applicable to the study of younger less-metamorphosed hostrocks.

Epstein et al. (1977), Tissot/Welte (1978), and many others, offered methods to establish the index of organic metamorphism in unravelling the basin geothermal history, for example, and thus the diagenetic history.

Sureda/Amstutz (1981) showed that granitic intrusions were not the source of the ores they investigated, but that ores were produced through contact-metamorphism of originally sedimentary — diagenetic ores. This is merely one example of the changes in diagenetic textures.

Beach (1979, 1982) and Fry (1982), among many researchers, deliberated on pressure solution as a metamorphic process, but contended that late-diagenesis and low-grade burial metamorphism can form similar features (see also Spry, 1969).

Hesse/Ogunyomi (1980) studied the pre-orogenic subsidence and orogenesis as parameters controlling diagenesis, including burial diagenesis.

Böhlke et al. (1980) and Evarts/Schiffman (1983) provided data on submarine hydrothermal metamorphic alterations of volcanic rocks. Note that many of the minerals are similar to those formed by other processes, including diagenesis/burial metamorphism. (See Hydrothermal.) Nahon et al. (1981) described zeolitic hydrothermal metamorphism in laterites, whereas Easton et al. (1977) and Valliant/Barnett (1982) have investigated low-temperature metasomatic garnets from marine sediments and from metamorphosed manganese sediment; the latter are a guide to gold mineralization.

Gole (1980) and Miyano/Klein (1983), respectively, dealt with BIF's mineralogy and petrology, and conditions of very low-grade metamorphism (see also Iron).

Ryall (1981) studied the form of Hg in stratiform $Pb - Zn - Ag$ deposits of different

regional metamorphic grades; Stanton (1982b) offered data on the sedimentary/diagenetic precursors of metamorphic facies; and Momles (1983) examined the sphalerite composition in relation to deposition/precipitation and metamorphism, e.g., changes of syngenetic – diagenetic sphalerite.

Ferry (1981) investigated desulfidation during prograde regional metamorphism. Can this process also occur during burial diagenesis?

Walter/Orville (1982) described volatile production and transport in regional metamorphism. Can this be extrapolated to a lower-grade burial diagenesis? The same question applies to Yardley's (1981) study on the effect of cooling, on the water content, and on mechanical behaviour of metamorphism.

Bailey (1982) reviewed mantle metasomatism and its chemical change within the Earth, and also discussed the effects on the processes along the Earth's surface.

J.C.M. Taylor (1983) opined on "bit-metamorphism", illustrated by lithological changes taken place during drilling. Beware of such man-induced alterations.

Kisch (1983) summarized comprehensively the data on burial diagenesis/low-grade metamorphism (including incipient changes) in clastic rocks. Many of the concepts are, of course, applicable to the study of hostrocks of ores — but only very few serious attempts have been made to match diagenesis of the hostrocks with ore mineralization. See also Ireland et al. (1983) and Duba/Williams-Jones (1983) for glauconite and illite stability, which could be applied to certain hostrock/ore pairs.

Slack et al. (1984) detailed stratiform tourmalinites in metamorphic terranes and included in their discussions the influence of syngenesis and diagenesis.

Langbein et al. (1984) examined the influence of magmatic intrusions on the "diagenesis" of shales. How can these contact effects be distinguished from "normal" diagenetic products?

Weaver (1984) offered a detailed study of the mineralogic, chemical, isotopic, petrographic, and structural changes during the late-diagenetic to low-grade metamorphic stages as a consequence of increase in temperature. Paleothermometric guides were developed.

Walther/Wood (1984) discussed the rate and mechanisms in prograde metamorphism, including low-grade catagenetic processes (i.e., the hydrologic systems were considered).

Althaus (1984) studied solution – rock interactions and neoformation of numerous minerals in a geothermal region (see Hydrothermalism). Schiffman et al. (1984) described the low-P/T conditions of a telescoped metasomatic facies series.

Blokh/Dagayeva (1984) offered criteria to discriminate authigenic and endogenic feldspathization in unmetamorphosed sedimentary piles and distinguished diagenetic and metasomatic products. In some investigations it has been proposed that feldspars in the hostrock supplied the Pb for the ore; thus the various genetic types of feldspars in the country rock must be recognized to permit a plausible interpretation of potential sources.

Fairchild (1985) offered relevant models (see his figs. 2 and 9) depicting the syngenesis – diagenesis – metamorphic evolution/paragenesis/development of dolomitic metasediments that show preserved diagenetic textures. Similar studies must be applied to many low-grade metamorphosed ore hostrocks.

Nyk (1985) investigated pelitic wall rocks (i.e. footwall) of syngenetic sulfide – barite ores that have reached anchizone-grade (burial/catagenetic?) metamorphism as based on illite crystallinity characteristics. He also discussed the methodological problems.

Robinson (1985) reviewed diagenesis and low-temperature metamorphism, comprising also hydrothermal changes of calcareous sandstones (what are their differences compared to burial metamorphosed types?), evidence for fossil submarine hydrothermal systems, carbonate alteration in the Salton Sea geothermal system (is the carbonate similar to ore-associated gangue?), and calcite – dolomite – ankerite vertical changes in a borehole.

MISSISSIPPI VALLEY-TYPE ORES

Anderson/Macqueen (1982), Kisvarsanyi et al. (1983), Sangster (1983) provided general comprehensive reviews of the M.V.-type deposits as well of a few other related types of sediment-hosted stratiform Pb – Zn deposits and offered models thereof. Diagenesis is treated extensively in their publications.

Reckman/Friedman (1982) translated from French a book on Exploration for Carbonate Petroleum Reservoirs, which contains sections on diagenesis, carbonate petrology in general, and petrophysical/geophysical information that ought to be applied in the search for new, or in the extension of known, Pb – Zn carbonate-hosted ores.

Kyle (1983) offered a review of the economic aspects of subaerial carbonates. See the whole Memoir on Carbonate Depositional Environments for excellent information.

Pratt (1984) reported on a Conference on M.V.-type Pb – Zn ore deposits. Earlier data is to be found in Sangster (1976), Hagni (1976), Hoagland (1976) and Kyle (1981) (all in Wolf, 1976, 1981) who have discussed specific aspects of the origin of M.V.-type deposits.

TABLE 63

Classification and comparison of stratiform lead – zinc deposits in sedimentary rocks (Skripchenko, 1981)

Characteristics	Types of deposit				
	clay	clay – carbonate	stratified carbonate	carbonate of dissolution structures	reef carbonate
Rock associations (primary)	Coaly argillite – sandy series	Coaly silliceous – clay – carbonate stratified groups	Dolomites, limestones		
Deposits and age of country rocks	Precambrian: Sullivan (Canada), Broken Hill (Australia), Kholodnenskoye (USSR); Jurassic: Filizchay (USSR)	Precambrian: Mt. Isa (Australia), Gorev-skoye (USSR); Devonian: Zhayrem (USSR), Rammelsberg (W. Germany); Triassic: Rupica* (Yugoslavia)	Precambrian: Balmat-Edwards (USA), M'Passa (Zaire); Cambrian: Sardinia (Italy); Carboniferous: Navan (Ireland); Triassic: Upper Silesia (Poland)	Riphean, Cambrian: Sardona (USSR), Austinville, Urich, Pioche (USA); Ordovician: Upper Mississippi region, Jefferson City (USA); Devonian: Mirgalimsay (USSR); Carboniferous: Tri-State (USA), Achisay (USSR), Riasi (India)	Cambrian, Ordovician: region of southeastern Missouri (USA); Devonian: Ushkatyn (USSR), Pine Point (Canada); Carboniferous: Dzhergalanskiy region (USSR), Bingham (USA)
Limiting and typical Pb/Zn ratios	From 1.3 to 0.25; typically 1:1	From 5 to 0.33; typically 1:2	From 0.33 to purely zinc ores; ores are essentially zinc	From 10 to 0.2; typically 1:4	From 4 to 0.4; typically 4:1
Examples of reserves or recovered mass of metals; contents	Broken Hill (Australia) 40×10^6 t Pb + Zn; 11.1% Pb, 11.9% Zn	Mt. Isa (Australia) 14×10^6 t Pb + Zn, 4×10^6 t Cu; 7% Pb + Zn, 3% Cu	Balmat-Edwards (USA) 1.5×10^6 t Zn; up to 10% Zn	Tri-State region (USA) 10.5×10^6 t Zn, 2.5×10^6 t Pb	Viburnum region (USA) 12×10^6 t Pb, up to 8% Pb, up to 2% Zn
Shape of ore bodies	Lens-like, stratified bodies	Lens-like stratified, irregular bodies	Stratified bodies	Arched, ribbon, annular stratified bodies, serrated veins, pipe-shaped bodies	Lens-like, ribbon, roll bodies

Major parageneses of sulfides	Pyrite + pyrrhotite + sphalerite + galena ± chalcopyrite	Pyrite + sphalerite + galena ± chalcopyrite	Pyrite + sphalerite	Sphalerite + galena ± pyrite	Galena + sphalerite
Shapes of aggregates of ore minerals	Stratified, continuous	Stratified, lens-like, concretion, continuous, impregnated	Stratified, impregnated, continuous, cementation	Impregnated pocket, vein-shaped, crust	Continuous, banded, pore-filling, impregnated
Isotope type of lead	Ordinary		No data	Anomalous "Joplin" type	
Difference between maximal and minimal values of the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios in ores of individual deposits or regions	0.33; 0.23; 0.52		–	3.61; 0.54; 3.50	1.50; 0.54; 1.92
Isotope composition of sulfur ($\delta^{34}S$, ‰) and its genetic type	About 0, endogenous sulfur			About +20, evaporite sulfur	
Dispersion of $\delta^{34}S$, ‰, in ores of individual deposits	to 10			to 50	
Temperature of basic mineralization	Reliable data unavailable on temperature of deposition of primary ores			$60° - 200°C$	

* Name not verified.

Bellana et al. (1981) studied the REE and minor elements in fluorites in limestones. Five differently colored fluorite types were recognized, and their Tb/Ca vs. Tb/La variation diagram outlined "hydrothermal", sedimentary syngenetic/diagenetic and other fields. Their method should be useful in the study of M.V.-type ores with fluoride gangue. Can we recognize several sub-varieties based on such geochemical (and isotope) data?
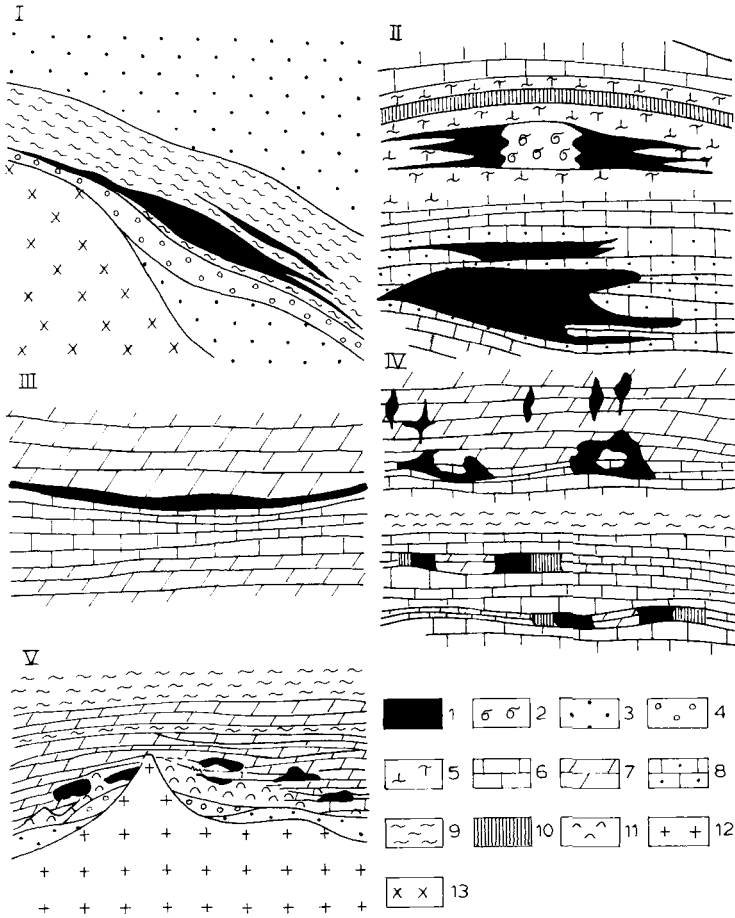
Fig. 154. Typical examples of stratiform polymetal deposits in sedimentary series: I = Sullivan (clay type); II = Zhayrem (at top), Gorevskoye deposit (clay – limestone type); III = Upper Silesian region (stratified carbonate type); IV = Upper Mississippian region (at top), Tri-State region (carbonate type, dissolution structures); V = deposits of southeastern Missouri (reef carbonate type). 1 = Polymetal ores; 2 = barite – lead ores; 3 = sandstones; 4 = conglomerates; 5 = siliceous – clay - calcareous flyschoid deposits; 6 = limestones; 7 = dolomites. Rocks: 8 = calcareous – siliceous; 9 = coaly clay; 10 = ferruginous – manganese siliceous rocks and jasperoids; 11 = reef structures; 12 = ancient crystalline rocks of the Ozark dome; 13 = diorites. (After Skripchenko, 1981.)

Diehl/Kern (1981) described the geology and origin of a carbonate-hosted (M.V.-type?) Pb – Zn ore in Thailand; see their model in fig. 14. Metal-bearing solutions entered the algal reef either laterally from the basin sediments (as compaction fluids?) and/or along early diagenetic fracture zones. The mixing of the metal-bearing fluids with diluted oxidizing subsurface waters caused precipitation of the ore minerals as disseminated and network-like irregular concentrations. Porosity and permeability controlled the localization. Paleokarst openings contain varve-like bedded sulfide or mineralized collapse-breccia concentrations.

Skripchenko (1981) classified and modeled the stratiform Pb – Zn deposits based on lithology and facies (Table 63 and Fig. 154). To what degree do these types reflect different styles (or sub-types?) of syngenetic – diagenetic – catagenetic – metamorphic – remobilized – hydrothermal, etc., mechanisms?

Radke (1982) offered a superb study of the late diagenetic history of a carbonate complex, including sulfides and gangue minerals, paragenetic stages/evolution,
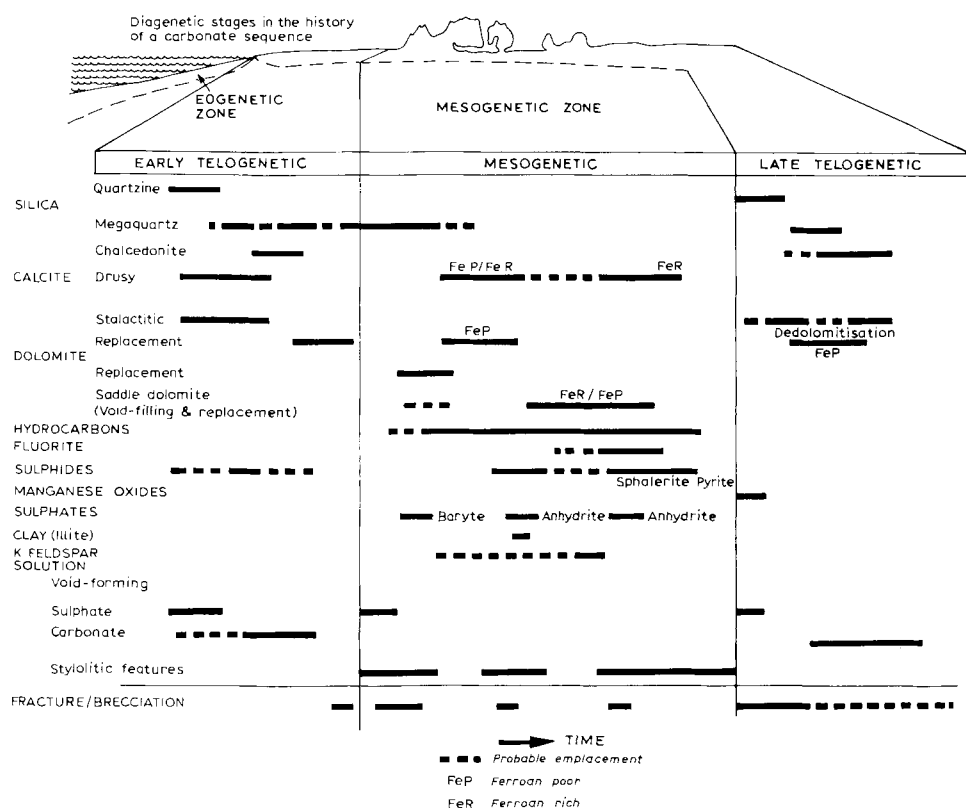
Fig. 155. Generalized paragenetic sequence in the Ninmaroo carbonates. (After Radke, 1982; for diagenetic phases, see Choquette/Pray, 1970.)

Shallow subsurface sulphate
reduction and calcitisation

Surface
dedolomitisation

Silicification (chert)

Nodular anhydrite

Dolomite (baryte,
celestite, fluorite?)

Gypsum mush

Carbonate cements

Seasonal fluctuation of
water table and salinity

VADOSE ZONE

0

1m

PHREATIC ZONE

SALINE GROUNDWATER

BRACKISH GROUNDWATER

Horizontal scale
several kilometres

Progression of diagenetic
facies with time

0

1m

VADOSE ZONE *

PHREATIC ZONE

SALINE GROUNDWATER

BRACKISH GROUNDWATER

* —— Selective dissolution of aragonite
and calcium sulphates

—— Moldic and cavern porosity

—— Calcrete

Fig. 156. (A) Eogenetic diagenesis on a sabkha. Idealized profile shows a high groundwater table, with a thin landward lens of brackish water. Seasonal fluctuations of the water table range from surface flooding to a lowered phreatic zone and a narrow vadose zone during the dry season. Bars indicate the spatial distribution of diagenetic fields at one point in time. These diagenetic fields migrate laterally with progradation of the shoal. (B) Early telogenetic diagenesis. Idealized profile of an emergent shoal surface during a drop in relative sea level shows a lowered water table and enlarged vadose zone. Selective solution of sulphates and aragonite produced moldic porosity, cavities and collapse breccias. Calcrete cements precipitated in the vadose zone. (After Radke, 1982.)

hydrological and structural controls of diagenetic facies, replacement and other textures, etc. (see his numerous models, only three of which are given here, Figs. 155, 156 and 157). Similar precise work is needed on M.V.-type ores.

Dzulynski/Sass-Gustkiewicz (1985), Sass-Gustkiewicz et al. (1982) and Kyle (1981), among others, studied karst features in association with M.V.-type ores (or vice versa: the ores are associated with the karst?).

R.N. Walker et al. (1983) and Bechstadt/Dohler-Hirner (1983) discussed, in general, a Proterozoic M.V.-type ore in Australia and the Bleiberg-Kreuth deposits in Central Europe, respectively. Sverjensky (1981b) treated the M.V.-type ores of the Southeastern Missouri Viburnum Trend; Wolff (1982) described the Long Lake Zn-deposit and offered a classification; and Rajlich (1983) studied a deposit in Morocco. All offered some data of interest to the diageneticists.

Riedel (1980a) and Rhodes et al. (1984) tackled, respectively, ore structures of the Irish Tynagh deposit (of non-magmatic hydrothermal – diagenetic origin with several stages involved), and the Pine Point orebodies as related to stratigraphy, structures, dolomitization, and karstification (see also Kyle, 1980, 1981).
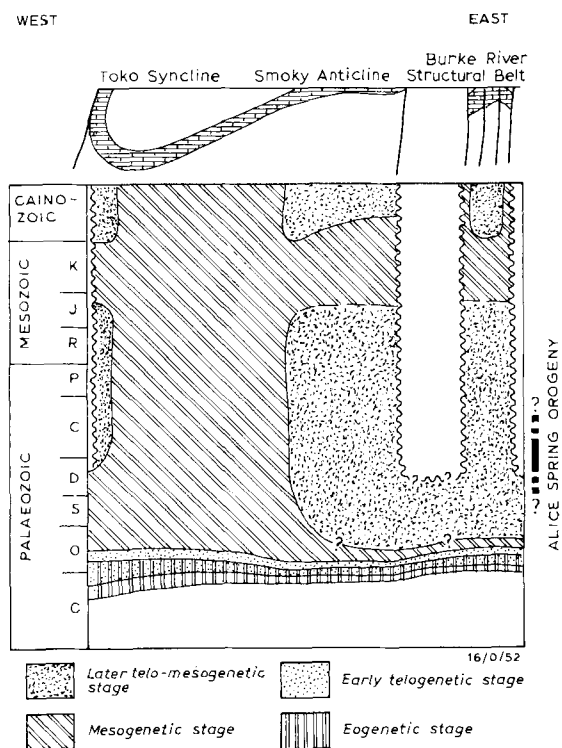
Fig. 157. Variations in duration and extent of diagenetic stages in the Ninmaroo Formation, Queensland – Northern Territory, Australia. (After Radke, 1982.)

284

Zimmerman/Kesler (1981) and Taylor et al. (1983) employed fluid-inclusion studies to prove fluid mixing in the origin of M.V.-type ores. (See also Fluid inclusions, and Mixing.)

Cathless/Smith (1983) studied the thermal constraints on the development of the M.V.-type deposits and their implications on episodic basin dewatering (see Compaction, and Hydrology); Whelan et al. (1984) examined the M.V.-type fluids of synsedimentary ores: Barrett/Anderson (1982) the solubility of sphalerite and galena in NaCl brines; and Giordano/Barnes (1981) studied the Pb-transport in ore solutions.

Macqueen/Powell (1983) and Powell/Macqueen (1984) considered the organic geochemistry of the Pine Point ore field, and the precipitation of sulfide ores and organic matter.
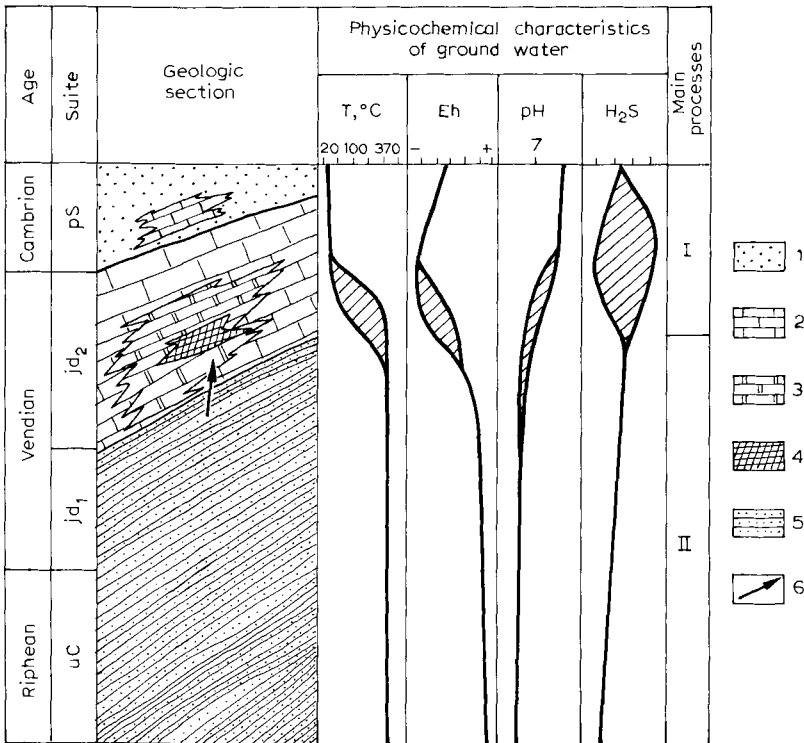
Fig. 158. Diagram showing formation of stratiform lead – zinc ore mineralization in Maya – Kyllakh zone. *1* = Oozes, *2* = limestones and other carbonates, *3* = epigenetic dolomites, *4* = ores, *5* = terrigenous clayey rocks; *6* = direction of movement of waters. *I* = Dolomitization and deposition of sulfides; *II* = enrichment of waters in metals leached from terrigenous clayey hostrocks, and other processes. (After Balashova, 1984.)

Zhabin et al. (1981) investigated the C- and O-isotopes in carbonates of an ore zone (three genetic types of calcite were identified); Kessen et al. (1981) studied the $^{87}Sr/^{86}Sr$ ratios of M.V.-ores; Sverjensky (1981a) the isotopic alteration of carbonate hostrocks as a function of water/rock ratios; Medford et al. (1983) the Sr-isotopic ratios of sulfides, carbonates, and fluid inclusions (the ratio increases with the mineralization process); Lange et al. (1983) discussed the S-isotopic evidence of barites and sulfides; and Schroll et al. (1983) outlined the S-isotope distribution of the Bleiberg deposits.

Shcheglov et al. (1983) offered a brief review of the connection between reefs and ore deposition.

Richardson/Pinckney (1984) and Hannah/Stein (1984) provided evidence for the chemical and thermal fluid evolution during M.V.-type ore formation.

Minerals	Sedimentation stage	Stages of ore formation		
		I stage 150–220°C	II stage 250–360°C	III stage 90–180°C
Calcite	■————————■		■—■	■——■
Dolomite	■————————■	■—■ ■—■	■——■	■——■
Quartz		■—■ ■—■	■——■	
Marcasite		■—■		
Pyrite	Rupturing	■—■ ■—■	■——■	Rupturing ■—■
Sphalerite			■—■ ■—■	■——■
Galena		■—■	■—————■	■——■
Arsenopyrite			■—————■	
Bitumen			Rupturing ■——■	
Phosphorites		■—■		
Glauconite		■—■		
Anthracolite				■——■
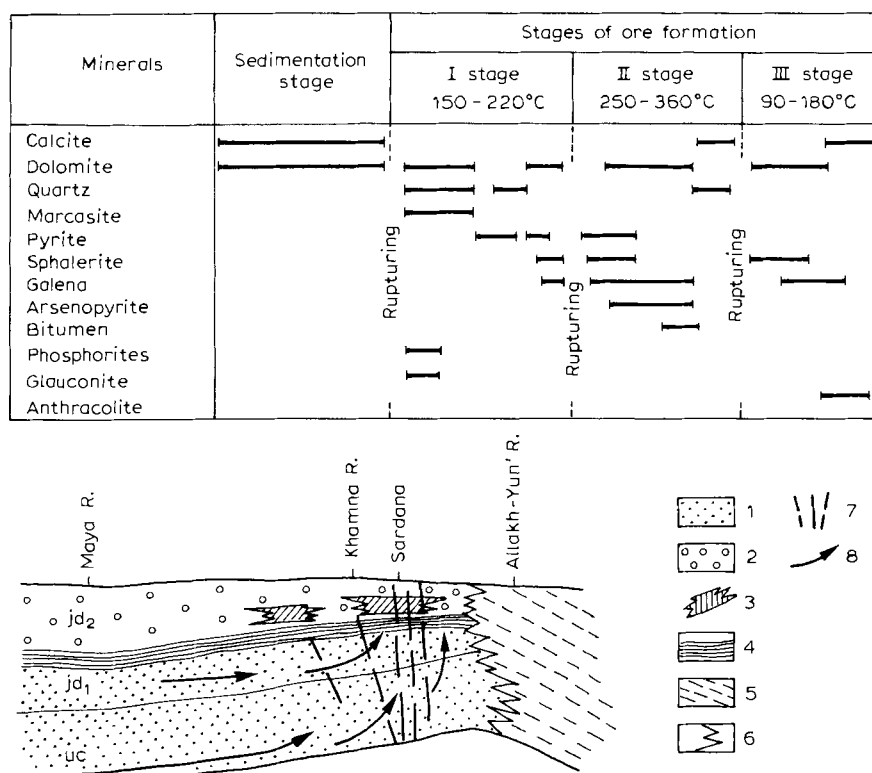
Fig. 159. Successive stages of mineralization in Sardana ore district, and paleogeohydrological structure determining them, according to model presented. *1* = Non-hydrogen-sulfide metalliferous waters of chloride – calcic – sodic composition, oxidizing; *2* = hydrogen-sulfide waters, strongly reducing; *3* = zones of mineralization; *4* = barrier; *5* = rocks of Chukhonoy – Khanda facies type; *6* = facies boundary; *7* = rupture zones; *8* = direction of movement of waters. (After Balashova, 1984.)

Balashova (1984) modeled the ores formed by non-magmatic fluids, including M.V.-type concentrations; e.g., she provided data on temperature, Eh/pH and H_2S genesis, etc. (Fig. 158), summarized the four stages and paragenesis of the minerals, and discussed the hydrology and facies/structural setting of the ores (Fig. 159).

Panno et al. (1983) opined on the genetic implication of halide enrichments near M.V.-type ores; Hartree/Veizer (1982) on the Pb and Zn distribution in carbonate rocks (can they be a source of the metals?); and Kucha/Wieczorek (1984) studied the sulfide – carbonate relationships of a Zn – Pb deposit in Ireland.

Lacerda/Bernard (1984) spoke of a syngenetic Pb – Zn origin of a French deposit. How do we discriminate between depositional – syngenetic and very early diagenetic ores?

Sangameshwar/Barnes (1983) discussed the supergene processes of Zn – Pb – Ag sulfide concentrations in carbonate rocks.

Drew/Both (1984) studied the M.V.-type Ag – Pb deposit of diagenetic – epigenetic origin, using petrological, fluid inclusion and S-isotopic information. A similar investigation was undertaken by Ambler et al. (1979), and they concluded that compaction – diagenetic fluids supplied the metals.

Kucha/Czajka (1984) described the genesis of sulfide – carbonate relations of the M.V.-type (?) deposits, including textures and contact features. Primary metal concentrations in carbonates formed a very large low-grade metalliferous accumulation. An overlying shale acted as a trap when H_2S-rich fluids arrived from an underlying coal basin and converted the metal carbonates into sulfides. Some enrichment may have occurred. This process of sulfidization was repeated several times. To what degree are such impermeable caprocks necessary in other ore districts? Like in oil genesis, do source, conductive, reservoir and cap rocks control the ore-forming hydrologic systems?

A few additional examples in regard to hydrology: Garven (1985) discussed the significance of regional fluid flow in the origin of the Pine Point ores (see his models); Baird/Dennen (1985) offered a geochemical survey of a younger overlying (cap rock?) dolomite that could have influenced brine movement and found that an unconformity controlled updip migration of basinal brines – they also described a source-direction identification method; and Rouvier et al. (1985) examined Pb – Zn deposits associated with salt-bearing diapirs, concluding that two types of ores are present, namely a syndiagenetic ore within organic-rich sediments and an "epigenetic" M.V.-type concentration, the latter resulting from evaporite rock-derived brines that were mobilized in four stages during diapiric growth or piercement (see their models showing, among others, that compaction was influential).

Giordano (1985) related organic ligands and metal-organic complexing particularly to the M.V.-type ore solutions.

Ruiz et al. (1985) discussed Sr-isotopic evidence in their reconstruction of the genesis of barites and sulfides of a M.V.-type deposit. A holistic approach is needed in all similar investigations: three sets of isotopic data ought to be obtained from the various mineral groups of the adjacent *hostrock* (and remoter country rock for comparisons), and of the *gangue* and *ore minerals*.

Aref et al. (1985) described surficial calcareous caliche-type crusts. The model in their fig. 2 outlined the evolution of caliche textures/fabrics/structures of interest to those attempting to unravel M.V.-type gangue and ore features in paleokarsts.

Gregg (1985) described the regional epigenetic dolomitization in the Missouri district. What are the differences between and similarities of the ore-bearing and barren dolomites?

Angiulli et al. (1985) combined sedimentological and geochemical methods to unravel the genesis of a Cambrian carbonate-hosted deposit: the metals are restricted to specific environmental facies. How can the information be utilized in exploration? Was the deposit of syngenetic, diagenetic and/or "epigenetic" origin; of multiple or single-stage origin; did remobilization occur?

Machel/Mountjoy (1986) reviewed the enigmas of dolomitization, many of which could "easily" be related to the hostrocks of ore deposits.

– See also Carbonates, Dolomites, and Karsts.

MIXING (OF FLUIDS)

Runnels (e.g., 1969) concluded that the mixing of natural waters can in some instances result in diagenesis. A simple classification of fluids provides 14 categories of natural fluids with 91 possible combinations of *mixing of pairs* of such waters (not to mention if more than two fluids mix).
    Note: Much more theoretical (e.g., system analyses and computer modeling) data is required on the consequences of mixing of solutions and on the dissolution, transportation, precipitation, coprecipitation, desorption, remobilization, and stabilization of gangue and ore minerals to explain, for instance, their complex and variable parageneses.

Won C. Park (pers. commun., 1973/74) summarized the four types (with five subtypes) of theories of sulfide precipitation in Fig. 160.
    Note: Park preferred to use the terms syngenetic, diagenetic, and epigenetic in a very strict or restricted sense, well realizing that his "epigenetic" was placed in comparison to or in context with the earlier-formed hostrock, thus merely meaning "later than the hostrock" as based on textural/structural observations. However, inasmuch as early and late diagenesis and catagenesis is used here (as done by many others) as a time or stage term, Park's "epigenesis" can be divided into "early

diaepigenesis'', ''late diaepigenesis'' and ''cataepigenesis'' as proposed by Wolf (1975, unpublished; see also Wolf, 1981, and the Glossary). Any of Park's theories also apply to this new scheme.

Kranck (1973, 1975) described flocculation of suspended sediments in the sea as a consequence of mixing of different types of water.

Powers (1957), Goldberg (1971), and Sholkovitz (1976) described, respectively, the adjustment of land-derived clays to the marine environment (see also Clay minerals) due to mixing of river and sea waters; river – ocean interactions in general; and the flocculation of dissolved organic and inorganic matter during river and seawater mixing. The previous history and derivation/source of material in sedimentary basins determines the subsequent diagenesis.

Sholkowitz et al., (1978), Mayer (1982) and Hunter (1983) refer specifically to estuarine mixing that affected, respectively, the removal of dissolved humic acids and Fe (due to flocculation); aggregation of colloidal Fe as explained by coagulation, ''suspension-type diagenesis'' in terms of kinetics and seasonality; and the colloid stability and surface properties of substances affected by estuarine mixing. Carpenter et al. (1984) opined on the mixing and cycling of U, Th and ^{210}Pb in sound sediments (e.g., on the diffusion).

Drummond/Ohmoto (1980) discussed mixing of various solutions, e.g., different types of hydrothermal fluids with meteoric, connate and seawater, as part of a computer model.
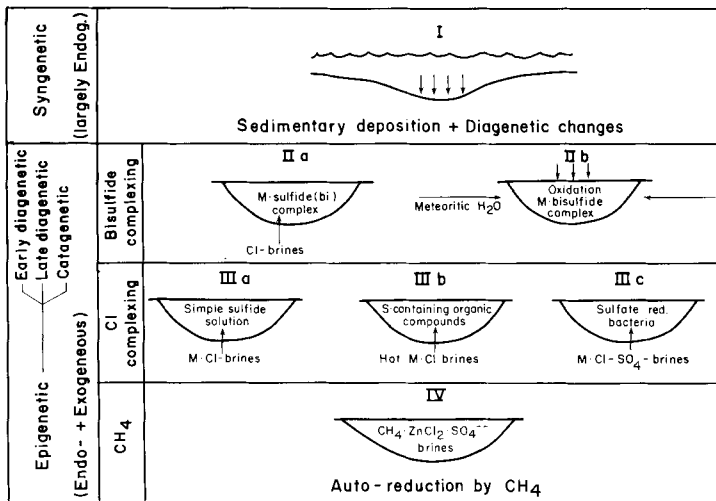
Fig. 160. Current theories of sulfide deposition. (After Won C. Park, pers. commun., 1973/1974.)

RSDW $\qquad$ $\downarrow O_2$ $\qquad$ $\downarrow HCO_3^-$ $\uparrow CO_2$

$$Mn^{2+}+\tfrac{1}{2}O_2+2H_2O \longrightarrow MnO(OH)_2(s)+2H^+ \qquad H^++HCO_3^- \longrightarrow H_2O+CO_2$$

INTERMEDIATE BRINE $\downarrow MnO(OH)_2(s)$ $\uparrow Mn^{2+}$ $\qquad$ $\uparrow CO_2$

$$H_2O+MnO(OH)_2(s) +2Fe^{2+} \longrightarrow Mn^{2+}+2FeO(OH)(s) +2H^+ \quad H^++HCO_3^- \longrightarrow H_2O+CO_2$$

DEEP BRINE $\uparrow Fe^{2+}$ $\downarrow FeO(OH)$ (s) $\uparrow HCO_3^-$

TO SEDIMENTS
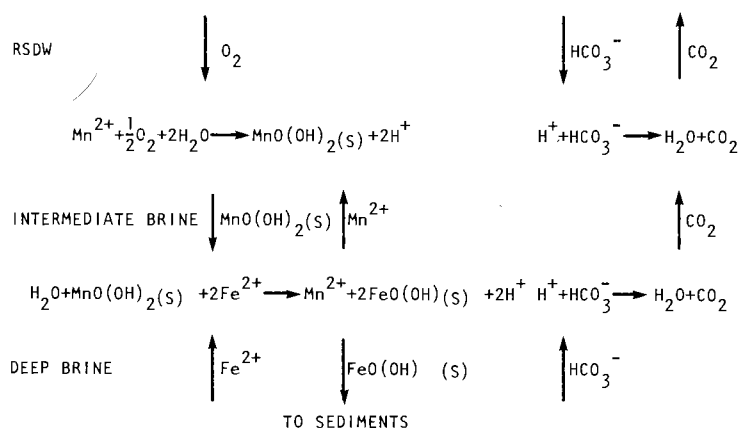
Fig. 161. Chemical model for the interplay of oxygen, manganese, and iron between brines and between brine and RSDW. (After Danielson et al., 1980.)

Danielsson et al. (1980) chemically modeled the interplay of Mn and Fe between three types of brines (Fig. 161).

Edmond et al. (1979) reported on the origin of metal-rich deposits at oceanic ridge crests believed to be the consequence of mixing of hydrothermal and seawater-derived "groundwater": the suite of associated metals depends on the degree of mixing. In contrast, Janecky/Seyfried (1984) studied the genesis of massive sulfide on such ridges and proposed incremental-reaction models for mixing of hydrothermal solution and (surface) seawater. Thus, mixing can be divided into several types: syngenetic, diagenetic, diagenetic – epigenetic, catagenetic, etc.

Volzhin/Korolev (1982) described an epigenetic uranium ore in jasper – quartzites as a product of mixing of exogenetic and endogenetic fluids.

Raup (1982) and Kalogeropoulos/Mitropoulos (1983), respectively, studied the origin of gypsum by mixing of seawater brines, and the geochemistry of barites of the Aegean Sea formed by mixing of ascending Ba-rich hydrothermal fluids and cold seawater.

MOBILITY (ELEMENTAL)

Groot (1966) discussed the mobility of trace elements in deltas.

Bonatti et al. (1971) studied deep-sea (e.g., Pacific) hemipelagic sediments which have an oxidized upper zone and a reduced lower zone, the latter being related to the presence of organic matter. Various elements (e.g., Mn, Ni, Co, P, and La) are

enriched in the upper oxidized zone, whereas Cr, V, U, and S are enriched in the lower reduced unit. Diagenetic (post-depositional) mobility of the elements occurs by diffusion in the interstitial solutions. Redox reactions directly mobilize Mn, Ni, Co, Cr, V, and U, and indirectly P and La. The Fe and Cu cations do not migrate significantly as they are immobilized as sulfides in the reduced zone. Th is not diagenetically mobilized. As a consequence, (a) the average elemental content when analyzed from the upper part of a sediment may be erroneous; some elements are overestimated, whereas others are underestimated. (b) Diagenetic redistribution of U may result in errors in age determinations. (c) The geographical variations in the trace-elemental composition (some potential economic concentrations) in Fe-Mn nodules is due to diagenetic mobility of Mn, Ni, Co, etc. (d) Depth and Eh controls are presented in Fig. 167. The above conclusions are generally applicable also to fossil sediments; any exceptions ought to be precisely established. The thickness increase of the oxidized top layer from the shore to the deep oceanic basin is shown in Fig. 167.

The following questions arise at this point: (a) Are these diagenetic changes also present in other environments, e.g., in lakes, fjords, etc.? (b) Are some types of zoning of metals explainable by diagenetic remobilization? (c) What are the conditions that cause a release of metals into compaction or other intraformational fluids, and what allows their long-distance movement? (d) Are these conditions different from those described by Bonatti et al. (1971)?

Burrows/Hulbert (1975) examined the release of heavy metals from sediments, whereas Subramanian (1976) modeled experimentally the interelemental relations in natural Fe – Mn materials, which also reflect the mobility of metals.

Yariv/Cross (1979) offered a basic text on the geochemistry of colloid systems, which also treated element mobility. (See also Eitel, 1975.)

Hartmann (1979) investigated early diagenetic mobilization of trace metals (Mn, Ni, Co, Cu, Fe, Zn) in pelagic sediments; Sawlan/Murray (1983) studied the trace-metal mobilization in interstitial fluids of red clay and hemipelagic marine deposits; whereas Sholkovitz et al. (1983) discussed the Pu- and Cs-isotopes of nearshore sediments.

Dowty (1980) handled the crystal-chemistry factors affecting mobility of ions in minerals.

Mann/Deutscher (1980) studied the solution geochemistry of Pb – Zn in water containing carbonate, sulphate and chlorine ions (e.g., the inter-ion/species effects, inter-complexes effects, mobility during weathering, etc.: the data is partly applicable to diagenesis). Kritsotakis/Platen (1980) described the barite mobilization by reduction, but at a higher temperature and pressure, which could be applicable to burial and regional metamorphism.

Chesworth et al. (1981) discussed the weathering of basalt and relative mobilities of

major elements. What are the similarities and differences in element mobility in subaerial in contrast to subaqueous (halmyrolitic-type) weathering?

Giblin et al. (1981) performed laboratory simulations of uranium mobility in natural waters, whereas Zielinski et al. (1980) studied the distribution/mobility of U in glassy and zeolitized tuff (no U-removal was recorded; this is in contrast to results of other studies). Many variables must be considered to explain the discrepancies of different investigations. (See also Uranium.)

Button/Erikkson (1981; and Table 64) provided data on the relative mobility of polyvalent elements of economic importance.

Long/Angino (1982) inspected the mobilization of selected trace metals from shales by aqueous solutions and considered the effects of temperature and ionic strength, whereas Kelepertsis (1983) studied the major and trace element association in an ancient carbonate sequence, determining the mobilization of elements and their concentration in pyrite and siderite.

Marchig/Rösch (1983) treated the early diagenetic origin of clays in a calcareous ooze, which reflects element mobility.

Holden et al. (1984) deliberated on the timing of the increase in S-deposition as reflected in lake sediments and on the post-depositional mobility in pore waters, and others.

Jacobs/Emerson (1985) studied the partitioning, transportation and thus the mobility of metals across O_2/H_2S-interfaces in an anoxic basin.

TABLE 64

Polyvalent elements of economic importance

SULFUR	-2	$\boxed{+6}$	
VANADIUM	$+3$	$\boxed{+5}$	
MANGANESE	$\boxed{+2}$	$+4$	$+7$
IRON	$\boxed{+2}$	$+3$	
ARSENIC	-3	$\boxed{+5}$	
SELENIUM	-2	$\boxed{+6}$	
MOLYBDENUM	$+4$	$\boxed{+6}$	
ANTIMONY	-3	$\boxed{+5}$	
URANIUM	$+4$	$\boxed{+6}$	

☐ RELATIVELY MOBILE

RELATIVELY INERT

– See Barriers, Coprecipitation, Eh, pH, Ion potential, Transportation, and Sources.

MULTI-FACTORIAL

Degens (1965), Larsen/Chilingar (1967, 1979), Füchtbauer/Müller (1970), and Berner (1971, 1980b), for example, provided good introductions to syngenesis – diagenesis, in general, with some sections on the origin of the hostrocks of ores. But most of the data is qualitative.

  Note: (a) Although many parameters related to diagenesis have been treated in the above-cited publications, these variables have too often not been modeled as part of an overall complex system, i.e., they are handled in isolation from each other. There are, of course, minor exceptions, among which the book by Berner (1980b) is especially recommended. He combined numerous diagenetic variables in a "general diagenetic equation", which relates the changes in solid and/or liquid component concentrations to the processes of diffusion (including bioturbation), advection, and diagenetic reactions (e.g., precipitation, dissolution, authigenesis, adsorption, ion exchange, bacterial reactions, and radioactive decay). (b) Most diagenetic problems can be satisfactorily solved only by a combination of *field and laboratory* work with a *rigorous theoretical treatment*. (c) Potter et al. (1980) summarized the "sedimentology of shale", including aspects of diagenesis, shales as hosts for metal deposits, and environments of black (euxinic) clay/mud deposits (see Clay minerals).

Beales/Onasick (1970), Beales et al. (1980), Wolf (1976a), and Hitchon (1977) considered many factors operative during basin evolution that result in the formation of Mississippi Valley-type ores. Wolf prepared several models depicting the complex interrelations between numerous parameters.

MacIntyre (1970) considered many variables that control the over seventy elements in ocean water as part of the global geochemical cycle. Figure 162 depicts his equilibrium ocean model consisting of nine phases and nine components.

  Note: (a) Although all elements, including metals, were listed in his various tables (e.g., periodic tables) only their *general* geochemical affinities were discussed. Too little as yet is known about most elements' global cycle as related to diagenesis and ore genesis. (b) For example, what are the sorption and desorption capabilities in regard to metals of the various clays in Fig. 162?

Hallberg (1972) described the formation of sedimentary sulfides in terms of geochemistry and biological processes as well as energy requirements. Numerous factors were considered and diagrammatic models were formulated.

Söhnge (1974) reviewed the research trends in the origin of sedimentary ore deposits, i.e., the approach used, tectonic setting, paleophysiography, sedimentary petrology,

submarine volcanism – exhalatism, biogeochemistry and paleoecology, and diagenesis.

Lambert (1976) described the McArthur Zn – Pb – Ag deposit's features and metallogeny. Lambert's work represents a good example of taking numerous
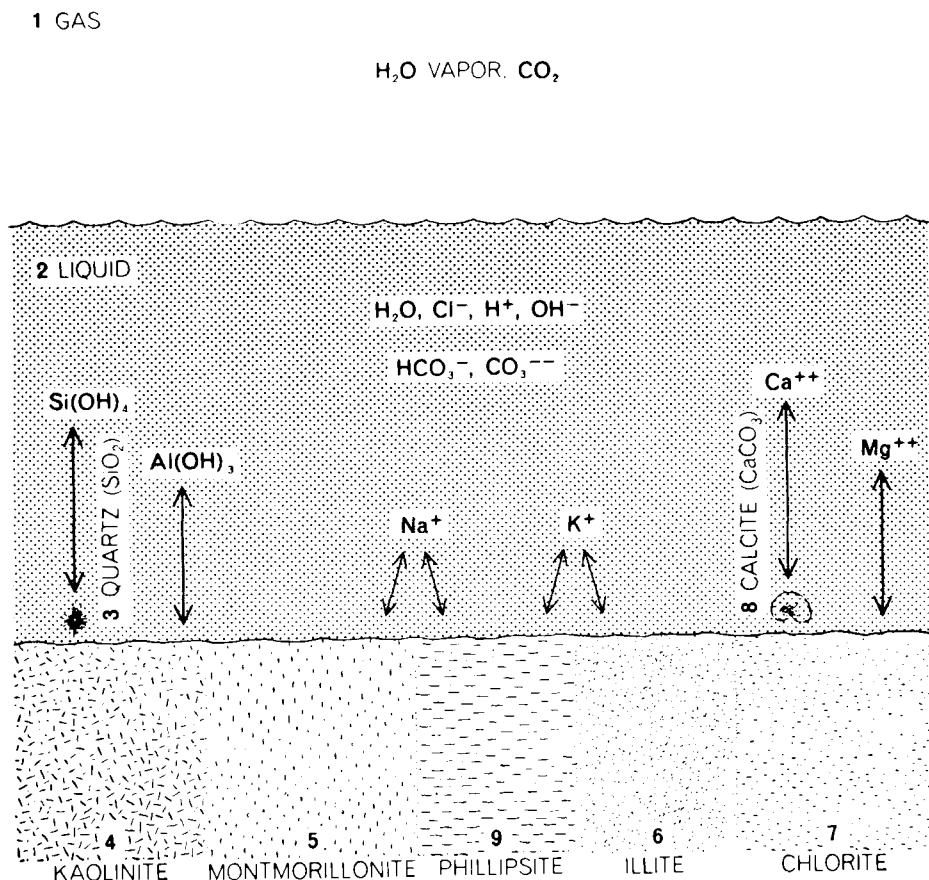
1 GAS

H₂O VAPOR. CO₂

2 LIQUID

H₂O, Cl⁻, H⁺, OH⁻

HCO₃⁻, CO₃⁻⁻

Si(OH)₄

Ca⁺⁺

Mg⁺⁺

Al(OH)₃

3 QUARTZ (SiO₂)

Na⁺

K⁺

8 CALCITE (CaCO₃)

4 KAOLINITE   **5** MONTMORILLONITE   **9** PHILLIPSITE   **6** ILLITE   **7** CHLORITE

Fig. 162. Equilibrium ocean model, consisting of nine phases and nine components, shows how the principal constituents of the ocean distribute themselves among the atmosphere, the ocean and the sediments. Three of the constituents [HCO_3^-, CO_3^{2-} and $Si(OH)_4$] are not included among nine listed components but appear as equilibrium products of those that are listed, as do seven ions (H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, OH^-). Two of the solids are shown as biological "precipitates": quartz (3) in the form of silicate structures built by radiolarians and "calcite" (8) in the form of calcium carbonate chambers built by foraminifera. The method of precipitation is unimportant as long as the product is stable. The equilibrium model goes far to explain why the ocean has the composition it does. (After MacIntyre, 1970.)

variables into account. Other excellent examples include: the Kupferschiefer (Jung/Knitzschke, 1976), Zambian Copperbelt (Fleischer et al., 1976), and many chapters in Wolf (1976, 1981), such as on the Western States-type uranium deposits (Rackley, 1976).

Vaughan (1976) offered a brief review of the sedimentary geochemical variables influencing the origin of sedimentary Pb, Zn, Cu and Fe sulfide deposits.

Gabelman (1977) presented a superb treatment of all variables controlling the origin of the known and of a few newly suggested types of uranium – thorium mineralizations. Insofar as all ore types are discussed, only part of this book is concerned with syngenesis – diagenesis; however, these sedimentary environments, processes, and stages are *put into context* with all other geological mechanisms and milieus. Nevertheless, much of the information is directly and indirectly applicable to
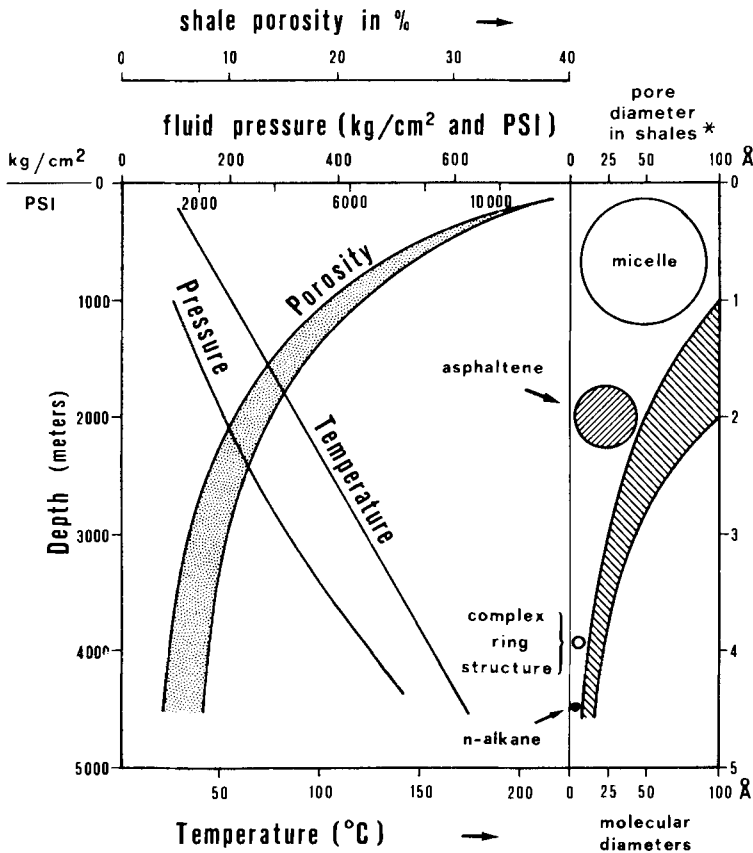
Fig. 163. Interrelationship of various physical parameters with increasing depth of burial for shale-type sediments. (After Tissot/Welte, 1978.) * Pseudo-pore diameters.

diagenesis – catagenesis – burial metamorphism of sedimentary – volcanic piles during basin evolution: sources, transfer – transportation mechanisms, mobilization processes, fixation, numerous geochemical cycles in orogenic – taphrogenic – cratonic settings, geochemical distinction of U-mineralization processes, and underemphasized processes in U-ore genesis useful in exploration.

Tissot/Welte (1978), based on many publications, summarized the interrelationships of various physical parameters with increasing depth during the burial of fine-grained (shale) sediments (Fig. 163). For example, the following are complexly interconnected: burial depth, pressure, fluid pressure, temperature, shale porosity, and the pore geometric configuration, which is shown in the diagram as "pseudo-pore diameter – depth curve".

Finlow-Bates/Stumpfl (1979, 1981), Finlow-Bates/Stumpfl (1979/80), Fisher (1960), Neudert/Russell (1981), Solomon (1965), and many others studied the origin of the Mount Isa deposits and offered various interpretations, especially by considering preferentially specific genetic parameters (often at the unfortunate expense of equally important other variables). Many of these parameters are related to diagenesis; see also Solubility, Zoning, Entropy, Structures, Textures, Facies, and Replacement.

McGowen (1979) discussed the relationship between water depth in which large volumes of fine-grained sediments formed, and the total organic carbon, sediment type, and trace-element composition (Fig. 164). The study was undertaken to

TRACE ELEMENT ASSOCIATIONS

	Md	H2O	C	B	Ba	Be	Ca	Co	Cr	Cu	Fe	Hg	La	Mg	Mn	Nb	Ni	Pb	Sr	Ti	V	Y	Zr
Md																							
H2O																							
C	X	X		X	X	X		X			X				X					X		X	
B	X	X	X		X	X		X															
Ba	X	X	X	X		X		X															
Be	X	X	X	X	X			X															
Ca																			X				
Co	X			X	X	X	X													X			
Cr	X	X								X	X		X	X	/X		X			X	X	X	
Cu	X	X						X			X		X	X	X		X			X	X	X	
Fe								X	X				X	X	X		X			X	X	X	
Hg	X	X	X																				
La	X	X						X	X	X													
Mg	X	X						X	X	X							X						
Mn	X	X	X					X	X	X			X								X	X	
Nb																							
Ni	X	X						X	X	X													
Pb	X	X																					
Sr							X																
Ti	X	X	X					X	X	X	X												
V	X	X						X	X	X					X								
Y	X	X	X					X	X	X					X								
Zr																							

(Left vertical axis label: TRACE ELEMENTS, ORGANIC CARBON, WATER DEPTH, AND FINE-GRAINED SEDIMENT. Top left axis label: DEEP Md H2O / DEEPER H2O)

Fig. 164. Relationship between water depth, total organic carbon, sediment type, and trace metals; Matagorda Bay system, Texas. (After McGowen, 1979.) Statistically significant correlations between the trace metals and other factors. For example, the cross in column 3, row 4, means that a positive correlation was found between boron and carbon content. Similarly, all trace elements except Ca, Fe, Nb, Sr and Zn are enriched in muds (column 1).

understand the U-mineralization processes (including the source) of the Texas Coastal Plain sandstone-hosted deposits.

Lerman (1979) in his book on geochemical processes reviewed numerous factors related to the aqueous and sedimentary milieus, including diagenesis, interface processes, cycles, fluxes, transport, diffusion, and weathering.

Odin/Letolle (1980) demonstrated the complex interplay of regional (geographic) and local (Eh, influx of detritus and Fe, etc.) factors which was reflected by the presence of glauconites, phosphates and types of marine clays in relation to other deposits as part of the normal geochemical evolutionary sequence (Fig. 165). For the specific interpretation, see the original paper.

Ohle (1980) discussed the origin of the Mississippi Valley-type ores, emphasizing that there is still great disagreement on most facets, i.e., source, timing, solutions, precipitation, and localization. Consequently, more research is required in this area, using a multi-factorial and multi-stage approach.

Strnad (1980) discussed numerous geological variables to be taken into account in the genetic models of the Athabasca-type uranium deposits and those used during exploration. He presented a useful generally applicable philosophical discussion.

Taylor/Rowntree (1980) reviewed the major features of uranium mineralization of the Pine Creek geosyncline in Australia, compared the models proposed, and reconstructed the genesis of the deposits. It is a fine example of a lack of consensus in the early stages of exploration, as based on *preferentially selected* methods and genetic factors considered.
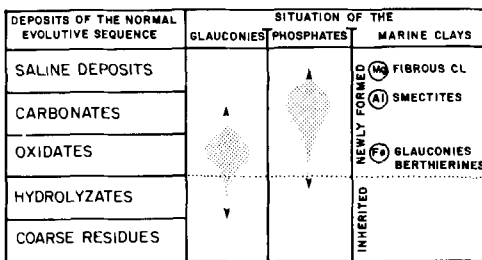
Fig. 165. Position of glauconites and phosphates in relation to deposits of the normal evolutionary sequence. The left column lists the classical members of Goldschmidt's sequence as revised by Millot (1964). They are deposited from the base to the top as indicated by the figure for a normal sequence. In this sequence, glauconitization is essentially related to the oxidate stage, whereas phosphatization occurs in the carbonate stage. This indicates that phosphate deposition is related to a period in the evolution of sedimentary basin characterized by a higher confinement; the nearby continent is more eroded and only the most soluble ions are transported by the rivers. The right column shows the position of glauconitic minerals in the theoretical sequence of deposition of the clay minerals. (After Odin/Letolle, 1980.)

Curtis (1981) provided a review of the variety of rock types, ages, and geologic settings of uranium in volcanic and volcaniclastic lithologies. He discussed the desirable features in evaluating potential uranium deposits. He concluded that diagenesis may have been operative in some varieties of uranium deposits, e.g., in those associated with red-beds, and in those of subaqueous, synsedimentary – exhalative, and synvolcanic – exhalative origin (see his models in figs. 10 and 11).

Förstner (1981a, b) wrote two chapters on the recent heavy-metal concentrations in limnic/lacustrine sediments and on trace metals in freshwater environments. He also discussed mine effluents and pollution. Numerous aspects treated by Förstner have a direct bearing on the understanding of diagenesis, such as precipitation, adsorption, complexing, transportation, and dilution mechanisms. He also discussed autochthonous and allochthonous components, authigenetic products, influence of organic matter, bacterial processes, influence of rate and type of sedimentation, mineral phases, and metal associations.

Gustafson/Williams (1981) and Bjørlykke/Sangster (1981) discussed numerous factors operative in sediment-hosted $Cu – Pb – Zn$ deposits. For example, in Table 65 three types of deposits are compared.

Kimberley (1981) wrote a chapter on the origin of oolitic iron formations and listed the proposed modes of iron transportation (see his table IV, p. 44) and iron concentration/precipitation (cf. his table V, p. 46). He compared and contrasted several basic genetic hypotheses, including syngenetic and diagenetic – epigenetic replacement types. He weighted many variables in his excellent contribution.

Kyle (1981) considered all possible factors in the origin of the Pine Point $Pb – Zn$ ores in this superb review chapter.

Large (1981) compared the major features of eight to nine sediment-hosted, submarine exhalative $Pb – Zn$ deposits. If the emphasis lies on "exhalative", in the future these ores ought to be compared with those of purely non-volcanic exhalative origin. To what extent these two major groups of ores differ in their zoning and diagenetic alterations, remains to be examined.

Laznicka (1981a) presented an excellent discussion of the concept of types of ores. Although not directly related to diagenesis, Laznicka's comments and critical evaluations are very important: the total petrographic and petrologic information required to properly evaluate ore types has to be improved in both quantitative and qualitative terms, including the methodologies. Computers only manipulate what they are being fed (in 1985 – 1986 at least); they do not obtain the field and laboratory data! Also, they do not improve badly recorded information or supply data that was not obtained in the first place!

Laznicka (1981b) contrasted the metallogeny of platform versus mobile belt-type of stratabound/stratiform ore deposits and considered many megavariables that determine, among others, the diagenetic processes (see pp. 537 – 539, especially). Very

TABLE 65

Comparison of the major features of intracratonic sedimentary Cu, Pb, Zn deposits (Bjørlykke/Sangster, 1981, p. 208)

Deposit type	Red-bed copper	Sandstone lead	Carbonate-hosted zinc – lead
Metal ranking	Cu >> Zn + Pb	Pb > Zn > Cu	Zn > Pb > Cu
Hostrock	Arkose, feldspar sandstone, shale	Quartz sandstone	Dolomite
Depositional environment	Continental	Continental – shallow marine	Shallow marine
Tectonic environment	Rifting	Stable	Stable
Climate	Arid to semi-arid; warm	Semi-arid, warm to cool(?)	Arid to semi-arid; warm
Cement	Calcite – dolomite – quartz	Quartz	Dolomite
Ultimate metal source	Basement	Basement	Basement
Immediate metal source	Oxide coating from mafic minerals	Feldspar in arkose or basement	Carbonate, evaporite, shale
Sulfur isotope composition	Light	Light and heavy	Heavy
Transport medium	Groundwater	Groundwater	?

little is known as yet on the regional broad-scale variables that influence directly and indirectly more local processes, including diagenesis. For example, hardly any utilizable information is available on the regional "in tandem, multiple-causal" geologic factors that control local geologic, geochemical, and biological systems (see pertaining sections in this chapter).

The Bureau of Mineral Resources of Australia (1981) offered a symposium reviewing the current states of syngenetic – diagenetic theories of the sediment-hosted sulfide mineralizations.

Chongying (1981) and Badham (1982), respectively, considered the depositional and diagenetic metallogenesis of a stratiform copper deposit and of the Rio Tinto district. Various models have been discussed.

Arthur/Jenkyns (1981) discussed the numerous parameters which control paleo-phosphogenesis: climate (warm humid versus arid), sealevel changes, transgressions – regressions, tectonism – plate tectonics, paleotopography, paleoceanography (e.g., upwelling, currents and supply of nutrients/phosphorus), terrestrial sources, reworking, remobilization and diagenesis, stratigraphy and lithological associations, among others.

Baturin (1982) schematized the environment of phosphate genesis on ocean shelves (Figs. 166 and 167). Many geological, oceanographic, chemical, and biological
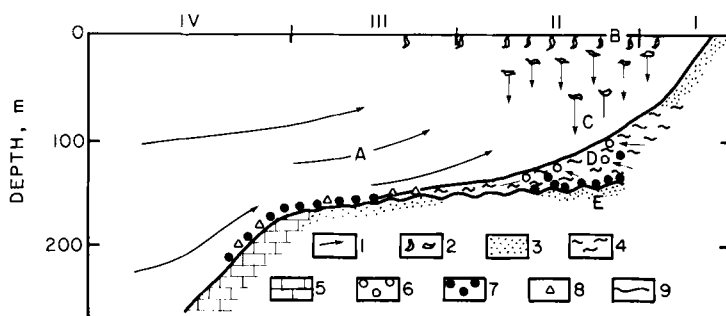
Fig. 166. Scheme of the process of Quaternary phosphorite formation on the ocean shelves: A = supply of phosphorus to the shelf zone by upwelling waters; B = consumption of phosphorus by organisms; C = deposition of phosphorus on the bottom in biogenic detritus and its burial in sediments; D = formation of phosphate concretions in biogenic sediments; E = reworking of sediments and concentration of phosphate concretions when sea level is low. Zones: I = zone of shallow-water clastic deposits; II = zone of biogenic sediments with high content of organic matter and disseminated biogenic phosphorus; III = zone of reworked sediments rich in phosphate concretions; IV = zone of carbonate sediments, locally with phosphate concretions. Legend: 1 = paths of movement of phosphorus in sea and interstitial waters; 2 = plankton; 3 = clastic sediments; 4 = biogenic siliceous, siliceous – clastic, and siliceous – carbonate sediments; 5 = carbonate sediments; 6 = unconsolidated phosphate concretions; 7 = dense phosphate concretions; 8 = glauconite; 9 = erosional surface. (After Baturin, 1982.)
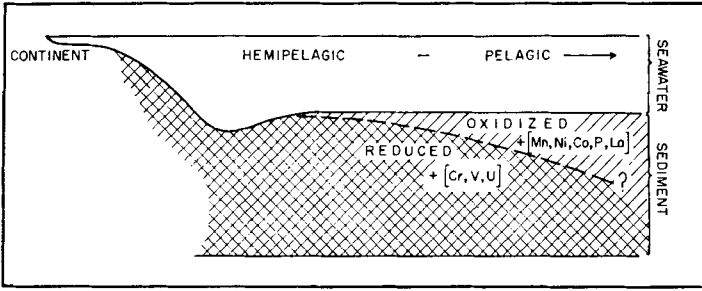
Fig. 167. Schematic and qualitative representation of the consequences of diagenetic processes on the distribution of some elements in the sedimentary column. The oxidized upper zone increases in thickness away from the continent. Mn, Ni, Co, P and La are enriched in the upper zone; Cr, V and U are enriched in the lower zone. (After Bonatti et al., 1971.)

parameters that in combination are responsible for the formation of phosphorites were considered in his book. Upwelling and mass mortality of organisms are not the only important controls and may have been overemphasized. Diagenesis is important also.

Bogdanov/Feoktistov (1982) divided the "Kupferschiefer"-type and related copper deposits of Central Europe into two varieties: the Cu-slate and the Cu-sandstone types. The latter has been wrongly included in the former group, i.e., the Kupferschiefer-type. The distinction between the two types, however, is important because the slate-hosted ore is of the sedimentary – diagenetic origin, in contrast to the sandstone-hosted copper that is truly epigenetic as shown by various criteria. More studies are required as certain features are valuable exploration guides that have been ignored in the past.

Lambert (1982) discussed the constraints on the genesis of Pb – Zn – Ag deposits, which have been variously interpreted as of epigenetic or synsedimentary origin. In the past, the same features have been interpreted to be guides to at least two different genetic mechanisms! Consequently, this problem must be resolved.

Voultsidis et al. (1982) contrasted the diagenetic, supergene, and hypogene genetic hypotheses advanced for the U – Ni deposits of Key Lake, Saskatchewan, Canada.

Siever (1983) discussed the burial history and diagenetic reaction kinetics; multiple parameters were treated well.

Barnes (1983) studied the stratiform/stratabound tungsten mineralization in the Precambrian Broken Hill area. The conclusion is that all depositional – sedimentological and secondary changes must be considered.

Goudie/Pye (1983) offered a good source book for data on chemical precipitates; most geological, chemical and biological variables have been examined in the context of near-surface residual deposits.

Loring (1984) outlined the multi-factorial processes determining the trace-metal composition of a bay.

Butuzova (1984) modelized the environment of the hydrothermal – sedimentary system and mineralization processes of the contemporary Atlantis-II Deep (Figs. 168 and 169). The models illustrate the multiple factors, stages and processes involved in the origin of the metalliferous deposits (see also Hydrothermalism).

Zelenov/Maslov (1984) studied the Black Sea hydrochemistry, e.g., sulfate-reduction and formation of H_2S and sulfide, as controlled for example by bacteria. The observations are compared with several genetic hypotheses.

Walter/Stoffers (1985) outlined the chemical characteristics of metalliferous sediments from the Galapagos Rift and the East Pacific Rise by considering detrital, hydrothermal, biogenous, hydrogenous and residual elements, of which the last four fall into the diagenetic category (see also Hydrothermalism).

MULTI-STAGE

Jackson/Beales (1967) and Beales/Jackson (1968) advocated a multi-factorial and multi-stage approach. They integrated a number of variables involved during the evolution of a sedimentary basin, in developing a genetic hypothesis for the Mississippi Valley-type Pb – Zn Pine Point deposit (Table 66).

Cook (1970) discussed a number of diagenetic replacement stages involving repeated
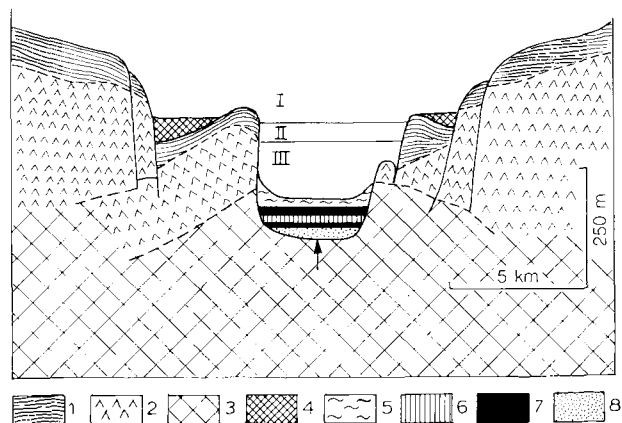
Fig. 168. Schematic cross-section across the southern Atlantis-II Deep: *I* = marine waters; *II* and *III* = upper and lower layers of brine unit, respectively; *1* = Pliocene – Quaternary clay – carbonate rocks; *2* = Miocene evaporites; *3* = oceanic basalts; *4* = oxides; *5 – 8* = zone of metal-bearing sediments (*5* = amorphous silicates; *6* = oxides; *7* = sulfides; *8* = detrital – oxide – pyrite-bearing unit). (After Butuzova, 1984, pt. II.)
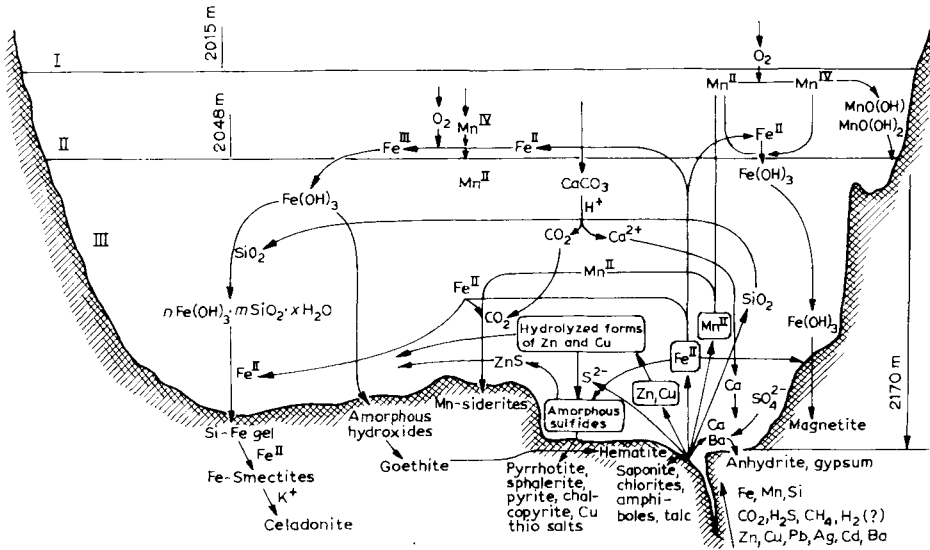
Fig. 169. Diagram of basic mineralizing processes in the Atlantis-II Deep: I = marine water; II and III = upper and lower layers of brine unit, respectively. (After Butuzova, 1984, pt. II.)

TABLE 66

Flow diagram depicting the general factors involved in ore genesis by basinal fluids (expanded after Beales/Jackson, 1968)

COMPACTION				
Source →	Transportation → Concentration →	Release →	Transportation →	Precipitant → Precipitation
Terrigenous rocks undergoing chemical weathering	Adsorption of ions on clay minerals and organic matter	Release of ions into compaction fluids	Fluid movement: rate, direction and distance of migration is controlled by compaction history in combination with basin configuration and other factors	Precipitation is controlled by different geochemical and physical conditions, e.g., by mixing of fluids, change in temperature, and pressure

phosphatization, calcitization and silicification, probably primarily in response to pH changes. He established the following diagenetic paragenetic sequence (the numbers refer to generations): phosphatization (1) → calcification (1) → phosphatization (2) → silicification (1) → phosphatization (3) → silicification (2) → phosphatization (4) → calcification (2) → silicification (3) (see Cook's fig. 3 depicting the textural relationships). Four phosphatization, two calcitization, and three silicification diagenetic replacement stages, therefore, occurred. Less important diagenetic processes were dolomitization, feldspathization, hematization, leaching-cum-oxidation, and fluoridization.

Amstutz/Park (1971) presented a complex paragenetic sequence of ore and gangue minerals. They also discussed textures and structures of the carbonate-hosted Mississippi Valley-type ores and multi-stage diagenesis.

Skripchenko (1972) described numerous chemical changes which occurred during sedimentation – diagenesis – catagenesis in flyschoid sediments (Fig. 170). This resulted in the formation of ore through several stages of segregation, crystallization, and concentration into concretions.

Smirnov (1972) explained the association of syngenetic – diagenetic ores with epigenetic mineralization (Fig. 171). Volcanic – sedimentary rocks accumulated in one part of a marine basin; whereas hydrothermal exhalations, syngenetic – diagenetic carbonaceous – siliceous carbonate rocks, and oxides of Fe and Mn ores were formed elsewhere, associated with pyrite and sphalerite. The ore beds were covered by roof rocks, but the supply of ore-forming hydrothermal solutions con-
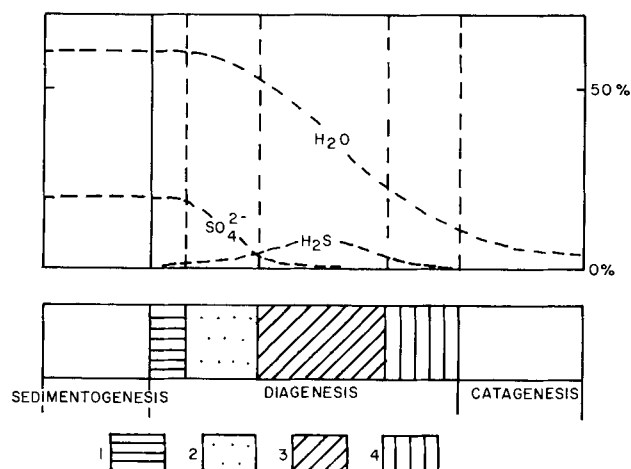
Fig. 170. Diagram of the ore-forming processes in flyschoid rocks. 1 = the earlier sulphate – carbonate mineral formation; 2 = formation of framboidal pyrite; 3 = converting of the non-sulphide lead and zinc salts into the hydrosulphide complexes; 4 = crystallization of the galena – sphalerite ores. The scale in percent only for H_2O. Concentration of SO_4^{2-} and H_2S is approximate. (After Skripchenko, 1972.)

tinued. In the subsurface, these solutions formed the epigenetic barite — sphalerite — galena concentrations.

Gulson (1977) conducted isotopic and geochemical studies of the Woodlawn Pb – Zn – Cu deposit. These investigations indicated that the ore was formed either from solutions associated with the volcanism and/or were derived (leached?) from the volcanics and sediments by circulating seawater. In the latter case, the shallow convective cell originated soon after or during the formation of the sedimentary – volcanic pile. The multi-stage processes effectively homogenized the Pb-isotopes. Diagenetic fluids are probably of lesser importance.

Hanor/Baria (1977) studied the origin of "sedimentary" barite, which formed in a number of different ways over a considerable period of time: (a) During the early diagenetic history of the sediment, as indicated by textures which suggest primary precipitation from seawater; (b) early diagenetic replacement of other minerals by barite; (c) penecontemporaneous (diagenetic – mechanical) reworking and redeposition of barite; and (d) later (late diagenetic?) recrystallization of barite. (See their references to publications providing textural evidence.)

Banas (1980) proposed for the origin of the Kupferschiefer three diagenetic substages: syndiagenetic, anadiagenetic, and catadiagenetic (epidiagenetic). Each substage is characterized by its own structure, texture, and typical chemical elements, compounds, and minerals (Table 67).
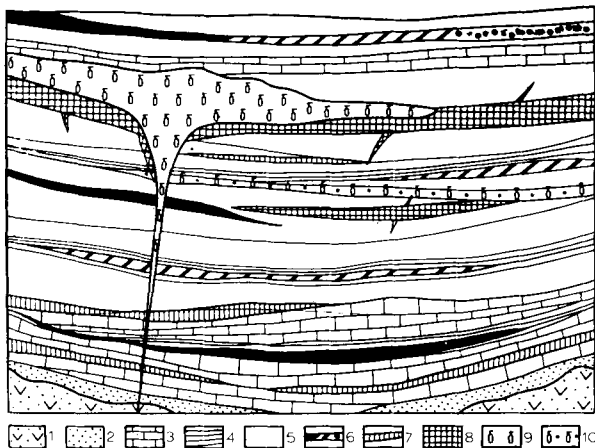
Fig. 171. The relations among syngenetic and epigenetic orebodies at the deposits of Atasu type. *1* = Volcanics; *2* = aleurolite sandstones; *3* = limestones and dolomites; *4* = cherts; *5* = argillaceous – carbonate rocks; *6* = iron, iron – manganese and manganese ores; *7* = sedimented zinc and lead – zinc ores; *8* = metasomatic lead – zinc – barite ores; *9* = barite metasomatites; *10* = barite – sulphidic ores. (After Smirnov, 1972.)

TABLE 67

Genetic assemblages of ore minerals in mineralized Zechstein beds, Fore-Sudetic Monocline, Lower Silesia, Poland (after Banaś, 1980, p. 139)

Stages of mineralization	Syndiagenesis	Anadiagenesis	Catadiagenesis (Epidiagenesis)
Typical structures	Disseminated	Cemented	Secretional
Typical textures	Metacolloidal	Crystalline	Crystalline
Typical elements	Cu, Fe, Pb, Zn	Cu, Ni, Co, As, Sb, Bi, Mo, U	Cu, Ag, Au, Pd, Hg, Ge
Typical compounds	Sulphides	Sulphides Sulphosalts Arsenides Sulphoarsenides	Sulphides Native metals Arsenides Sulphoarsenides
	Chalcocite Bornite Chalcopyrite Pyrite Galena Sphalerite	Chalcocite Djurleite Digenite Bornite Chalcopyrite Tennanite Tetrahedrite Bi-tennanite Zn-tennanite Ag-bornite Enargite Luzonite Stibgluzonite Smaltite – Chloanthite – Skutterudite Rammelsbergite – Safflorite Pararammelsbergite Cobaltite – Gersdorffite Niccolite Carrolite – Siegenite Cattierite – Vaesite Bismuthinite Wittichenite Molybdenite Jordisite Castingite New phases: $CuMoS_3$, $CuMoS_6$, $Cu – Mo – As – S$ Thucholite Uraninite Pyrite Galena Sphalerite Stromeyerite	Chalcocite Digenite Covellite Bornite Idaite Chalcopyrite Tennanite Stromeyerite Cu-stromeyerite Jalpaite Mckinstryite Akanthite Argyodite Morozewycz Pb_3GeS_4 Polkowycz Fe_3GeS_4 Rammelsbergite – Safflorite Cobaltite – Gersdorffite Smaltite – Chloanthite Ag-bismuthinite Au-bismuthinite Ag – Au-tennanite Castangite New phases: $CuMoS_3$ Cu_2MoS_4, $Cu – Mo – As – S$ Niccolite Wittichenite Silver, gold, bismuth Ag-amalgams Palladium Vincentite Pd_3As Majakite Pd/Co, Ni/As New phases: $PdAs_2$, Pd_5As_2, Pd_2As_3 Pd-sulphoarsenides Ag-bornite Au-bornite Pyrite

Minerals

Crick/Muir (1980) studied the uranium deposits of the Pine Creek geosyncline of Australia which originated during a number of stages related to the complex history of carbonates and evaporites: (a) Primary enrichment of U in evaporite sediments; (b) extrusion of U-rich brines during diagenesis; (c) further release of U-rich brines during metamorphism; and (d) possibly still further releases of U-rich brines during post-metamorphic phases. Additionally, evaporitic brines released during stages 2 to 4 scavenged U and other metals from circumjacent sediments and subjacent basement before redepositing them along with the evaporite-derived uranium. The major phase of U-concentration occurred during stage 4, when the evaporites were replaced by magnesite, which was associated with the formation of high-Mg chlorites. Pre- and post-metamorphic diapirs were the consequence of density contrasts between evaporites and sediments. Base-metal mineralization, commonly associated with uranium deposits, may have had a similar origin. In addition, this model may apply to metal concentrations associated with replaced evaporites (see Fig. 172).

DeVoto/Paschis (1980) presented a complex polygenetic history of the
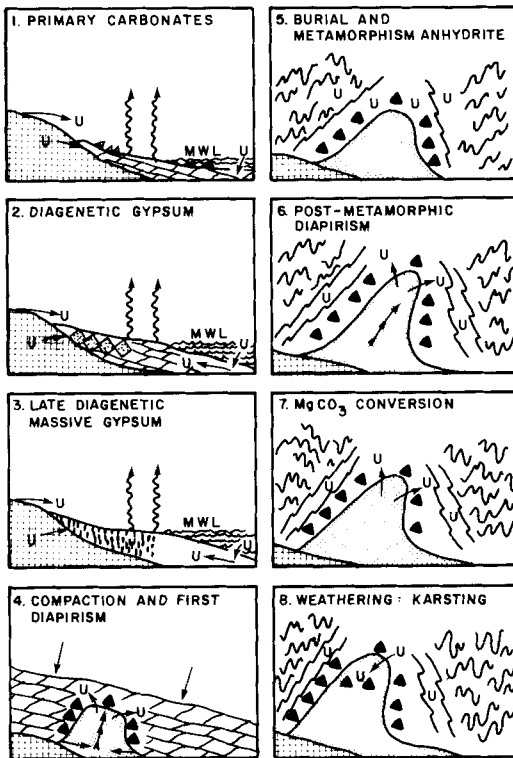
Fig. 172. Stages in the development of the uranium deposits in the Alligator Rivers and Rum Jungle Uranium Fields, Pine Creek Geosyncline, Australia. (After Crick/Muir, 1980, p. 537.)

Schwartzwalder-type uranium vein deposits: (1) An initial syngenetic – diagenetic enrichment of U in marine shales and sandstones; (2) regional metamorphism, heating, and dewatering along pressure-dilation zones with movement of metals in metamorphic – hydrothermal fluids; (3) precipitation of uranium minerals in structures (veins); and (4) local uranium mineralization.

Gustafson/Williams (1981) and Bjørlykke/Sangster (1981), among others, emphasized the multi-factorial and multi-stage origin of the sediment-hosted Pb – Zn – Cu ore deposits, ranging from the syngenetic, through the diagenetic to the epigenetic/catagenetic/metamorphic stages. Many criteria have been discussed (see models in Wolf, 1976b).

Gruszczyk (1982) concluded that the Upper Silesian Zn – Pb deposits are of sedimentary origin, with secondary processes having distorted or obliterated the primary features. During stage I, the disseminated ores formed synchronously with the dolomites; whereas during stage II further concentration of the "primary" ores and secondary alteration of the primary dolomites took place. The following substages have been recognized: syngenesis, diagenesis, epigenesis, catagenesis, and hypergenesis. These deposits must be considered of polygenetic origin.

Ogunyani et al. (1980) outlined the stages of pre-orogenic and synorogenic diagenesis as well as anchimetamorphism (see Metamorphism). Similar studies are to be undertaken on ore hostrocks.

Torres-Ruiz (1983) studied the spatial/temporal evolution ranging from depositional – syngenesis through diagenesis to metamorphism (Fig. 173).

Ratkin/Malakhov (1984) discussed the stages of hydrothermal – sedimentary ore genesis and its relation to vulcanism, including diagenesis, fluid mixing, numerous sources of fluids, etc. (See also Hydrothermalism, and Volcanic – exhalative.)

Chartrand/Brown (1985) unraveled the diagenetic origin of a stratiform Cu-deposit which evolved through several stages as demonstrated by the parageneses of both the hostrock and ore constituents. A sabkha model is proposed comprising compactional diagenesis, for example.

NUCLEATION – NUCLEI

Solomon (1965) is one of the few investigators who discussed the problem of nucleation, accretion, and seeding or a "collector mechanism" that "coalesces" dispersed precipitates into crystalline grains.
    Note: (a) The nucleation/accretion/seeding by both biological and physicochemical methods are important for the whole spectrum of syngenetic – diagenetic – catagenetic – metamorphic – igneous processes. Are the mechanisms the
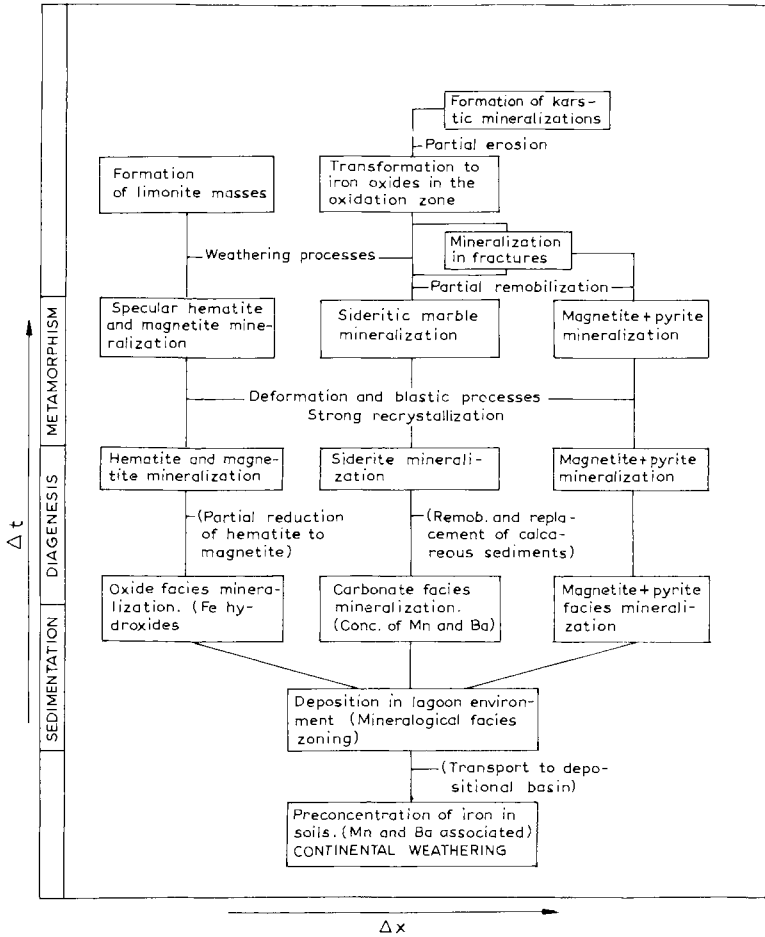
Fig. 173. Spatial and temporal evolution diagram of the Marquesado and adjacent iron ore deposits. (After Torres-Ruiz, 1983.)

same, or do they change according to the conditions of the environment? (b) Sorption (adsorption, absorption, and desorption) is only one "collective mechanism" of importance during diagenesis. (c) What are the precise relationships between nucleation – seeding and "metasomatic" (diagenetic) replacements of, say, pre-ore pyrite by $Cu - Zn - Pb$ sulfides (e.g., Finlow-Bates et al., 1977)?

Spry (1969) offered a general introduction to nucleation in his book on metamorphic textures, and Yariv/Cross (1979) referred occasionally to nucleation applicable to diagenetic systems.

OIL – ORE RELATIONSHIPS

Wolf (1976b) reviewed the origin of hydrocarbons and metalliferous concentrations as part of basin evolution, discussed by many researchers, e.g., Jackson/Beales, 1967; Pospelov, 1969 (see in Wolf, 1976c, pp. 490 – 513, figs. 5 – 2 to 5 – 17, and table 5-VI). There are, for example, many similarities in (1) structural – lithological – stratigraphic controls of ore and oil occurrences of the bedded, stratigraphic, vein, stock, and stringer type traps; (2) lithological screens and traps; (3) fissures as channels and screens for both oil- and metal-carrying solutions; (4) multi-level and pillar-shaped deposits produced during ascending fluid migration, and (5) the migration paths of fluids. In many instances, the genesis of both oil- and metal-bearing waters are believed to be related to the diagenetic – catagenetic – metamorphic evolution of sedimentary basins (see especially Tissot/Welte, 1978, for oil evolution, mentioned below).

Bailey (1977) concluded that hydrogen sulfide and hydrocarbons are formed during early to late diagenetic thermal maturation in sedimentary basins.
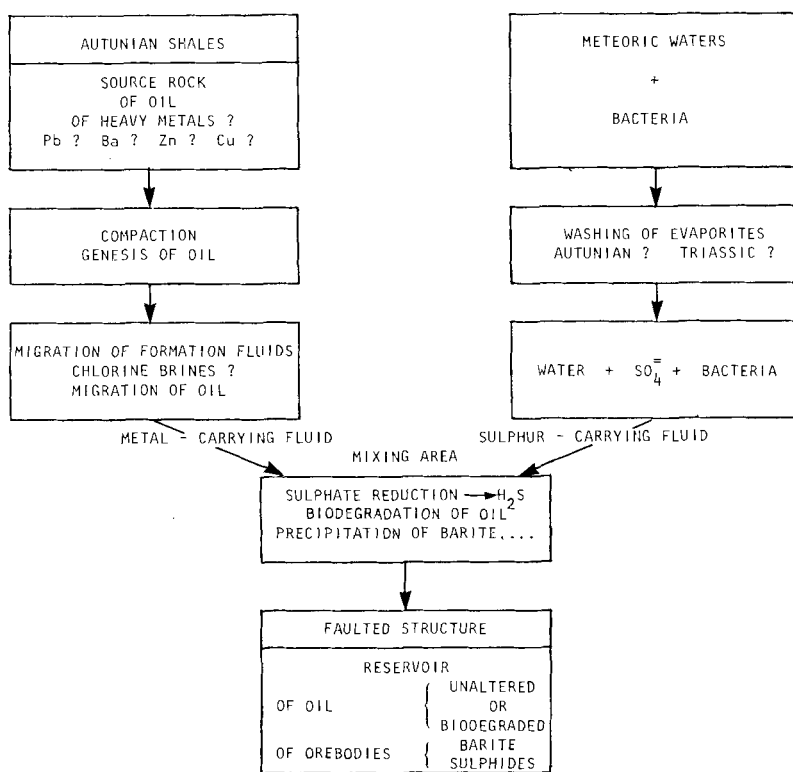
Fig. 174. Genesis of the barite deposit according to models proposed by Beales (1970) and Hitchon (1977). (After Onasick, in Connan, 1977.)

Connan (1977) provided a model for the origin of a barite deposit (with some sulfides), as based on the basin-evolution concept of Beales et al. (1970) and Hitchon (1977), for example (see Fig. 174).

Dunsmore/Shearman (1977) offered the one-brine hypothesis in the origin of the Pb – Zn Mississippi Valley-type ores, in conjunction with oil genesis. (See also Carpenter et al., 1974.)

Hitchon (1977) stated that there are many similarities between oil-hydrocarbon and ore genesis in sedimentary basins (see also Wolf, 1976). He compared geothermal brines (believed to be ore-bearing fluids) with formation waters (see his table 2), and concluded that the deeper, hotter saline basinal fluids, which have leached evaporites to produce solutes (possibly assisted by membrane filtration through clays and shales to enhance the metal content), can act as ore-forming solutions. The source – migration – accumulation scenario for both oil and ore genesis is controlled by temperature, pressure, hydrodynamics and the fluid – rock-interaction continuum in all sedimentary basins. Fluid conduits are very important: the best are reefal or shelf-carbonate fronts close to evaporites and organic-rich muds, and faults.

Tissot/Welte (1978) pointed out that crude oils contain metals, especially Ni and V, ranging from less than 1 up to 1200 ppm V and 150 ppm Ni (Fig. 175). There is a good correlation between metals, sulfur (for a classification of high- and low-S oils, see their fig. IV.2.2), and asphaltene contents. As shown by metal – asphaltene correlation, the degraded oils (which are enriched in asphaltene) contain also more metals, in contrast to the non-degraded oils of similar derivation. Other metals, e.g., Fe, Zn, Cu, Pb, As, Mo, Co, Mn, Cr, etc., have also been reported; however, they have not been systematically studied.

Tissot and Welte offered a diagram showing the occurrence of high- and low-S oils, with respect to the crude oil classification (their fig. IV.2.2), and one depicting the main trends of alteration and thermal maturation of crude oils (their fig. IV.2.3), among many other data modelizing the source, evolution, etc., of organic material in basins, involving diagenetic – catagenetic – metagenetic processes.

Note: If oil and ore are generated during the evolution of sedimentary basins, then the following relationships must be worked out: (a) type of basin → types of fluids produced; (b) stages of basin development → types of fluids evolved or released → types of hydrocarbons formed → metals released; (c) types of clay minerals → stages of basin maturation → metals released; and (d) many other complexities.

Macqueen (1979) in a review of base-metal deposits hosted by sedimentary rocks deliberated on the oil – ore associations and considered burial maturation of basins and the role of organic matter (see also Organic matter). Sverjensky (1984a) proposed oil field brines as ore-formers; Bloch et al. (1983) studied petroleum-related U-organic-rich nodules; Ryabchikov/Novgorodova (1981) considered the effect of reducing fluids in hydrothermal ore genesis (i.e. the association of oil and ores); Simoneit/Lonsdale (1982) mentioned hydrothermal petroleum in mineralized

mounds; Hermann (1961) studied the influence of metalliferous petroleum fluids; Aleksenko et al. (1981) dealt with the behaviour of S during ore genesis in oil and gas fields (as a function of temperature, depth, time and diagenesis/catagenesis); Bein/Amit (1982) described the environment of chert, phosphorite and oil shale and contrasted the diagenesis of these components; whereas Parnell (1983) studied a stromatolite-hosted ore in an oil shale unit.

Gottikh et al. (1980) outlined some trends of uranium accumulation in petroleum, whereas Pen'kov (1981) provided evidence of the generation of U-bitumen from hydrocarbon – water emulsion.
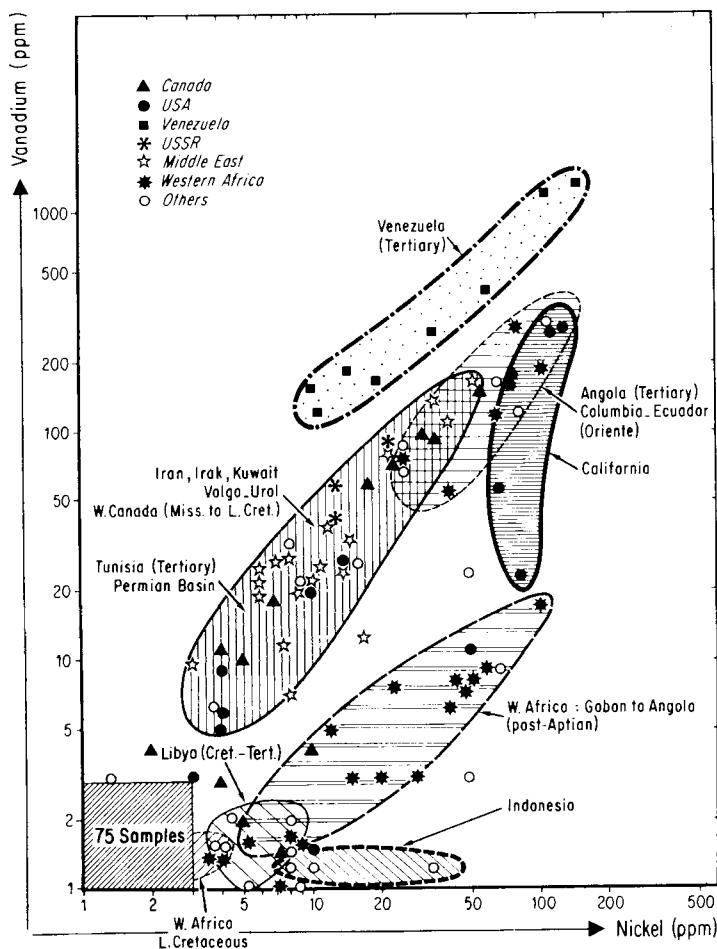
Fig. 175. Vanadium and nickel contents of 175 crude oils of various origins. The shaded area contains 75 crude oils of paraffinic, naphthenic, or paraffinic – naphthenic types from Devonian and Cretaceous of Alberta, Paleozoic of Pennsylvania and Oklahoma, Tertiary of Gulf Coast, Mesozoic and Paleogene of Paris and North Aquitaine basins and from the Rhine Graben and North Sea, Tertiary of Pannonian basin, Paleozoic of Algeria and Libya, Lower Cretaceous of West Africa, Tertiary of Australia, Paleozoic and Mesozoic of Bolivia, etc. (After Tissot/Welte, 1978.)

Sassen (1980) studied the biogradation of crude oil and mineral deposition in a shallow salt dome, whereas Pankina/Mekhtiyev (1983) discussed the genesis of H_2S and CO_2 in hydrocarbons as indicated by isotopes. The H_2S has been mentioned by many researchers to be involved in ore genesis.

Klemme (1980) reviewed petroleum basins and offered a classification of the basins and discussed their characteristics. If it can be proven eventually that there is a genetic relation between oil and ore, and/or the two are associated in time and space, then it seems reasonable to assume that numerous aspects related to hydrocarbons are also applicable to ore deposits in sedimentary basins. If some types of basins have a greater petroleum potential, would they also have a greater potential for metalliferous concentrations?

Chakhmakhchev et al. (1983) described the catagenesis in terms of trace-element composition of oils and bituminoids, including their sources, remobilization, and oil – ore association.

Sakhibgareyev (1983) dealt with the alteration of reservoir rocks along the oil – water contacts. How can this be applied to the genesis of diagenetic – catagenetic types of ore? If the metals of ore deposits are supplied by *aqueous* solutions, then any evidence of a fossil oil – water contact would be important to locate mineralization in cases where the ore is found to be associated with petroleum.

Borovikov et al. (1984) modeled (see their fig. 1) the types of oil and gas traps based on geochemical and geophysical prerequisites. Such traps may be partly identical to those occupied by sediment-hosted ore deposits.

Samarkin (1984) mentioned ore-replacing sulfate minerals and ores associated with oil in their lithologic – geochemical study of Soviet sulfur deposits.

Masse/Perrodon (1984) outlined the subsidence, sedimentation and petroleum systems in the context of basin evolution; Blackbourn (1984) discussed the sedimentary facies variations and reservoirs in continental sediments, offering a predictive model, and concluded that diagenesis was responsible for the reservoir evolution; Ivanov/Shcherban (1982) described the characteristics of oil formation in various types of sediments and their associations; Hunt et al. (1980) mentioned three processes in the genesis of hydrocarbons in marine sediments (how do they affect diagenesis?); North (1979) discussed episodes of source-sediment deposition (these sediments can act as metal-source beds or supply H_2S or saline solutions, for example, thus satisfying some requirements in ore genesis); and Grunan (1983) estimated the abundance of source rocks for oil and gas on a worldwide basis.

   If the compaction and related processes are responsible for the origin of both oil and metalliferous concentrations during basin evolution, then the concepts outlined in the above-listed publications for the origin of hydrocarbons should find application in ore genesis investigations. (Doesn't that sound like a "scientific tautology"?!)

Nalivkin et al. (1984) estimated the destructive processes of oil/gas pools and hydrocarbon loss. The causative geological conditions are given in their table 3. How can such hydrodynamic systems be applied to ore genesis interpretations?

Petukhov/Tikhomirova (1984) demonstrated the influence of hydrocarbon deposits on the formation of superimposed secondary metal mineralization.

Kelly/Nishioka (1985) investigated Precambrian oil inclusions in late-formed veins and the role of hydrocarbons in Cu-mineralization. To what degree could the carbon have been derived from younger overlying source rocks?

Parnell (1985) examined U/REE-enriched hydrocarbons in a sandstone sequence, including nodules rich in organic matter, concretionary-type processes controlled by Eh/pH, and reduction spots in sediments.

Eugster (1985) studied the origin of oil shales, evaporites and ore deposits.

Ellrich et al. (1985) investigated trace elements in crude oils. This is indeed a rare study because many geochemical data of oils do not list metals.

Angier (1985) reviewed briefly the proposal by Cornell University astronomer Thomas Gold who has suggested that large amounts of hydrocarbons "settled in the earth's interior" when our globe originated at the time the primordial gaseous swirl (with carbon as the fourth most abundant element in the solar system) condensed into the sun and its satellites. "Some of these compounds seeped upward into porous rocks and sediments", says Gold, "and became such accessible pockets of riches as the oil fields of the Arabian Peninsula". He predicted that "if greater depths were drilled, fuel reserves far beyond current estimates would be found." In at least one country such deep drilling is under way to test Gold's concept! What does Gold envisage in regard to the origin of hydrothermal fluids, sources of metals and sulfur, and their connection or interrelationships with the hydrocarbons? How can diagenetic studies settle the contradictions?

ORGANIC MATTER

Bolton (1880) (yes, 1880!) reported on the organic acids in minerals; Kizil'shtein (1982) described the contribution of the composition of organics to authigenetic mineralization processes; Volkov/Fomina (1974) discussed the organic matter — sulfide processes and associations in controlling some trace-element distribution; and Creech et al. (1984) treated the formation of CS_2 and OCS from the decomposition of metal sulfides.

Curtis (1966), Pillai et al. (1971), Segar/Pellenbarg (1973), Nissenbaum/Swaine (1976), Calvert/Morris (1978), Premuzic et al. (1982), and D.J. Smith et al. (1983) all studied various aspects of organic matter in sediments and their effects on trace-element association.

Long et al. (1964) studied during hydrocarbon exploration the "geochemical characterization of the depositional environment of ancient sediments through the analysis of evidence left by organic matter during its evolution", e.g., they plotted (from drill data) the regional mean insoluble organic carbon content ($0-1\%$, $1-2\%$, $> 2\%$) and the mean pyrite content ($0-2\%$, $2-4\%$). Thus, they outlined the "reducing facies" and, possibly, the "source-rock" facies? No such similar work is known from the metal-exploration industry.

Curtis (1966) discussed the influence of soluble organic matter in sediments and its effects on trace-element assemblages. He concluded that the trace elements are incorporated via a mechanism largely controlled by the interaction of clay particles with soluble organic matter. There is a positive association of inorganic trace constituents with organic material, which has previously often been attributed to biological concentration and has been explained by Curtis on the basis of purely physical phenomena (e.g., adsorption). The trace elements between the constituent phases of the sediments were probably redistributed during diagenetic alteration (e.g., early sulfide formation), and thus masked early mechanisms of element concentration. The presence of organic films around clay particles affects the ion-exchange capacity of the clay lattice. Syngenetic – diagenetic processes between metallic and other elements, on one hand, and organic matter plus clays, etc., on the other, must be fully understood before, for example, the boron and other elements can be used for paleoenvironmental (e.g., salinity) reconstructions, and before one can recognize potential metal-source beds.

Kranz (1968) studied the participation of organic matter in the transportation of metallic elements in hydrothermal solutions.
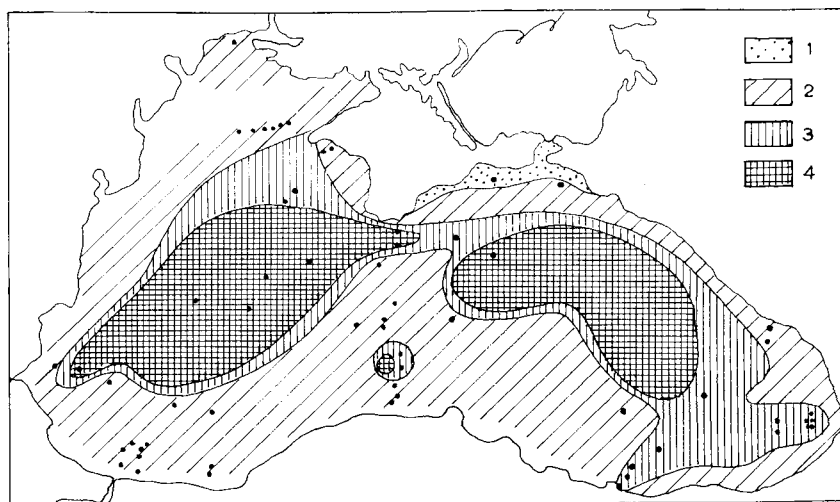
Fig. 176. U (ppm) in non-carbonate matter of the Black Sea. $1 = < 1$; $2 = 1 - 5$; $3 = 5 - 10$; $4 = > 10$. (After Strakhov, 1971.)

Saxby (1969, 1976, 1981, and other papers by him), among numerous additional researchers, reviewed the association of metals with (1) carbonaceous material, (2) metal-organic compounds in living organisms and in sediments, and (3) potential organic metal-binders in sediments. He also studied organic matter in numerous ore deposits and the influence of organic matter in the genesis of metalliferous deposits.

Publications on organic matter ought to be studied in conjunction with those dealing with the bacterial processes in ore genesis.

Strakhov et al. (1967, 1969, 1971, in three volumes) discussed numerous aspects of organic matter as related to lithogenesis of sediments. For example, the distribution of organic matter in the Black Sea and that of pyrite, U, Pb, Zn, Cr, V, Co, Se, O_2, $CaCO_3$, TiO_2, ZrO, Ge, P, Cu, Ni, Mn, Fe, WO_3, MoO_3, and As_2O_3 indicates that the distribution of some elements or compounds corresponds closely to that of the organic matter (e.g., U), whereas other elements do not show that relationship (e.g., Pb, Zn; see Figs. 176–179). There are several "natural diagenetic laboratories", e.g., the Black Sea, Baltic Sea, and Red Sea, where actualistic or contemporary diagenesis occurs.

Kitano et al. (1970) studied the influence of organic matter on the inorganic precipitation of carbonates, including its control on the crystal form (habit) and the distribution of Zn.

Insofar as carbonates have been suggested as the metal source for the Mississippi Valley-type Pb – Zn deposits, more has to be known of the incorporation of metals during the origin of biologically and chemically precipitated calcite, aragonite, dolomite, etc., and the coprecipitation of metals. Kitano et al. found that the body
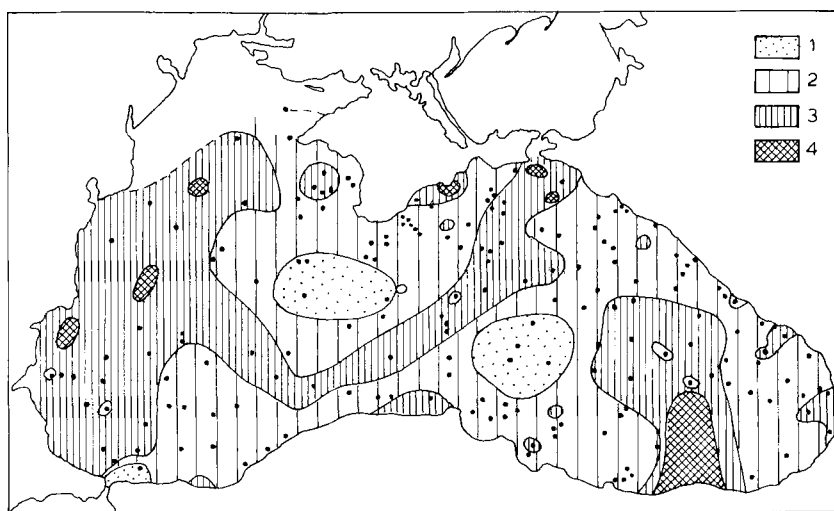
Fig. 177. Pb (ppm) in non-carbonate matter of the Black Sea. $1 = < 20$; $2 = 20-40$; $3 = 40-60$; $4 = > 60$. (After Strakhov, 1971.)

fluids in organisms, not the seawater, control directly the organic/skeletal carbonate type formed. Are only the biochemically formed carbonates potential precursors of metals in contrast to the physicochemically originated ones?

Berner (1971/72) discussed the sulfate reduction, influence of organic matter, etc., in the diagenetic origin of pyrite. He also considered the ocean floor budget, the composition of interstitial fluids, and the pressure versus depth of the intertidal and subtidal sediments.

Rickard (1973) mathematically modelized several variables related to the formation of synsedimentary metal sulfide deposits, namely, simple physical and chemical factors, such as porosity, sedimentation rate, and especially organic carbon concentration. The Black Sea-, Baltic- and fjord-type environments were used as analogues.

Bondarenko (1972) studied the stability of soluble coordination compounds of Cu organic acids; Reuter/Perdue (1977) and Putilina/Varentsov (1980) examined the metal – organic matter interactions in natural waters; whereas Disnar/Trichet (1983) described the influences of algae in the origin of organo-metalliferous complexes (U, Cu, Pb, Ni, Mn, Zn, and Co).

Cloud (1974) discussed the evolution of the ecosystems, whereas Söhnge (1977) outlined the Earth resources of Southern Africa as based on the paleoecology and the paleoecosystems.
    Note: Eventually a correlation ought to be attempted between the four Earth resources' categories; (1) organic fuels; (2) direct precipitates like carbonates, iron, and silica; (3) biogenic residues like bauxite/laterite ; and (4) indirect resources
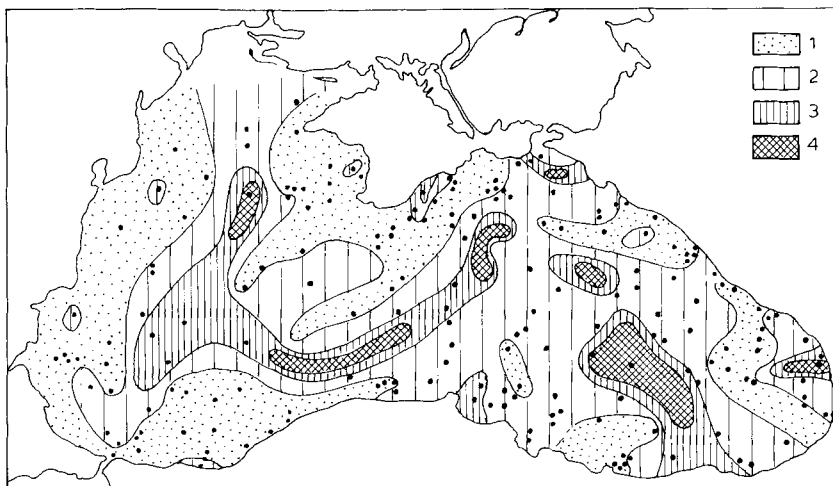
Fig. 178. Zn (ppm) in non-carbonate matter of the Black Sea. *1* = < 100; *2* = 100 – 200; *3* = 200 – 300; *4* = > 300. (After Strakhov, 1971.)

associated with organic-rich sediments, e.g., Au, U, Cu, Pb, Zn, and F. These variables should also be correlated with the evolution of the climate, lithologies, volcanism, ocean and subsurface fluid changes through geologic time, and the changes of diagenetic systems; all of which are complexly interconnected.

Timperley/Allan (1974) studied the metal-dispersion halos in organic-matter-rich lake sediments (e.g., in gyttja). The Cu- and Zn-contents increase with the amount of organic matter in the sediment, and the quantity of interstitial water in the sedi-
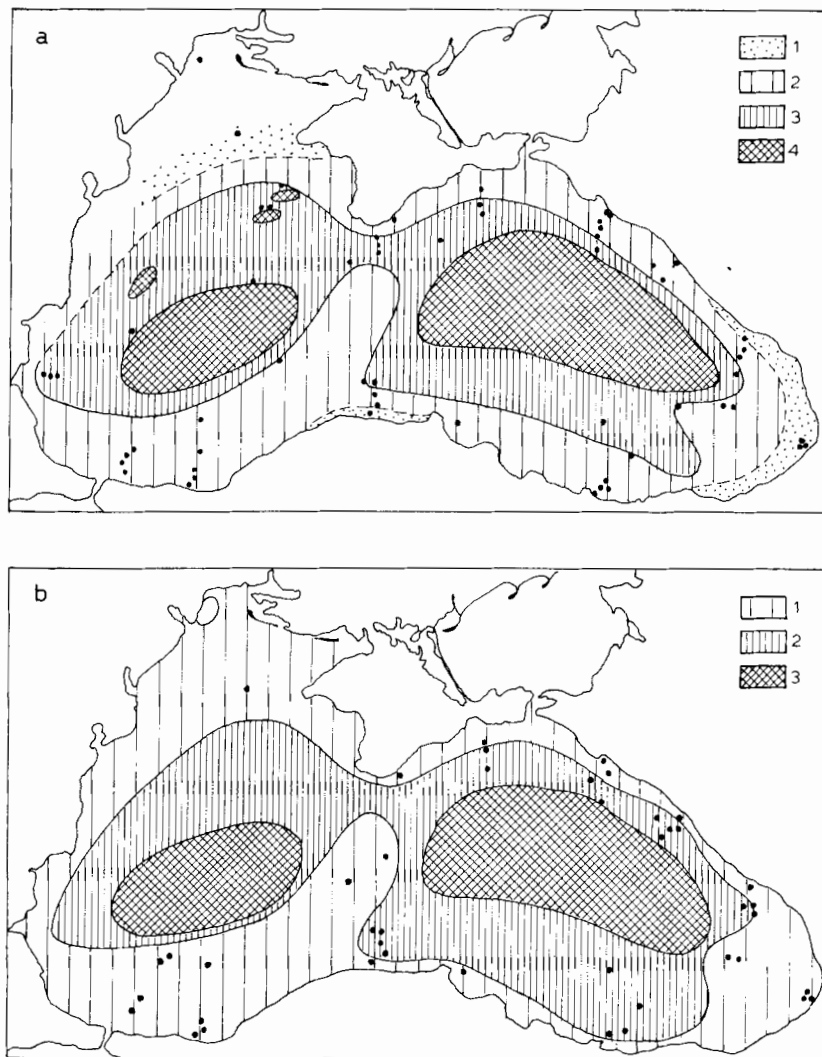
Fig. 179. S_{pyr} (b) and C_{org} (a) in natural sediments of the Black Sea (% in dry sediment). (a) $1 = < 1$; $2 = 1-2$; $3 = 2-4$; $4 = > 4$; (b) $1 = < 1$; $2 = 1-2$; $3 = > 2$. (After Strakhov, 1971.)

ment increases linearly with the organic content. The organic matter is dispersed in the interstitial water. Two major trace-element sources were identified: (1) metals in the lattices of clastic minerals, and (2) metals in the sediments derived from the surrounding water. The latter, chemically dispersed metals are dominated by either organic complexing or by metal-sulfide precipitation. Sulfides precipitated in the order $Cu^{2+} > Pb^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Fe^{2+}$ in contrast to the following order of stability of metal-organic complexes: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Fe^{2+} > Zn^{2+} > Mn^{2+}$. For any metal, the balance between the two models of accumulation is determined largely by the sulfide-ion concentration in an organic-rich sediment.

Note: (a) Although the work by Timperley and co-worker was carried out to assist exploration geochemists in the interpretation of gyttja samples, the results of similar investigations can be useful in understanding diagenesis of euxinic environments. (b) Can finely dispersed *organic-matter-rich* interstitial fluids be pressed out and move into originally "clean" porous sedimentary and/or volcanic rocks to provide the necessary particulate or dissolved organic fraction so often required for ore genesis? In a marine basin environment, oil-bearing formation waters can take up this function. (c) Can the above-cited metals be remobilized to be concentrated into economic deposits as long as organic matter is present? (d) Are there diagenetic processes, e.g., bacterial, that consume totally all the organic matter present and leave the metals as "residues"? In which form would the metals be retained? (e) Coprecipitation, for example, can be studied in lakes more easily than in ocean environments, because of easier accessibility. (f) To what extent are metal-dispersion halos in lakes responsible for diagenetic zoning — or vice versa?

Alberts et al. (1974) described the evolution of Hg mediated by humic acids.

Claypool et al. (1978), Bonham (1980), Meinhold (1977), and many others, studied the organic geochemistry of basins through time and space — the evolution from deposition, through diagenesis, into incipient/burial metamorphism controls the generation of intrastratal fluids and the origin of various types of oil and gas as well as their zonal distribution (e.g., Fig. 180).

Note: If there are relationships between basin development and burial history, maturation of clays and organic matter, evolution of intrastratal fluids, and zonal depth--temperature distribution of oil and gas, on one hand, and between basin development and evolution of ore-forming fluids and metal concentrations, on the other, then the detailed studies done by the oil industry should be applied to ore genesis to provide data on sources of metals and sulfur, on the stage when they are released or mobilized, on the total amount of each available, and on zonation. Can we establish a "rule" (or even a Law) that states: no oil, no sulfur; no clay and no organic-matter transformation, no metals released?

Jackson et al. (1978) presented an up-to-date review of the metals – sediment – water interactions in freshwater bodies, including the role of organic matter. A wide range of topics pertinent to diagenesis are treated: complexing; stability order of complexes of metal ions as influenced by pH, temperature, and type of organic

acids; mixed ligand systems, adsorption – desorption, reactions of organic acids with mineral surfaces, and mineral dissolution; stabilization of Fe, Mn, Hg, U, Mo, V, etc., species; and geochemical dispersion. The information on freshwater systems ought to be compared/contrasted with normal-marine and other types of waters, e.g., saline systems.

Annels (1979) and Garlick (1979) disagreed on the mode of origin of the organic matter that controlled the formation of the Zambian/Rhodesian copper deposits. The former believed that "epigenetic" hydrocarbon-bearing fluids moved into the sandstone hostrock, whereas the latter advocated the importance of "syngenetic" detrital organic matter.

Note: The role of syngenetic, diagenetic and epigenetic/catagenetic types of organic matter and hydrocarbons may be more important than hitherto recognized – the time of availability will influence the time of ore genesis. Wolf (1976) pointed out that clastic/detrital organic matter may have a different distribution pattern and a different diagenetic-cum-metamorphic preservation chance in contrast to catagenetic hydrocarbons originating at different stages during basin evolution. The availability of different types of organic matter varies widely (see Hydrology).

Hallberg et al. (1979) pointed out that when a sulfide-bearing brine comes in contact with a solution of heavy metals (e.g., Cu, Zn) in the *absence* of organic compounds (i.e., in an inorganic system), metals are precipitated and fixed as metal sulfides in a *common* sedimentary layer. When organic compounds are *present*, especially when they serve as nutrients to sulfate-reducing bacteria to create H_2S, the precipitation and fixation of metals are more complex and the Cu and Zn are enrich-
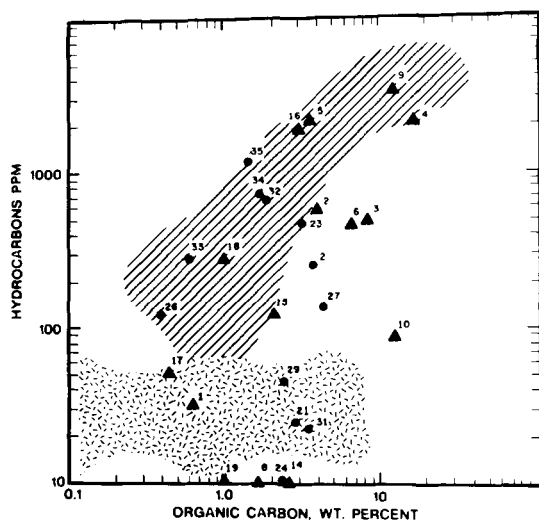
Fig. 180. Hydrocarbon concentration versus organic carbon content in unmetamorphosed and metamorphosed sediments of Phosphoria Formation. (After Claypool et al., 1978.) Triangles = Retort Member; circles = Meade Peak Member; dashed area = unmetamorphosed; and stippled area = metamorphosed.

ed in *different* sedimentary layers. The significance of this and other observations are discussed by Hallberg et al., e.g., the influence of sedimentation rates and zonation.

Holland (1979) discussed the enrichment of metals in black mud or black shale environments. Certain of his conclusions are relevant to ore genesis and source-bed analysis: (1) A definite assessment of trace-element enrichment by organisms is lacking; (2) the concentration of metals in *living* organisms is not large enough to account for the observed enrichment; (3) the concentration of metals in organic-rich sediments owes more to chemical precipitation and to reactions with *dead* organic remains than to their incorporation in living organisms and; (4) sediments like the Kupferschiefer must owe their extreme metal-enrichment to sedimentation in chemically odd basin and/or metal addition after deposition.

Note: (a) Clearly, the investigators only have begun to comprehend the precise chemical processes involved in the direct (e.g., as a sulfide mineral) and indirect (adsorbing – absorbing – desorbing) precipitation of metals, let alone the mechanisms that involve preconcentration – mobilization – transportation – reprecipitation of metals, possible in several cycles. (b) What are the processes of differential – preferential – selective adsorption, for example, on organic matter in contrast to various types of clays? The same query applies to desorption. (c) Also what are the differentiation/fractionation/partitioning processes in organic and inorganic sedimentary systems? These questions remain to be answered.

Carnegie Institution (1980) held a symposium on the "geochemistry of organic matter in ore deposits" which covered a wide spectrum of problems briefly summarized herewith: organic matter controlling ore accumulation and ore-fluid composition, uranium – organic matter associations, microbiological processes concentrating metallic ions, effects on manganese, bacterial leaching, metal – organic associations, organic matter recorded from ore deposits, and role of soluble/insoluble organic matter in ore genesis.

This symposium represents an excellent recent synopsis that permits a quick introduction to further, more detailed publications on the interrelationship among organic matter – diagenesis – ore genesis.

Nagy (1980) proposed that the organic matter (= algal mats) in the Precambrian Witwatersrand Au – U deposits trapped detrital gold. To a lesser degree, the decomposing biochemicals affected crystallization of gold, introduced probably in aqueous colloidal suspensions (see also Pretorius, 1976a, b).

Powell/Macqueen (1980) studied the geochemistry, degree of maturation, distribution, etc., and orebody – organic matter relationships of the Pine Point region. Present data suggests that the latter association is casual rather than genetic. The question of possible reduction of sulfate by reaction with organic matter to produce H_2S and altered bitumen in the barrier complex, is as yet unanswered.

Price (1980) proposed that organic matter was not, or was only slightly, involved

in the origin of the South Texas-type uranium deposits. Pyrite served as a major reductant during ore deposition.

Nash et al. (1981) discussed the origin of syngenetically – diagenetically – epigenetically influenced sandstone-hosted uranium deposits (among others). These sandstone-hosted uranium deposits are divided into two major groups (Table 68) based on the role organic matter could have played during their origin: (a) Deposits with organic matter serving as adsorbant – reductant, and (b) deposits with non-essential organic material.

TABLE 68

Sandstone-type uranium deposits

I. Deposits with organic matter serving as adsorbant – reductant
  A. Uranium deposition in an organic-rich matrix
    1. With syngenetic detrital organic matter
      a. Examples:
        (1) Niger deposits
        (2) Permian sandstones, Europe
        (3) Karoo sandstones, South Africa
        (4) Sandstone of Chinle Formation, Arizona – Utah
        (5) Tallahassee Creek Conglomerate, Colorado
        (6) Basal deposits, Japan
    2. With epigenetic – authigenic organic matter
      a. Examples:
        (1) Permian sandstone (epigenetically enriched), Europe
        (2) Temple Mountain, Utah
        (3) Grants mineral belt, New Mexico

II. Deposits with non-essential organic material
  A. Uranium deposition at a chemical solution gradient (hostrock-solution reaction)
    1. Redox gradient in a single solution – (geo)chemical cell, roll-type deposit, roll-front deposits
      a. Bordered on one side by oxidized rock
        (1) Examples:
          (a) Primary roll-type deposits
          (b) Secondary roll-type deposits (redistributed)
    2. Chemical gradient between two solutions (intersolution reaction)
      a. Bordered on both sides by reduced rock
        (1) Examples:
          (a) Uravan mineral belt
          (b) Entrada belt
  B. Deposition by adsorption of uranium-(VI) from infiltrating solution
    1. Involving iron hydroxides and oxyhydroxides
      a. Examples:
        (1) Cutler Formation
    2. Involving zeolites or clays
      a. Examples:
        (1) Basal deposits, Japan

For original references to these deposits see Nash et al. (1981).

Burke et al. (1981) and Comita et al. (1984) studied, respectively, light hydrocarbons in the Red Sea brines and associated sediments while referring to thermal cracking in a nearby hydrothermal system, and discussed suspended organic matter from hydrothermal vent waters in the ocean.

Bordovskiy/Domanov (1981) studied the decay rate of organic matter during early diagenesis; Jørgensen (1982) examined the role of sulfate reduction in the mineralizing of organic matter; and Mango (1983) tested the diagenesis of carbohydrates by H_2S.

Baturin (1982) discussed the relation between organic matter and the origin of phosphorites. Organic matter supplied organic phosphorus and determined the pH and Eh of the environment, thus causing the precipitation of Ca-phosphate. Perhaps it provides the energy used in forming concretions and the CO_2 produced as a result of the decay of organic matter forms part of the molecule of carbonate – fluorapatite. The organic matter may have also supplied the trace elements incorporated in the phosphate.

During the various stages of the formation of phosphorite concretions (from unconsolidated ooze to dense concretions), the content and composition of organic matter changes systematically in correspondence with the extent of lithification and age of the concretions (Fig. 181). An example of the distribution of organic C is
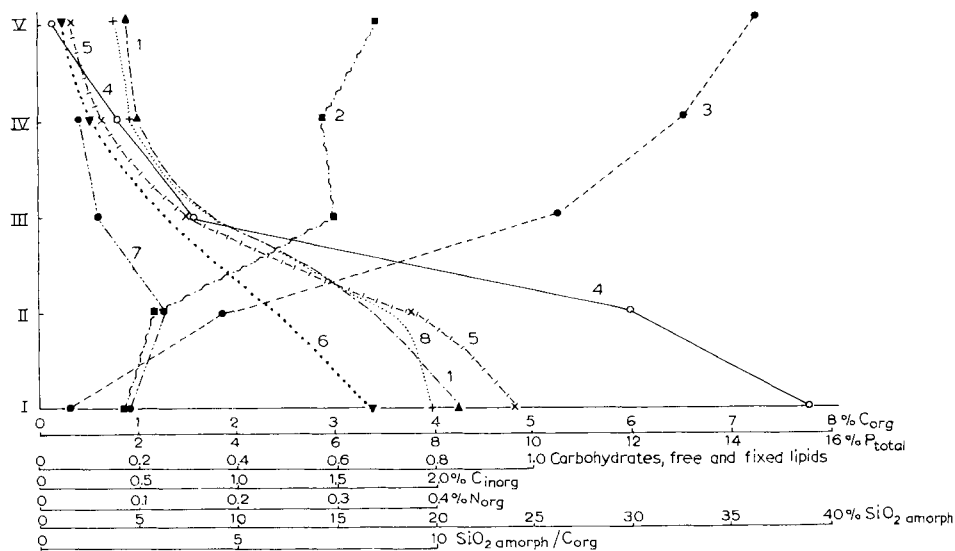
Fig. 181. Evolution of the composition of organic matter in Holocene phosphorite concretions (shelf of southwest Africa) as they lithify. Samples: I = diatomaceous ooze; II = phosphatized ooze; III = unconsolidated concretions; IV = compacted concretions; V = dense concretions. Components: 1 = C_{org}; 2 = C_{inorg}; 3 = P_{total}; 4 = $SiO_{2\ amorph}$; 5 = carbohydrates; 6 = free lipids; 7 = fixed lipids; 8 = N_{org}. (After Baturin, 1982.)

given in Fig. 182. Similar maps are available on numerous Recent oceanic and lacustrine environments; however, little work has been done on correlating carbon with trace-metal distribution in ancient rocks, for example, on a regional scale.

Mackenzie et al. (1982) described the "chemical fossils" and the geologic fate of steroids during diagenesis and catagenesis (at lower and higher temperatures) as modeled in their fig. 3.

Puchkov et al. (1983), like so many others, discussed the effect of organic material on the origin of Pb – Zn ore, but also offered new data on the regional and vertical distribution of organic matter. They unraveled a decrease of the latter from older to younger ore hostrocks.
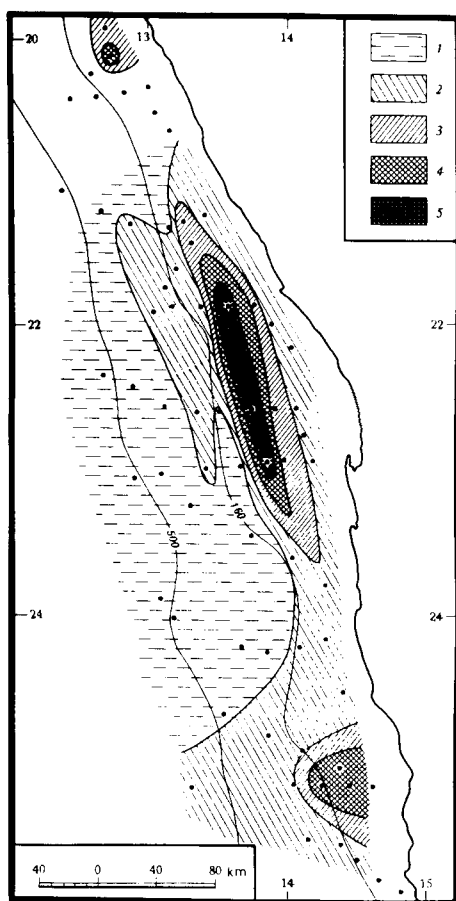
Fig. 182. Distribution of C_{org} in the sediments on the shelf of southwest Africa in the region of Walvis Bay: $1 = < 5$; $2 = 5-10$; $3 = 10-15$; $4 = 15-20$; $5 = > 20\%$. (After Baturin, 1982.)

Ortner et al. (1983) referred to interactive effects of metals and humus on marine phytoplankton carbon uptake.

Laznicka (1985a) summarized comprehensively the geological association of metal elements and ore deposits with coal sequences.

Barnes et al. (1984) reviewed (as part of a series of articles on diagenesis) the chemistry and evolution of organic matter; Gauthier (1984) reported on the relation of organic matter and mineral diagenesis; Singer (1981?) summarized trace metals and metal-organic interactions in natural waters; whereas Duursma/Dawson (1981) offered a book on marine organic chemistry, including the evolution, composition, interactions and chemistry of organic matter in seawater. For a study of ancient rocks, see Schlanger/Cita (1982) who studied the nature and origin of a Cretaceous carbon-rich sedimentary facies.

Simoneit (1984) studied the hydrothermal effects on organic matter, comparing low-with high-temperature components (see his models). Under what conditions are carbon compounds destroyed and thus unavailable for the formation of metalliferous ores, in contrast to those environments that permit the preservation of organic matter which later can engage in the precipitation of metals?

Davidson et al. (1985) determined the implications of C/S ratios in pyrite genesis in freshwater sediments.

Westbroek et al. (1985) investigated the biopolymer-mediated Ca and Mn concentrations in regard to biomineralization, which had occurred on an immense scale resulting in a metal depletion of the surface waters. This mechanism is conducive to the formation of ore deposits. Semasheva/Popov (1984) examined the role of Iofor (= fossil analog of present-day "soluble organic matter in seawater", called SOMS) in ore-creating processes.

Ivankin/Nazarova (1984) discussed carbon-metasomatism and dispersion of metals in sedimentary-metamorphic rocks, whereas Shuguang et al. (1984) studied the graphite in Precambrian BIF, possibly derived from siderite.

Bustin et al. (1985) reviewed "organic diagenesis" (see their quantitative treatment and models), which is, of course, applicable to the study of ore hostrocks as well as to oil-bearing sequences in general.

— See also Complexing (e.g., Turner-Peterson, 1977), and Remobilization.

OSMOSIS

Graf (1982) discussed chemical and reverse-chemical osmosis in the genesis of subsurface brines.

PARAGENESIS

Amstutz/Park (1971) provided the paragenetic sequence of the minerals and numerous sedimentary structures formed during several diagenetic stages in the carbonate hostrocks and the ores of one Mississippi Valley-type district (Fig. 183).

Dimroth (1976) presented an excellent example of textural changes in cherty iron-formations, supported by numerous flow-chart-like conceptual models (see Textures, and Dimroth, 1976).

Diagenetic stages	General*	Pre-burial	Shallow - burial		Deep- burial
	Sandstone*	Redoxomorphic	Locomorphic		Phyllomorphic
	Oolitic limestone	Depositional	Early cement	Intermediate cement	Late cement. (Pre-metamorp.)

Row labels (grains / Oolites / Calcite / Silica SiO₂):
Nuclei; Micrite rings; Erosion and Deformation; Dissolution and Recrystallization; Dog-tooth; Drusy mosaic; Dissolution and Recrystallization; Dolomite - CaMg(CO₃)₂; Chalcedony; Quartz; Sphalerite - ZnS; Pyrite - FeS₂; Bravoite - FeNiS₂; Chalcopyrite - CuFeS₂; Galena - PbS; Fluorite - CaF₂; Strontianite - SrCO₃; Witherite - BaCO₃; Barite - BaSO₄

Sedimentary structures and processes:
Submarine erosion; Slump-'Cut-and-fill'; Intraformational brecciation; Tension fracture; Fault; Geod - Vug; Cementation; Pressure solution; Stylolite formation; Porosity** shale / limestone

Porosity values: shale ~85%, ~60%, ~30%, ~5%; limestone ~85%, ~40%, ~10-5%

Fig. 183. Paragenetic sequence of the minerals and of the various sedimentary structures during the various stages of diagenesis found in the carbonate hostrocks and the ore-bearing rocks from the Cave-in-Rock fluorite district, Illinois, U.S.A. The thicker portion of a bar indicates the main stage of formation, whereas the initial and final stages are shown by the thinning of a bar. *Subdivision of diagenetic stages were proposed by Dapples (1959, 1962). **Porosity values for shale are after Müller (1967). (After Amstutz/Park, 1971.)

Hagni (1976) offered a paragenetic diagram (see his fig. 3) of the Tri-State Zn – Pb district (see also Kyle, 1981, fig. 44).

Jung/Knitzschke (1976), among others, discussed the ten types of parageneses and the "evolution" of the Kupferschiefer ore minerals and their elements (see their figs. 6, 13 and 15).

Rastad et al. (1980) described four stratabound Pb – Zn (Ba – Cu) deposits that are part of a Cretaceous transgressive series comprising very shallow-water dolomites formed in a tidal milieu: (a) Black, algal laminated siltstone to dolomitic siltstone (intertidal?), with sphalerite, galena, and some barite; pyrite is very abundant; (b) black algal laminated dolomite, with some chert lenses (intertidal), with sphalerite, galena, and minor barite; pyrite is very abundant; (c) collapsed, brown, gypsum-bearing dolomite (supratidal) with smithsonite, barite, and Fe-oxides (no pyrite); and (d) dark grey rudist dolomite (subtidal), with sphalerite and galena; pyrite is not abundant. In each of these four ore horizons, the diagenetic crystallization sequences and textures demonstrate that sphalerite, galena, barite, and smithsonite
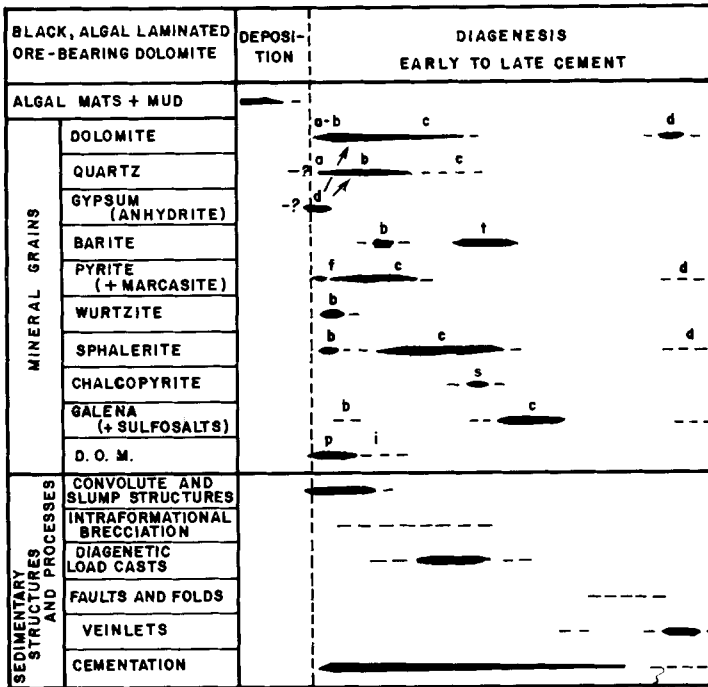
Fig. 184. Schematic paragenetic sequence of the minerals and of sedimentary structures during diagenesis in the main ore-bearing black, algal, laminated dolomite facies. (After Rastad et al., 1980.) a = Aphanocrystalline; b = very fine to fine crystalline; c = medium crystalline; d = coarsely crystalline; f = very fine to fine crystalline, often with framboids; i = inclusions in grains; p = in intergrain spaces; s = inclusions in sphalerite; t = medium to coarse tabular crystals. Arrows indicate diagenetic replacement. $D.O.M.$ = disseminated organic matter.

are also diagenetic (= rock-forming) minerals, like the gangue minerals dolomite and quartz. Four paragenetic sequences have been established (see their figs. 5 – 7 and Figs. 184 and 185 presented here).

Vaughan/Ixer (1980) presented a detailed "comparative parageneses" study done on several Pb – Zn – Ba – F (M.V.-type) ore districts. They established differences and similarities, and a "sequence of precipitation of elements from ore fluids". It was concluded that there was a systematic change in ore-fluid composition or in the sequence of precipitation (see Table 69), as reflected in both ore and gangue minerals. The ore-forming fluids were at least partly of magmatic origin. Some believe that "hydrothermal" (non-magmatic?) solutions were responsible for the M.V.-type ores.

Amstutz/Fontbonté (1982) studied a large number of stratabound Pb – Zn – (F – Ba) deposits showing a striking similarity as to five controlling factors: paleogeography, hostrock lithology, geometric characteristics of the ore bodies, ore
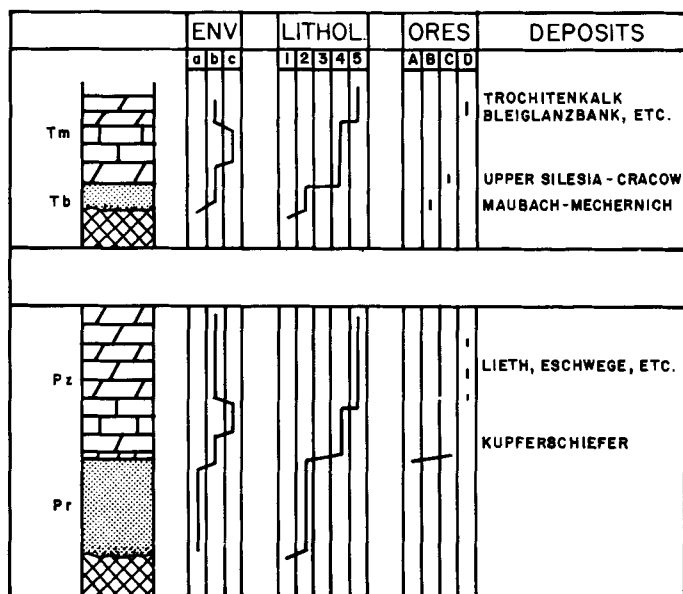
Fig. 185. Comparison between lithology of the country rock and ore paragenesis of the stratabound deposits occurring in the Rotliegendes – Zechstein and Buntsandstein – Muschelkalk transgressive sequences in Central Europe. A parallel evolution in the course of decreasing complexity of the composition of the country rock and of the ores can be observed. Such an evolution in the composition of the ores outlines a clear "sedimentologic ore zonation", which is perfectly congruent with the sedimentologic evolution of the basin in itself. Similar "sedimentologic ore zonation" can be recognized in many other stratabound belts occurring in transgressive sequences. (After Amstutz/Fontboté, 1982.) *Pr* = Rotliegendes, *Pz* = Zechstein, *Tb* = Buntsandstein, *Tm* = Muschelkalk. Environment: *a* = continental, *b* = marine peritidal, *c* = marine relatively deeper. Lithology: 1 = conglomerate, 2 = sandstone, 3 = marls, 4 = carbonate rocks, in part dolomites, 5 = dolomite and/or evaporites. Ore paragenesis: A = (U –) Cu – (Pb – Zn – Ni – Co – Ag), B = Pb – Zn – Cu – (Ni – Co), C = Zn – Pb – (Cu), D = Zn – Pb – (F – Ba), F – (Ba – Zn – Pb) or Ba – (F – Zn – Pb).

328

composition including sedimentary ore zonation, and diagenetic evolution. The semi-holistic interpretation indicated that the diagenetic history of the ores occurred in two phases: (a) "Diagenetically *open* system" when ore accumulated, followed by (b) "diagenetically *partly closed* system" when crystallization of the sediment constituents, including the ore matter, took place. A process of differentiation by "diagenetic crystallization – fractionation" can be recognized in many cases.

The geometric congruency of the ore with the enclosing sediment is too great and the ore bodies are too closely linked to specific paleogeographic (environmental) facies to allow a genesis by migrating brines, at least not on a scale larger than the individual lithologic units and not after the complete lithification of the sediment. The ore-forming process must be a *surface-linked mechanism,* i.e., the ore precipitation occurred probably within the first millimeter-to-decimeters (in some cases up to a few meters) of burial.

Milliken et al. (1981) investigated the history of burial diagenesis reflected in the isotopic geochemistry. Among others, they discussed multiple factors and unraveled passive and active diagenesis, temperature-gradient zones, depth of formation, and elemental pathways.

Timofeyeva (1983) reported on quantitative paragenetic relations, silicate vs. sulfide vs. carbonate iron minerals of authigenetic and diagenetic origins within humid-climate silt – clay sediments.

pH

Tischendorf/Ungethüm (1965) provided, among many other data, Fig. 185 illustrating the dependence of the composition of siderite (i.e., the MgO-content) on pH.

TABLE 69

Sequences of precipitation of elements from ore fluids as shown by paragenetic studies of various Pennine orefields (Vaughan/Ixer, 1980)

Orefield	Sequence of precipitation of elements from ore fluids				
South Pennines	Fe	→ Ni (Co)	→ Cu	→ Pb	→ Zn
	S	→ S	→ S	→ S	→ S
Askrigg	Fe	→ Ni (Co)	→ Cu	→ Pb	→ Zn
	S	→ S	→ S (Sb/As)	→ S	→ S
Alston	Fe	→ Ni/Co	→ Cu (Ag)	→ Pb	→ Zn
	S (As)	→ S/As (Sb)	→ S/Sb (As)	→ S (Sb/Bi)	→ S

Note: More experiments, however, are required to establish the dependence of trace, minor and major elements in mineral lattices on pH, Eh, etc., both at lower and higher pressures and temperatures.

Perel'man (1967) offered much information on pH – Eh-controlled processes related to ore genesis, including diagenesis. Spencer et al. (1968) concluded that pH is only one of many variables that not independently, but in inter-reactions, controls the distribution of elements in sediments. Figure 187 shows the pH in upper layers of Recent sediments (see also Fig. 188). MacIntyre (1970) described two mechanisms controlling the pH in the ocean (Fig. 188), whereas Rösler/Lange (1972) presented the useful Table 70 depicting the pH of waters and sediments.
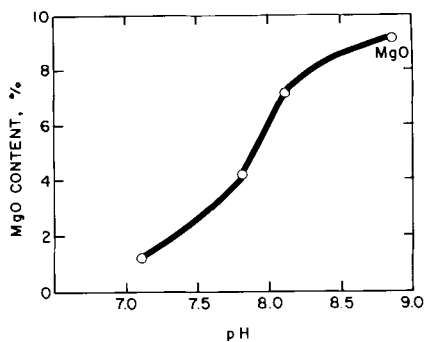
Fig. 186. The pH-characteristic of siderites depending on their MgO-content. (After Tischendorf/Ungethüm, 1965.)
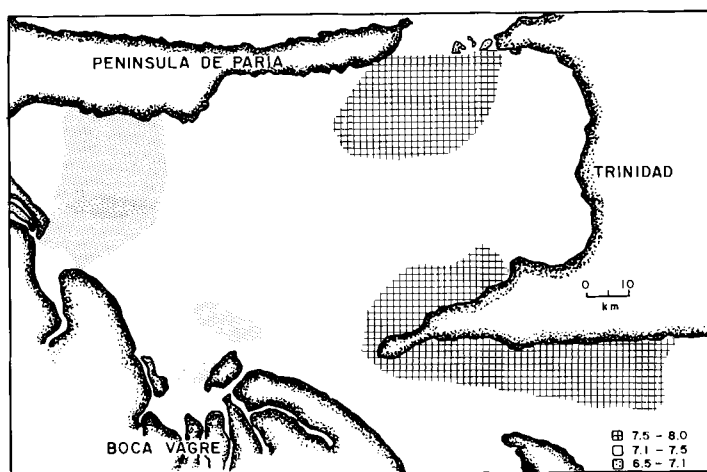
Fig. 187. Map of pH in upper layer of sediments. (After Spencer et al., 1968.)

Zirino/Yamamoto (1972) offered a pH-dependent model of Cu, Zn, Cd and Pb chemical speciation in seawater. Ben-Yaakov (1973) studied the pH-buffering of pore water in anoxic marine sediments. Khalid et al. (1978) discussed the pH/Eh influence on the chemical transformations of Cd and Zn in river sediments.

Goleva (1980) evaluated hydrogeochemical exploration methods. The various metal compounds/complexes, which formed during supergenesis, were plotted on the pH – Eh diagram (Fig. 189) to indicate the strongly acidic-weakly acidic and alkaline, and oxidizing and reducing environments of migration of these complexes. These supergene "remobilization" conditions ought to be compared/contrasted with the original milieus of syngenetic – diagenetic – epigenetic/catagenetic solutions that formed the ore (see Hydrology, and Eh).

TABLE 70

pH values in natural waters and sediments (combined on the basis of data from Saukov, 1953, Rankama-Sahama, 1949, and information from Wünsche, Freiberg; after Rösler/Lange, 1972)

pH Value	Types of waters and sediments
0	Sulphuric acid waters in desert soils
	Crater lakes
1	
	Waters in alum shale open pits (in dry seasons) — acid thermal waters
2	in open pits of disseminated copper ores and in quarries
3	of sediments containing pyrite — soft brown coal — mine drainage
	Marshy waters, peat waters, waters in peaty meadows
4	
	Waters in brown-coal — soils on gneiss, porphyry, granite, sandstone
5	open-cast mines — Tertiary sands — loess soils
	Rainwater
6	Sea and river water — wells in calcareous regions — normal arable soils — soils on basalts and diabases
7	Seawater of the type of the Black Sea (at a depth of 1000 m)
8	Sea and river water — seawater (surface) — boulder clay — Pleistocene clay in calcareous regions
9	Basic subsoil water
10	Waters in arid alkaline soils
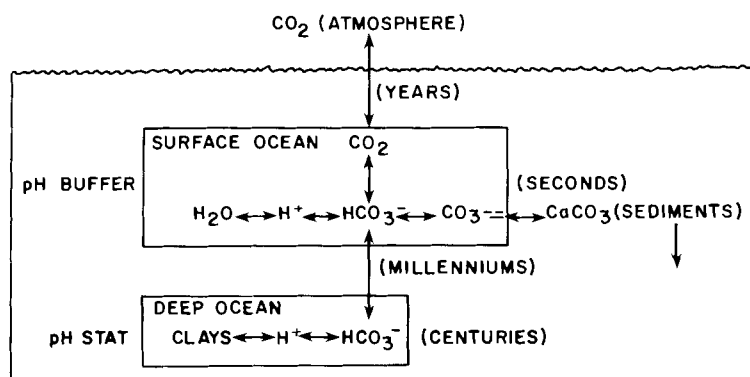
Fig. 188. Hydrogen-ion concentration, or pH, of the ocean is controlled by two mechanisms, one that responds swiftly and one that takes centuries. The first, the "pH-buffer", operates near the surface and maintains equilibrium among carbon dioxide, bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}) and sediments. The slower mechanism, the "pH-stat", seems to exert ultimate control over pH; it involves the interaction of bicarbonate ions and protons (H^+) with clays. Clays will accept protons in exchange for sodium ions (primarily). (After MacIntyre, 1970.)

Sakharova et al. (1981) studied the pH effect on Au and Ag precipitation from aqueous solutions, whereas Shmariovich et al. (1982) tested the control of pH changes during primary uraninite genesis.

Turner et al. (1981) studied the equilibrium speciation of many dissolved components (Fig. 190; see Thermodynamics) and modeled the metals' behaviour in freshwater and seawater at varying pH/Eh conditions (see Complexing).

Lewan/Maynard (1982) offered excellent Eh – pH diagrams approximating the stability field for at least ten metal elements (Fig. 191) applicable to diagenetic low-temperature and low-pressure environments (see also Eh and Concentration).

Nealson (1982, in Holland/Schidlowski, 1982) described the iron bacteria (i.e., biologically active Fe-binding and Fe-transporting bacteria); some are acid (2 – 4) or neutral (6 – 8) pH types.

Boles/Johnson (1983) discussed mica surfaces influencing pore-water pH during early to late diagenesis and compaction, which in turn determines the origin of mineral associations, paragenesis, etc.

Birnbaum/Wireman (1984) described bacterial reduction in terms of pH which has numerous implications for early diagenesis.

Dickson (1984) described pH-scales and proton-transfer reactions in saline media, such as seawater.

Somina (1984) depicted the "position of altered rocks" (i.e., the horizontal and vertical zoning) as controlled by pH of the ore-forming solutions, time and facies (see his fig. 3). Can similar models be established for diagenetic – catagenetic ores?

– See also Eh (for Eh – pH relations), and Solubility.

PHOSPHATES – PHOSPHORITES

Baturin (1982) and the publication by the Geological Society of London (1980) summarized the phosphorite deposits with discussions on diagenesis. For those in-
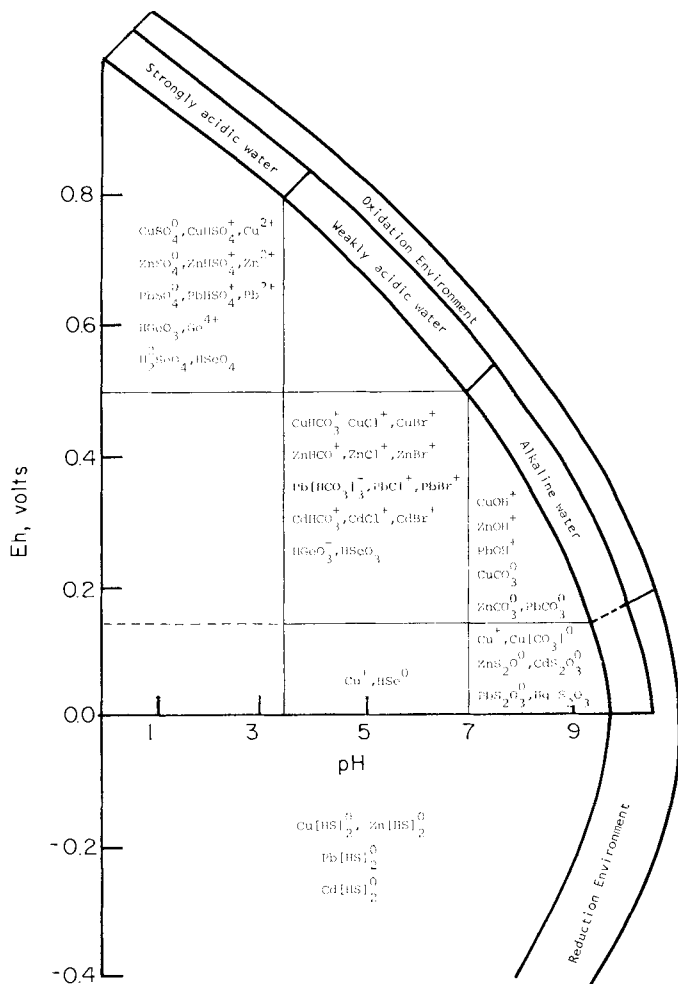
Fig. 189. Diagram depicting the form of migration of the most important indicator elements in natural waters under different Eh – pH conditions. (After Goleva, 1980.)

terested in the complex interrelationships of many factors, ranging in scale from global and regional to the local and microscopic, the study of the phosphorites offers indeed a rare opportunity because just about all sedimentological – environmental principles have been utilized to explain (what is in the final analysis a very local diagenetic mechanism) the origin of phosphate grains. The following disciplines and concepts have been employed: oceanography, climate, hydrodynamics, paleotopography, upwelling, eustatic/tectonic changes, transgressions and regressions, cyclicity, changes in latitudes and thus plate tectonics-cum-continental drift, Eh/pH, water depth, temperature and pressure conditions, salinity, etc. Consult Riggs (1984) and Cook/Shergold (1984) for recent discussions on phosphate diagenesis.
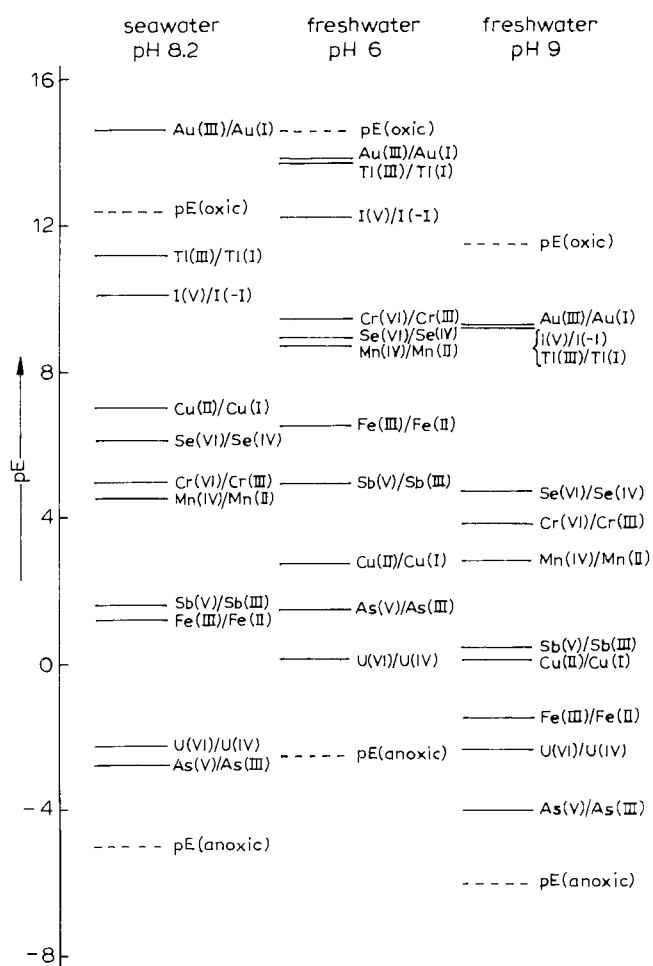
Fig. 190. Calculated values of pE_{eq} for trace elements with potentially variable oxidation states in model seawater and freshwater. pE_{eq} = redox level at which the oxidized and reduced forms of elements are present at equal concentrations (see p. 859 in Turner et al., 1981; see also their table 1.)
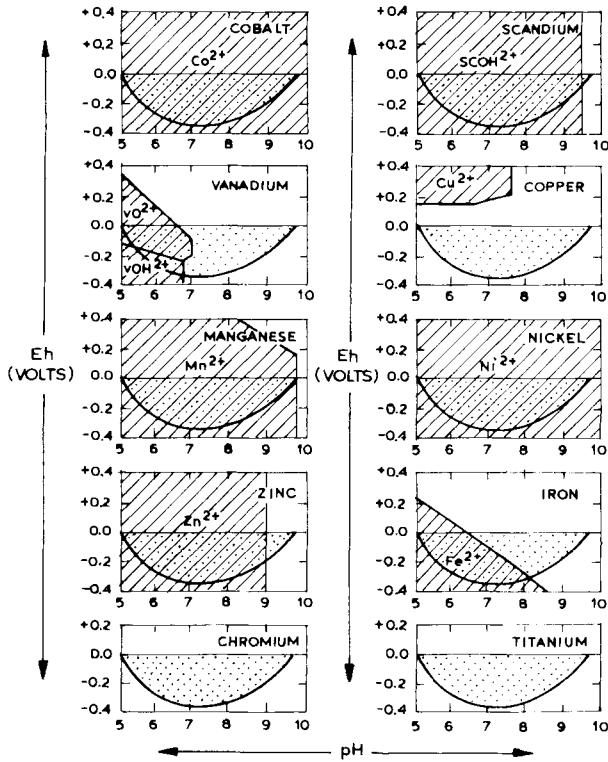
Fig. 191. Eh - pH diagrams showing approximate stability field for tetrapyrrole preservation (stippled area) and stability field for bivalent cations of the first transition-series of elements (hatched area). Diagrams were constructed from thermodynamic data compiled by Garrels/Christ (1965) at 25°C and 1 atm. Total metal concentrations are equal to those reported by Goldberg (1961) for average seawater. (After Lewan/Maynard, 1982; see for original sources.)

McArthur (1985) reviewed the francolite geochemistry and its compositional controls during formation of phosphate, including its diagenesis, metamorphism and weathering or supergenesis. See also Yonkang (1981) for some mineralogical characteristics of fluorapatite in different genetic types of phosphate deposits.

Krom/Berner (1981) and Filipek/Owen (1981) specifically referred to the diagenetic controls of phosphate in nearshore and outer shelf marine sediments. Moody et al. (1981) provided data on long-term P-flux to deep-sea sediments.

Burnett et al. (1982) discussed the growth rates of P-nodules from a continental margin off Peru, whereas McArthur (1983) reappraised the age and genesis (formed not authigenically but by the phosphatization of earlier carbonates).

Berge/Jack (1982) provided a study of one of the many ancient phosphorite deposits known on several continents, in contrast to the more restricted younger oceanic occurrences.

Israili/Khan (1980), Tambiyev/Baturin (1981), and Rasmy/Basily (1983), among others, studied the trace elements in phosphorites (or in associated black shales). Many metallic and non-metallic elements have been reported as concentrations in phosphate minerals or particles (e.g., pellets or oolites), some of which, like uranium, may be of economic interest.

Bol'shov (1979), Starinsky et al. (1982) and Avital et al. (1983) investigated the U and Th; Tambiyev (1981) the B; Roe et al. (1982) the protactinium (offering a model on the geothermal pathways between water, nodules and associated sediments in a coastal upwelling zone); and McArthur/Walsh (1984/85) the REE content of phosphorites. The latter authors discussed the early diagenesis, deep-burial diagenesis, remobilization, and differentiation/fractionation of elements (e.g., P) from surface, ground and formation waters.

Aharon/Veeh (1984) and Shemesh et al. (1983), respectively, studied the isotopic variation of insular atoll phosphatization, and the O-isotopic variations in phosphate of biogenic apatites. They concluded that the isotopes must be used with great caution in environmental and genetic interpretations.

O'Brien et al. (1981) and Soudry/Champetier (1983) described the bacterial origin of continental margin phosphorites and the microbial processes of an ancient phosphate accumulation.

Sandstrom (1980) opined on the organic geochemistry of some Cambrian phosphorites, whereas Waples (1982) discussed the significance of P-rich sedimentary rocks in relation to organic-rich and petroleum facies, including topics of importance in exploration.

Manning/Jones (1982) provided data on the binding capacity of ferric hydroxide for non-apatite inorganic phosphorus in lakes.

Ten Have et al. (1982) described the alterations of guano-type phosphates.

Pacey (1985) modeled the origin of pelletal apatite/phosphates, depicting numerous variables, including upwelling (Fig. 192).

— See also Glauconites.

PHOTOCHEMISTRY

Cooper/Zika (1983) discussed the photochemical formation of hydrogen peroxide in surface and ground waters exposed to sunlight, whereas Schidlowski (1984) described the early atmosphere oxygen levels and their constraints from Archean photoautotrophy. How much information is available on "photochemical diagenesis"? Are photo- and electrochemical processes independent of each other, depending on the specific natural conditions?

Water surface

Planktonic algae (coccolithophorids) enrich PO_4^{3-} & biophilic trace elements (I, Br etc.) from upwelling waters

Input of nutrient rich upwelling waters from proto-Atlantic Ocean to S.W. of shelf area

Grazing of coccolithophorids by copepods. Further enrichment of trace element levels

Biogenic debris consisting of dead fish & plankton, faecal pellets of fish etc. Delivered to cuvette areas by fallout through water column. Adsorption processes lead to further uptake of PO_4^{3-} & trace elements

Uptake of plankton by higher trophic levels (fish & other nekton)

Periodic concentration of plankton by winds & currents, so leading to Red Tide events. Resulting masses of biogenic debris delivered to cuvette areas by downwelling

Unique fauna of benthonic feeding worms & crustaceans. Coprophagy results in extensive reprocessing of biogenic debris from overlying water column so leading to further enrichment of trace element levels in final generation faecal pellets

Chalk ooze

Erosional cuvette formed in Chalk ooze by frontal eddy system in overlying water column. Eddy also produces closed biological & chemical environment within cuvette area

Breakdown of organic matter within sediment by mainly SO_4^{2-} reducing bacteria. Increase in free inorganic PO_4^{3-} levels followed by replacement of calcite by phosphate precursors of apatite e.g. struvite

Thick blanket of faecal debris undergoing phosphatisation

Uptake of F^- & CO_3^{2-} results in conversion of precursors to carbonate-fluorapatite This then takes up U, Sr & R.E.E. Adsorption of other trace elements by humic acids

Fig. 192. Box diagram summarizing the main oceanographic, biogenic and inorganic chemical processes responsible for the formation of concentrated deposits of pelletal apatite in the chalk. (After Pacey, 1985.)

Krumbein (1983b) offered an interesting, important overview of stromatolites and their evolution in space and time. He also discussed the *"energy source"*, electron donor, and carbon source for microbial communities; one of the energy sources is light. To what extent is photochemical diagenesis controlled by microorganisms?

POLLUTION

Förstner/Wittman (1981) offered an excellent comprehensive review of metal pollution in the aquatic environment. Why list data on pollution in a treatment of diagenesis? In the cited book, for example, there are dozens of references on numerous topics that have a direct bearing on diagenesis. True, the studies are related to man-caused (pollution) systems, but the mechanisms of inorganic and organic adsorption/desorption, element mobility, etc., are of use to diageneticists. Additionally, geochemical sedimentologists who are studying contemporary sediments must always consider the possibility of pollution and the exploration geochemists must likewise take into account such contaminations and decide on techniques to discriminate the natural geochemical background and anomalies from the anthropogenic metal pollution.

Jedwab (1980) described rare anthropogenic and natural particles suspended in deep ocean waters, providing a long list of metals classified according to mode of derivation or origin.

Wijbenga/Hutzinger (1984) reviewed the interconnection between man, chemicals and the environment in their historic perspective of pollution and related matters.

Fisher et al. (1982) reported on a downcore variation in sedimentary organic nitrogen and contrasted anthropogenically influenced with pre-cultural factors that controlled diagenesis.

Irion (1984) studied the heavy metal pollution of surface sediments of the Baltic Sea; Thornton/Seyfried (1983) investigated the thermodiffusional transport of pelagic clay as an implication for nuclear waste disposal in geological media — the data is also applicable to diagenetic studies; Ferguson et al. (1983b) described the heavy-metal enrichments, bacterial sulfate reduction and iron sulfide genesis in an Australian shallow-water carbonate deposit present offshore from a smelting complex; and Taylor (1976) outlined the heavy-metal distribution in a polluted estuarine sediment.

Müller et al. (1983) determined the chronology of anthropogenic heavy metals in a lake.

Frape/Fritz (1982) examined the chemistry and isotopic composition of a polluted saline groundwater brine in crystalline rocks.

POROSITY – PERMEABILITY

Motts (1968) provided data on the regional porosity – permeability variations in a limestone – dolomite – evaporite – sandstone, shelf – reef – basin facies, which control the present hydrology (Fig. 193).

Note: (a) To what extent can ancient hydrologic systems be unravelled to understand the regional, lithology – environment-controlled diagenesis? (b) How can "primary" hydrologic systems be distinguished from the "secondary" superimposed systems? (c) Are all the paleokarst systems formed by *surface and near-surface* hydrologic systems? (d) Do certain primary porosity – permeability zones control specific types of karsts, and how do they influence ore localization? In other words, how in general can one distinguish between karst types that are likely to contain ore versus those that do not? (e) How can one establish the time of the formation of hydrologic systems?

Blanche/Whitaker (1978) offered a detailed reconstruction of sandstone diagenesis as related to the original lithology (grain size and shape, mineralogy, primary porosity, ± organic matter), subsequent burial history (including temperature), and pH-increase of circulating pore solutions. Diagenetic products include calcite, , quartz, kaolinite, illite, dolomite, siderite, and pyrite. Their formation resulted in the loss of porosity and a drastic permeability reduction.

Note: Similar detailed studies are required on sandstone – hostrocks of ores to determine pre-ore, syn-ore, and post-ore changes, including the *preparation* of hostrocks for mineralization, e.g., the origin of early diagenetic pyrite which is later replaced by, say catagenetic, Cu-minerals.

De Boer (1976) provided data on the variation in porosity with time, pressure, temperature of solutions, etc. (Fig. 194).

Note: Such information can demonstrate the changes in the porosity and permeability of rocks with geologic time and with increase in subsurface depth or burial, etc., which in turn determine the *"receptability"* of the rocks in regard to ore-forming fluids. If the evolution of the permeability is known, on measuring the
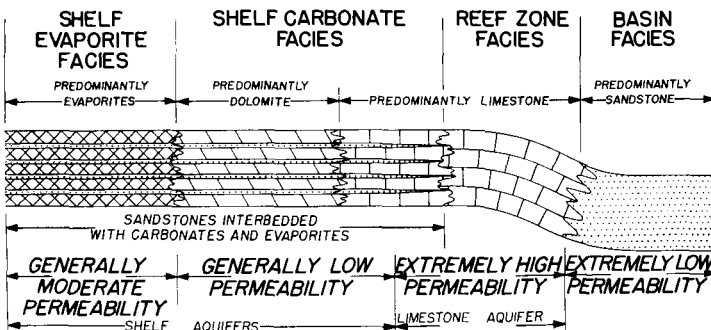
Fig. 193. Idealized diagram showing permeability of major Guadalupian lithofacies. (After Motts, 1968.)
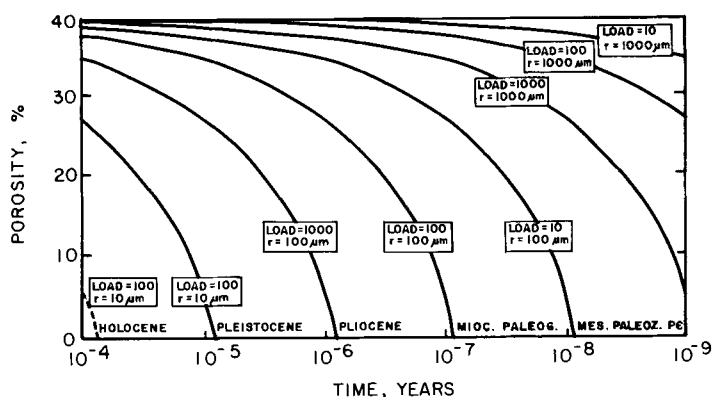
Fig. 194. Calculated decrease of porosity with time as a result of pressure solution [consequence of equation 10 in De Boer, 1976, when initial porosity is set at 40% load $(P-p)$ in atm, grain radius (r) in μm].

porosity – permeability of any particular ore-containing sedimentary rock, one may be able to calculate at what depth, etc., the mineralization took place.

Sharp/Domenico (1976) calculated the porosity distribution, etc., in response to pressure- and temperature-dependent parameters in basins (see discussions above).

Rickard et al. (1979) provided many interesting details on the sandstone-hosted Pb – Zn Laisvall-type deposits, e.g., on the arrangement of sand and shale permeability variations which controlled the flow of the ore-forming solutions. The permeability also was the overall major control of the localization of the ore. These fluids were similar to oil brines (compaction fluids?). Both congruent and non-congruent sedimentary structures and textures controlled ore precipitation on a local and microscopic scale (see their figs. 21 and 22), which occurred at around pH 5 at 150°C. The ore fluids are believed to have been deep basinal brines, i.e., the ore was of a late diagenetic to catagenetic origin (see also Gustafson/Williams, 1981; Bjørlykke/Sangster, 1981).

Wolf (1976) and Gustafon/Williams (1981) pointed out the importance of the "pre-ore diagenetic preparation" of the sedimentary – volcanic source, aquifer-conductor, host-reservoir and cap rocks, by either enhancing or decreasing the various types of rocks in a basin to become eventually involved in ore genesis (see Multi-factorial, and Multi-stages).

Porter/Weimer (1982) related a diagenetic sequence to structural history and petroleum accumulation (i.e. they outlined the paragenesis and modification of porosity). Could similar studies be carried out on ore hostrocks?

Curtis (1983) determined a link between Al-mobility and destruction of secondary porosity.

Silayev/Savel'ev (1984) described a porosity-measuring test for the hydrothermal – metasomatic origin ore deposits (including stratiform ores in dolomites) and concluded that the evolution of porosity was important in the genesis of ore.

Glezen/Lerche (1985) offered a model of the control of sand, in contrast to matrix and other components, for example, on the effective and vertical permeabilities. Such data should be obtained from sandstone units that host ores, which may allow the determination of the burial depth of the rock at the time the metalliferous ore minerals were introduced.

Guide elements	Resi-states	Hydro-lysates	Oxides	Carbo-nates	Eva-porates
Au					
Sn					
Zr,Hf					
Ti					
Ce					
Th					
Y					
W					
Nb,Ta					
B					
Be					
Ga					
V					
U					
Sc					
Cr					
Mo					
Cu					
As,Te					
Zn					
Pb					
Co					
Ni					
Cd					
Sr					
Ba					
Tl					
Rb					
Br					
I					
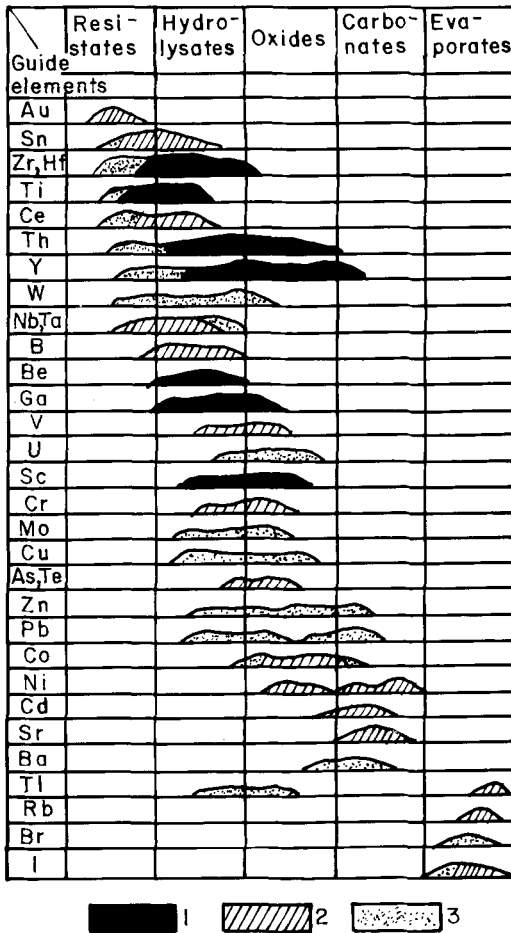
Fig. 195. Sequence of precipitation of some chemical elements in sedimentary milieus. *1* = After Goldschmidt; *2* = after several authors; *3* = after Smulikovski. (After Ginsburg, 1963; for original references to Goldschmidt and Smulikovski see therein.)

PRECIPITATION

Ginsburg (1963) offered a "sequence of precipitation" of some elements in the sedimentary environment, which results in five types of facies (Fig. 195). Many of these elements are precipitated either syngenetically or diagenetically, or by both mechanisms. Those that are syngenetically accumulating can be diagenetically remobilized – transported – concentrated – reprecipitated. The sequence in Fig. 195 thus depicts a geochemical differentiation (= fractionation, partitioning) that led to the formation of different facies. Zoning may be the consequence.

Note: Many more publications deal with this topic (see also Solubility, Zoning, etc.).

Li (1981) examined the ultimate removal mechanisms of elements from oceans. Are these "removal" processes and environmental conditions the antitheses of those that cause precipitation?

Goudie/Pye (1983) offered a review of chemical sedimentation in numerous near-surface (surficial) environments that resulted in the origin of laterites/bauxites, silcrete, calcrete, evaporite crusts (e.g., gypsum, nitrate), desert varnish, red-beds, aeolinite, cave deposits, lake precipitates, phosphate on coral islands, among others. Much of the data is related to terrestrial or continental diagenetic systems. Eventually a comparative study must be undertaken to establish the differences, similarities and transitions/gradations of the marine in contrast to the continental diagenetic systems.

PRESSURE

Ridge (1973), Haas (1971), Finlow-Bates/Large (1978), Large (1979), and Finlow-Bates (1980) discussed the influence of depth of water − and thus the hydrostatic pressure − on the "boiling" of hydrothermal fluids onto the seafloor (see the various diagrams and models in the publications). For example, boiling controls indirectly the temperature as well as timing and localization of the least and most soluble chemical precipitates. In extremely shallow basins (i.e., with small water depth and low hydrostatic pressure), the deposition of the less-soluble species occurs in the *subsurface* conduit, so that the solution is depleted of $Zn - Pb - Cu$, leaving only Fe and Ba to reach the seafloor to form exhalative, diagenetically influenced barite and iron-rich deposits.

Bradley (1975) discussed abnormal pressures, which require a seal (i.e. a caprock). Several interrelated processes lead to abnormal pressures, with temperature change being an important one. Epeirogeny, climate, overburden thickness, osmosis, precipitation, reactions between solutions or trapped fluids, carbonatization, etc., all affect the temperature and pressure in a complexly interconnected fashion.

De Boer (1976) provided data on the interrelationships among pressure, time, porosity, and temperature (see Porosity).

Sharp/Domenico (1976) and Sharp (1978) discussed the origin of and the controls on abnormal pressures, temperatures, etc., all of which control late diagenesis – catagenesis.

Beach/King (1978) discussed pressure solution in general and Narasimhan et al. (1980) reported on a conference on the role of pore pressure in the deformation of rocks. Not only are these data important in relation to ore-forming fluids and metal derivation, transportation and precipitation, but also in reference to the origin of openings in rocks to form veins, for example.

Dorokhin/Bogomolov (1980) examined the effect of bed pressure and temperature on the chemical composition of groundwater with rare metals.

Filippov (1980) described the pressure influencing the genesis of barite – polymetal mineralization.

Millero (1982) deliberated on the effect of pressure on the solubility of minerals in water and seawater, and Whitfield (1982) discussed the seawater under extreme pressure which in turn influences dissolution, hydrothermalism, among others.

Jaenicke (1983) studied biochemical processes under high pressure and concluded that, for example, bacteria must adopt to both high pressure and low temperature in deep oceanic environments, except near hydrothermal vents where they also must tolerate high temperature.

– See also Depth, Metamorphism, and Temperature.

PYRITE – PYRITIZATION

Bogush (1981) utilized growth zoning of pyrite to evaluate the productivity and origin of endogene sulfide-ore sources: both diagenetic and metasomatic pyrite generations were identifiable. Roberts (1982) used the trace-element chemistry of pyrite as a guide to the occurrence of sulfide base-metal ores; e.g., he distinguished diagenetic – metamorphic from base-metal-bearing solutions. Udubasa et al. (1983) investigated stratabound Pb – Zn pyrite ores in Precambrian carbonate rocks. Note that the differentiation of various types of pyrites that formed at various stages has become increasingly important, because early diagenetic pyrite (without any economic metal association) can be replaced subsequently by late diagenetic or metamorphic Cu – Zn – Pb-bearing fluids. Thus, the recognition of the various phases of development are of theoretical as well as of practical significance.

Lew (1981) modeled the major phases or steps in pyrite genesis (Fig. 196) when he examined the elemental distribution in oceanic sediments, including S, S-isotopes, several trace and minor metals, and organic nitrogen.

Hallbauer/Von Gehlen (1983) studied pyrites and metamorphism of the Witwatersrand deposits and discriminated allogenic detrital, synsedimentary and post-sedimentary pyrites as based on variable mineralogical and geochemical criteria.

Raiswell (1982) provided models of pyrite textures, isotopes, and iron availability. Evans et al. (1982) used the ^{57}Fe Mössbauer parameters to identify pyrite and marcasite with different provenances and recognized hydrothermal, vein and sedimentary pyrite types by their trace-element contents, among other criteria (see also Natale, 1980).

Pandalai et al. (1983) studied the geochemistry of pyrite and black shales; Postma (1982) examined pyrite and siderite in swamp sediments (see his diagenetic facies distribution); Luther et al. (1982) studied the pyrite types in salt marsh and estuarine sediments; Lord/Church (1983) the ion diffusion, sulfate reduction and pyritization in salt marshes; whereas Altschuler et al. (1983) reported on S-diagenesis in peat and the origin of pyrite in coal.

Jørstad et al. (1982) investigated the vertical trace-element distribution in fresh and saline waters and sediments in a fjord, noting that albite content increases with depth and ankerite changes to pyrite.

Clark/Lutz (1980), Hudson (1982), and Thomsen/Vorren (1984) examined the relation between organisms or fossils and pyritization, i.e. in living bivalve shells, as well as in Jurassic ammonite-bearing shales (identifying pre- and post-compaction pyritization), and in tubes and burrows in Pleistocene continental shelf sediments.

Cortecci et al. (1983) studied the S-isotopes of pyrite deposits, whereas York et al. (1982) dealt with the ^{40}Ar/^{39}Ar dating of pyrite.
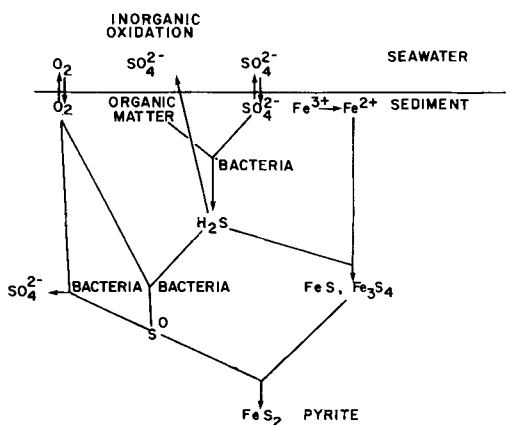
Fig. 196. Major steps in the formation of pyrite. (After Lew, 1981.)

Berner (1982) and Berner/Raiswell (1983) treated the burial of organic carbon and pyrite S in modern oceans and their geochemical and environmental significance, and changes during the Phanerozoic time as part of a new theory. Goldhaber (1983) experimented with metastable S-oxygenation during pyrite oxidation at pH 6 – 9 and 30°C.

– See also Textures, e.g. for framboids.

Graf (1984) examined the effects of M.V.-type mineralization on REE patterns (or vice versa?) of carbonate rocks and minerals; Hein et al. (1984) dealt with the REE-fractionation in fluorite as a geochemical indicator of ores in Triassic carbonates; Majumder et al. (1984) investigated the REE of BIF-deposits (e.g. the diagenetic REE-enrichment in iron oxides compared to silica); Clauer et al. (1984) studied Nd – Sr isotopic and REE-constraints on the genesis of recent hydrothermal Mn-crusts in the ocean; Michard et al. (1984) checked the REE in seawater near hydrothermal vents and Michard (1983) the REE and U in high-temperature solutions from the East Pacific Rise's hydrothermal vent field; whereas Courtois/Clauer (1980) investigated the REE and Sr-isotopes of polymetallic nodules from the Southeast Pacific Ocean. Kerrich/Fryer (1981) studied the separation of rare elements from base metals in an Archean lode-type gold deposit and discussed the implications of low water/rock source regions. From these publications one can see that the REE geochemical techniques have been used in diagenetic and hydrothermal – exhalative (and other) studies (i.e. in plutonic/volcanic and sedimentary petrogenesis). These REE-data ought to be supported by the information obtained from isotopic, and trace/minor element geochemical and geological data, such as textures and stratigraphy.

Elderfield/Greaves (1982) studied the REE in seawater and discussed the geochemical cycles; Baker/Groot (1983) discussed the Proterozoic seawater – felsic volcanics interaction and concluded that there was no essential change in REE in seawater since the Precambrian; and Murphy/Dymond (1984) deliberated on the REE-fluxes and the geochemical budget in the Pacific, including the sedimentary traps and nodules.

Brookins (1983) provided Eh-pH diagrams for the REE at 25°C at 1 bar pressure.

McLennan et al. (1980) correlated REE in sedimentary rocks and discussed the composition of the continental crust, the latter comprising also sedimentary rocks. Diagenetic processes were considered, among others.

RECRYSTALLIZATION

Ewers (1967) discussed in general terms the driving forces for the recrystallization of sulfide minerals as influenced by particle-size variation (surface energy), temperature gradients, and formation of a new phase. In general, little data is available on recrystallization.

Spry (1969) in an introductory text on metamorphic textures outlined some aspects of crystallization and recrystallization. A separate (unique?) comprehensive summary is needed of the available information on diagenetic/low-grade metamorphic crystallization and nucleation processes.

Eitel (1975) provided some data on aging and recrystallization of silicates.

RED-BEDS

Boyle (1968) discussed the red-bed-type sandstone-hosted $Cu - Pb - Ag - V - U$ deposits (see his table 42). He evaluated numerous aspects of diagenesis.

Chandler (1980) summarized the Proterozoic red-bed sequences of Canada as they offer important information on past climates, O_2-evolution in the atmosphere, and depositional – tectonic environments. Possibly, their greatest significance lies in their association with base metals and uranium and vanadium deposits. Thus the red-beds may provide a useful exploration guide. The clastic versus diagenetic origin of iron oxide in the sediments, which has been debated for many years, is reviewed by Chandler. It is accepted that the diagenetic origin of the hematite in red-bed deposits is the most plausible explanation.

Franke/Paul (1980) examined the deposition and diagenesis of a Devonian red-bed sequence (e.g., its iron mineral types and their distribution); whereas Mader (1982) and Holmes et al. (1983) studied the diagenesis and mineralization of some other red-beds.

Zielinski et al. (1983) treated the mobility and distribution of heavy metals during the origin of first-cycle red-beds. See for important references this publication; consult also Wolf (1976, 1981, 1985, 1986 – see the Indexes in vols. 4, 7, 10 and 14 for red-beds related to ore genesis).

Turner (1980) and Goudie/Pye (1983) offered two excellent books on red-beds and related diagenetic theories. Note, however, that only the continental red-beds were reviewed, so that a comparative investigation of the marine origin of some other red-bed varieties is needed.

REDUCING (ANOXIC, EUXINIC, STAGNANT, BLACK SHALE)

Thiede/Van Andel (1977) worked out the paleoenvironment of a Mesozoic anaerobic Atlantic oceanic sediment, whereas de Graciansky et al. (1984) studied the ocean-wide stagnation episode in the late Cretaceous. Cameron (1982) examined the sulphate and its reduction in early Precambrian oceans.

Berner (1979) treated the kinetics of nutrient regeneration in reducing marine sediments; Murray/Grundmanis (1980) discussed the O_2-consumption in pelagic sediments; and Morris et al. (1984) worked on the sapropelic sediments in an oceanic basin in the Pacific, comparing stagnant conditions with increased marine productivity. Tunnicliffe (1981) had investigated the high species diversity and abundance of epibenthic community in an O_2-deficient basin. Skei (1983b), on the other hand, examined the geochemical/sedimentological features of a permanently anoxic fjord (see also Fjords), including metal sulfide genesis.

Moore (1980) and Demaison/Moore (1980) studied the anoxic environments and oil-source bed genesis (i.e., black shale genesis in reducing milieus) and offered a classification of anoxic depositional models. Zimmerle (1985) presented new data on the origin of hydrocarbon source rocks: numerous anoxic/black shale-type milieus were classified and modeled. If black shales are associated with metal deposits or constitute the hostrocks, then the precise origin of these facies must be understood.

Southam et al. (1982) discussed the dynamics of anoxia, including Eh, black mud environments, and color of sediments, among others.

Carserud (1982) reviewed the research on black shales and ore genesis, including mobilization processes to form ores and diagenetic concretions.

Keith (1982) modeled the C- and S-transfers and reservoirs in an ocean as well as the development of reducing/anoxic conditions necessary for the origin of petroleum and stratabound ores (Fig. 197).

Cameron (1983a, b) outlined the distribution of dissolved oxygen, sulfides and iron in a stratified oxic – anoxic basin (see models in his figs. 2 and 3) with black sulfidic muds along the bottom.

Martin/Knauer (1984) examined the Mn-transportation through oxygen-minima (e.g., including the Mn-flux, equilibrium determined by oxygen levels); J.C.G. Walker (1984) studied the suboxic diagenesis in banded iron formation; and Kiyosu (1980) investigated the chemical reduction and S-isotopic effects of sulfate, in the presence of organic matter, under hydrothermal conditions (see also Hydrothermalism).

Thunell et al. (1984) outlined anoxic events as related to the evolution of climates

(see model in their fig. 1): three models of different basins or oceans are depicted (i.e., the Black Sea, Indian Ocean and SW African Shelf types) as characterized by the anoxic-silled basin, oxygen-minimum zone, and upwelling environments (the latter with organic-rich sediments along shelves).
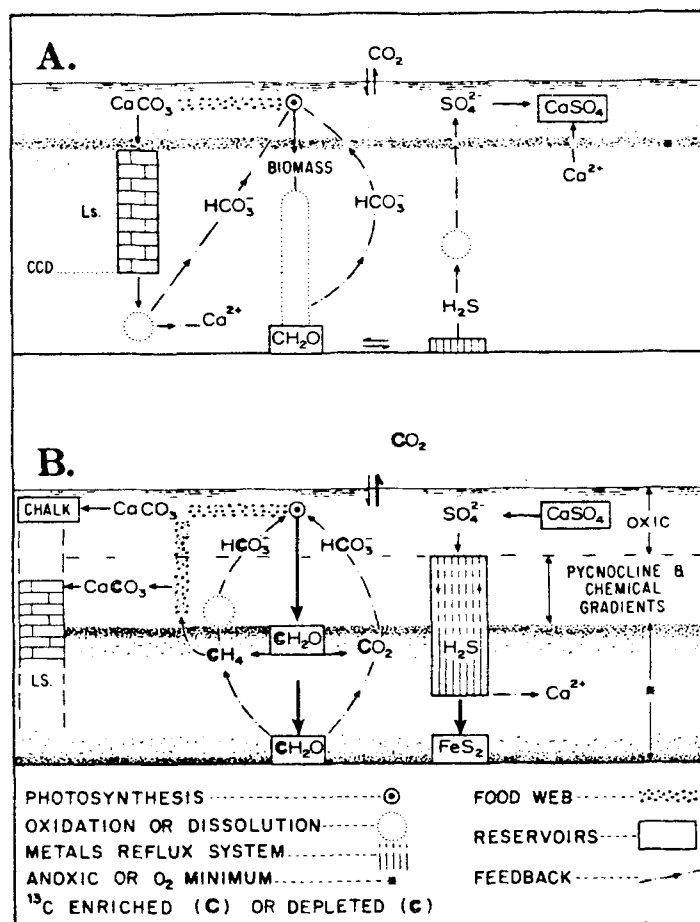
Fig. 197. Simplified diagram of carbon and sulfur transfer and reservoirs in a mixed ocean (A) and a developing stagnant ocean (B) with increasing volume of the anoxic deep layer or mid-depth layer. A horizontal food-web pattern represents dominant phytoplankton components, and a vertical pattern dominant bacterial components. Proposed carbon isotopic fractionation is shown schematically by light and bold-face carbon symbols for the example of methane and carbon dioxide from anaerobic fermentation. CCD = Calcite compensation depth. $CHALK$ is used as the type example of shallow-water biogenic $CaCO_3$. "Metals Reflux System" represents counter flow in a system with steep vertical gradients of O_2 and H_2S and mid-depth concentration of metals by transient sinking detritus and precipitates. (After Keith, 1982.)

Glenn/Arthur (1985) reviewed modern and ancient basins as to their sedimentary and geochemical indicators of productivity and O_2-contents, of which the Holocene Black Sea is the type anoxic setting.

— See also Eh, and Upwelling.

REMOBILIZATION – MOBILIZATION

Turner/Peterson (1977) studied the uranium mineralization in a rift basin, which was located in offshore lacustrine black mudstone and in nearshore lacustrine sandstones. Two agents (humic acids and aqueous sulfide) fixed U in the offshore black muds. The reducing agents generated within the black muds were expelled during diagenetic – early burial compaction into the adjacent, more permeable nearshore sands, providing the reductants necessary for U-fixation. Uranyl ions were carried into the basin by groundwater from U-rich crystalline rocks south of the basin. It is possible that the U-bearing groundwater reacted in the subsurface with the reductant, or moved upward to the surface into the lake to precipitate uranium there upon encountering the reductants. The former is a diagenetic and the latter a syngenetic deposit.

Lydon (1978b) studied the Pb – Zn deposits which are of the low-temperature hydrothermal origin (< 200°C). Mobilization of the solutions in some cases was probably tectonically induced, possibly by true "seismic pumping" or by the fracture release of geopressured reservoirs. In other cases, solutions were mobilized by burial compaction. "Seismic pumping" and "fracture release" can occur relatively early in a sedimentary basin's history; therefore, it can be late diagenetic in origin as well as catagenetic.

Walton (1978) discussed the fate of U during diagenesis of volcanic rocks as a consequence of remobilization.

Sherborne et al. (1979) studied U-bearing lacustrine tuffs that underwent compaction and dewatering and concluded that the expelled alkaline solutions came in contact with strongly reducing paludal sediments causing precipitation and fixation of the U. Associated zeolitization, silicification, calcification, and argillic alteration indicate early diagenetic origin of the mineralization. Some remobilization and reprecipitation of U-minerals in fractures occurred subsequently. More data is required on such diagenetic alterations, on one hand, in contrast to buried metamorphic and early to late diagenetic hydrothermal alterations, on the other.

Zielinski et al. (1980) provided a model of the distribution and mobility of uranium in a diagenetically zeolitized tuff: no statistically detectable fraction of the tuff's original U was lost, even though it has a high (about 9 ppm) U-content and was extensively altered. This seems to contradict results of studies on other tuffs. In order to determine the source potential of tuffs to supply metals, similar studies are re-

quired in a variety of different geological environments in order to identify the particular combination of conditions most favorable for liberation, migration, and reprecipitation of U from volcanic (and other) rocks.

Banás et al. (1982) described clastic quartz and other minerals that have been replaced by copper minerals. The ore-forming fluids, which originated through diagenetic mobilization of metals from Cu-bearing shales, migrated into underlying porous sandstones. Clay – organic micro-layers acted as semipermeable membranes.

Matisoff et al. (1981) examined the kinetics of nutrients (see Organic matter) and metal release from decomposing lake sediments (see Adsorption), whereas Zhorov et al. (1983) studied the distribution of various metals in the Black Sea bottom sediments, and diagenetic remobilization.

Brevart et al. (1982) utilized Pb-isotopic data to unravel the remobilization process and the origin of Pb – Zn ores in a French metallogenic province. Boni/Koeppel (1985) discussed ore – Pb-isotope relations and patterns as related to metal remobilization.

Carserud (1982) reviewed the Soviet research on black shales and ore genesis, which included mobilization to form ores as exemplified by diagenetic concretions.

Tsunogai et al. (1982) studied the diagenetic remobilization of metals as reflected by the regional differences in the composition of manganese nodules. Many other publications dealt with (re)mobilization of manganese in Recent sediments: Trefry/Presley (1982) studied Mn-fluxes in delta sediments including river vs. delta element-partitioning (see Differentiation); and Beran et al. (1983) discussed the dissolution – reprecipitation of Mn as a mechanism to form diagenetic Mn-carbonate mineralization. Stoffers et al. (1984) has compared the features of Mn-micronodules from the equatorial and Southwest Pacific regions, including the remobilization as affected by the rate of sedimentation.

Petrascheck (1983) issued a symposium on ore mobilization, which is a good source to the pre-1982 literature.

Moorby (1983) deliberated on the geochemistry of transitional sediments associated with the Recent Galapagos hydrothermal mound fields, including discussions on remobilization.

Zakrzewski/Nugteren (1984) interpreted a distal volcano-sedimentary deposit to be the product of several successive processes, ranging from syngenesis through diagenetic remobilization to hydrothermal remobilization.

The Geological Society of Australia (1984a) offered a short course on the mechanical and chemical (re)mobilization of metalliferous mineralization covering the whole spectrum of numerous, very different processes covered under the

umbrella-term "(re)mobilization". (See also Scheibner, 1986; Marshall/Gilligan, 1987; and the general review by Wolf, 1987, on his "ubiquity" of (re)mobilization.)

Frakes/Bolton (1984) modeled the environment of the origin of Mn-giants as based on sealevel changes and anoxic history, including on the diagenetic remobilization on a regional scale (Fig. 198). Clemmey (1981) discussed the genesis of heavy mineral assemblages in Proterozoic U – Au conglomerates and invoked resorting and mechanical and chemical reworking/remobilization to explain the placer and
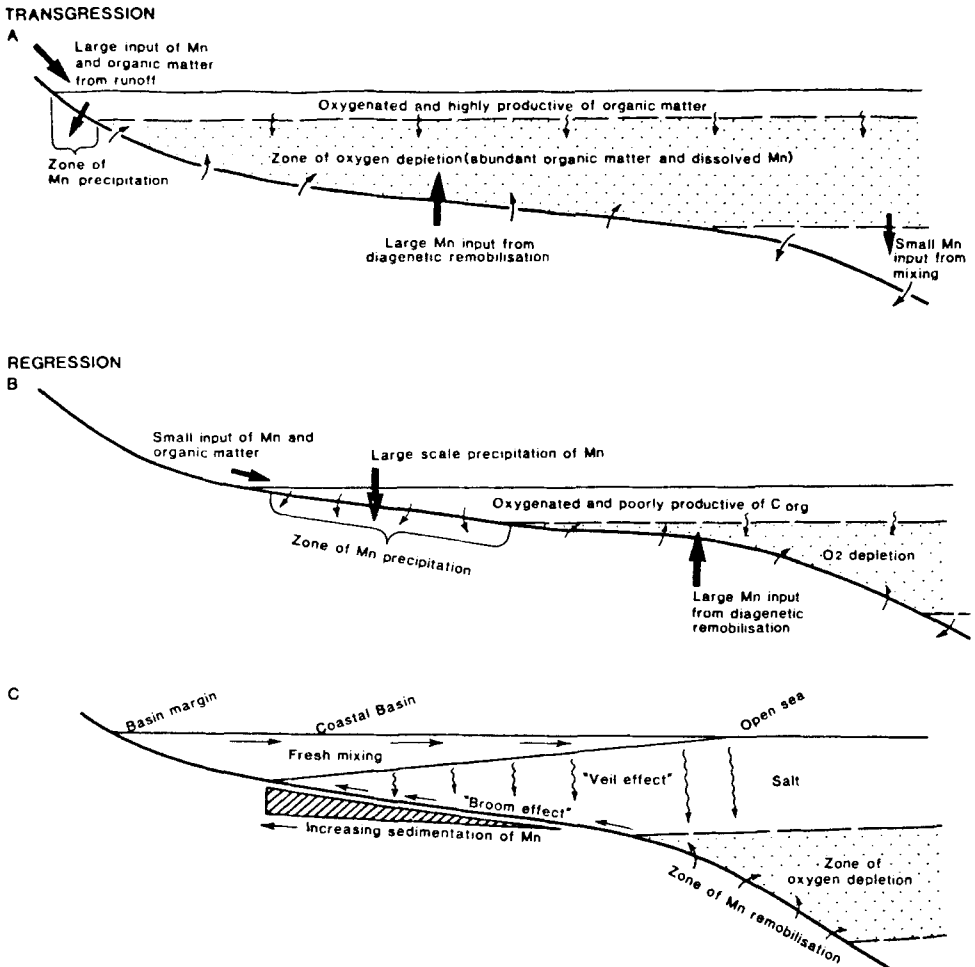
Fig. 198. (A) Relationships during marine transgression, showing narrow zone of Mn accumulation and concentration of dissolved Mn in water column. (B) Relationships during marine regression with abundant diagenetic remobilization and wide zone of final Mn precipitation. (C) Manganese sedimentation in coastal zone of intracratonic basin, showing *veil effect* (flocculant fall-out) from saline mixing and *broom effect* (bottom transport and concentration) from tidal activity. (After Frakes/Bolton, 1984.)
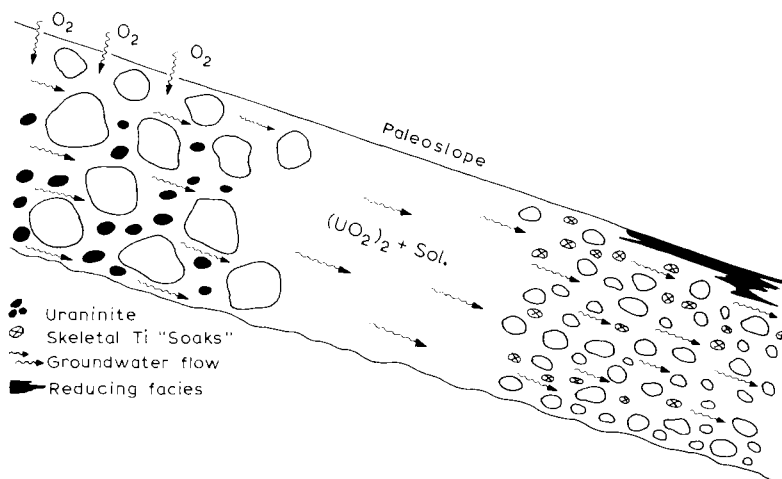
Fig. 199. A schematic model for the intrastratal oxidation of uraninite with remobilization and reprecipitation of uranium in more distal facies at Elliot Lake. (After Clemmey, 1981.)
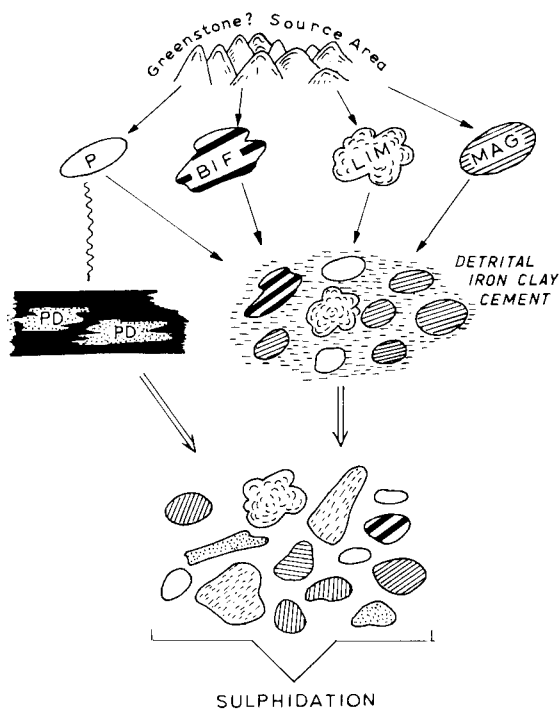
SULPHIDATION

Fig. 200. A schematic model for the generation of sulphidized conglomerates in the Proterozoic, which also demonstrates the processes involved in the complex intra-basinal reworking of the Rand sediments. P = pyrite; BIF = banded iron-formations; LIM = ferric iron clasts; MAG = magnetite; PD = diagenetic pyrite from intra-basin reduzate facies. Detrital iron clay cement of the first-formed sediment is derived from the breakdown of iron-bearing silicates common in the greenstone source areas. (After Clemmey, 1981.)

other types of origins, sulphidization/diagenetic pyrite types, intrastratal remobilization, roll-front genesis, etc. (Figs. 199 – 201; see also Uranium).

Bazarova et al. (1984) investigated the mobility and resulting association of elements as exemplified by a Cretaceous deposit, whereas Ivanov et al. (1984) offered a comparative study of minor-element distribution of three shales. Such bed-by-bed studies must be undertaken to unravel the primary, diagenetic and metamorphic effects on ore hostrocks in contrast to those on barren country rocks. Some such investigations have been performed on volcanic and sedimentary lithologies, but extensive detailed comparisons are rare. The concepts of Tischendorf/Harff (1985) on "dispersive and accumulative elements" must be considered.

Dasgupta et al. (1985) studied the immobility of O_2 during the metamorphism of non-calcareous Mn-rich sediments. What is the degree of (re)mobilization of other elements or what is their comparative immobility? Are certain elements, which are mobile during diagenesis, increasingly immobile with depth of burial and/or change in permeability, for example? Or is there an increase in mobility due to increase in temperature?

Kyte et al. (1985) examined the siderophile interelement variations across a sedimentary/stratigraphic boundary and concluded that element fractionation was the consequence of local redistribution, reworking and diagenetic (re)mobilization.
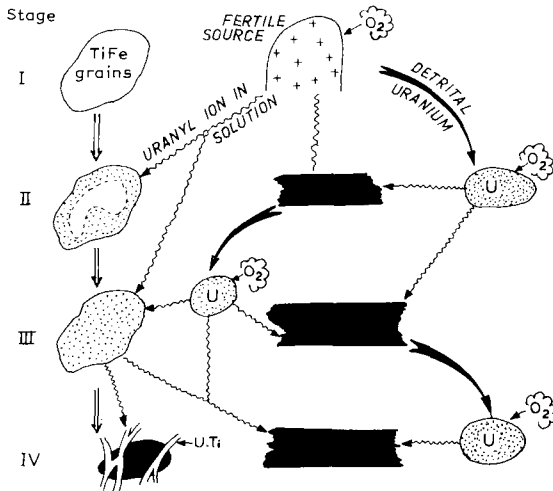
Fig. 201. Schematic model for uranium distribution in Proterozoic conglomerates. *Stage I:* derivation of uranium from source areas; *stage II:* first sediment of Rand precursor grain (see fig. 4 in original publication); *stage III:* reworked or diagenetically altered sediment; cf. Dominion Reef of Elliot Lake; *stage IV:* reworked, mineralogically mature sediment; cf. main Witwatersrand conglomerates. Stippling on the Ti/Fe phases indicates progressive alteration. Only small particles progress beyond stage III. The solid black arrows indicate reworking of primary and secondary uraninite and uranothorite grains; O_2 indicates oxidative diagenesis; cf. Fig. 199. (After Clemmey, 1981.)

Shanmugam (1985) pointed out the importance of dissolution of grains in the origin of secondary porosity in sandstones. However, the result may be two-fold: either the dissolved material is removed in solution or it is reprecipitated again if the physicochemical condition changes. Thus, permeability/porosity may either increase or decrease. Can metal ions be released from one specific stratigraphic unit during dissolution and reconcentrated in another?

– See also Sources.

REPLACEMENT

Ames (1961a – d) worked on anion/cation "metasomatic" replacement of limestones, etc., which may seem to be out-of-place in relationship to "diagenesis". The definition of the word metasomatism and related terms (including metasome and palasome), however, is not confined to higher- (how high?) temperature processes related to igneous or hydrothermal activities. It applies equally well to lower-temperature sedimentary diagenesis and volcanic – exhalative – sedimentary diagenetic processes (but compare pyrometasomatism). In any case, inasmuch as there are several types of non-igneous hydrothermal fluids formed within sedimentary piles, and that hydrothermal alteration passes or overlaps with sedimentary diagenesis, one may assume that the several "volcanism-related metasomatic" processes are transitional into "diagenetic metasomatism". Ames (1961c) also stated that some of his work applies to two geochemical environments: (a) to low-temperature settings consisting of gangue minerals in sulfide deposits (both veins and stratabound/stratiform ores and to bedded replacement products in carbonate rocks), and (b) to normal sedimentary milieus in which meteoric waters containing Ca^{2+}, Sr^{2+} and Ba^{2+} circulate (e.g., in barite formations).

Stanton (1966) offered a "numerical" method for discriminating between replacement and sedimentary processes in the deposition of stratiform ores. Chemical analyses are used, on the presumption that replacement involves selective substitution for certain constituents of beds following sedimentation, whereas sedimentary deposition involves simple addition of sulfide to detrital and other material during sedimentation. In the first case, increase in sulfide content should be accompanied by a systematic change in the proportion of certain constituents of the hostrock. In the second case, increase in sulfide content should have no effect on these proportions and there should be no change.

Finlow-Bates et al. (1977) described atoll textures characteristic of Pb – Zn ores due to partial to complete replacement of fine-grained pyrite by other sulfides, e.g., galena. They believe that the replacement took place during early diagenesis by downward percolating Pb and Zn from a sulfur-free surface into the underlying sediment, encountering a sulfide (i.e., the pyrite) of greater solubility than galena and sphalerite.
    Note: Similar processes have been frequently described in the literature and in-

dicate the importance of the pre-ore facies and pre-ore diagenesis, controlling the subsequent formation of ore mineralization. If no pre-ore pyrite had been available to the downward seeping or diffusing metals, no ore might have formed.

Wedepohl et al. (1978) offered criteria to distinguish syngenetic from diagenetic features in the Kupferschiefer.

Reynolds (1982) examined the post-depositional alteration, including replacement, of titanomagnetite in a Miocene sandstone.

REWORKING (CHEMICAL, MECHANICAL)

Knox (1977) studied the origin of caliche and calcrete. Although the geologic setting is different, similar studies should be carried out on the U-rich calcrete deposits.

Baturin (1982) outlined the mechanical reworking – transportation – redeposition of sediments containing phosphate grains and concretions, resulting in a higher-grade phosphate deposit by removing the finer-grained "matrix" (Fig. 202).

Note: (a) Numerous publications described the "reworking" (Fig. 203) of syngenetic and diagenetic sulfide ore deposits that resulted in the formation of
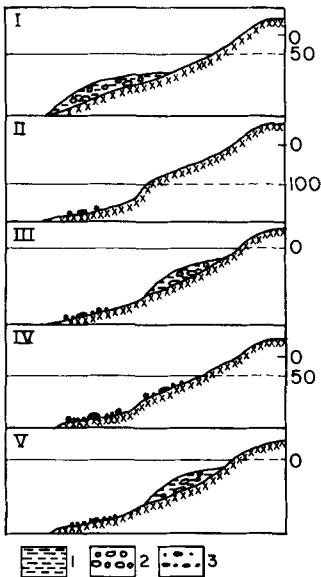
Fig. 202. Scheme of the process of concentration of phosphate grains and concretions by reworking of the sediments on the shelf of southwest Africa in Quaternary time. (After Baturin, 1982.) *1* = Diatomaceous oozes; *2* = unconsolidated phosphate concretions; *3* = compacted phosphate concretions. Present sea level indicated by zero (0).

"intra-environmental"[1] breccia (e.g., Kuroko ore deposits). The breccia fragments may either form a lag deposit or can be transported to another locality. (b) Although the (re)concentration of the phosphate grains and concretions, on one hand, and the transportation – redeposition of sulfide breccia fragments, on the other, have certain similarities in common, numerous differences exist that must be clearly outlined in the future.

McArthur (1980) proved that (diagenetic) "subaqueous (marine) reworking" and subsequent weathering results in changes in contents of the trace elements originally concentrated in carbonate – apatite.

Note: (a) For example, early diagenetic phase I may have been conducive to the concentration of U in phosphorite, whereas early diagenesis phase II could have caused depletion thereof. If in the future such apatite-bound U is considered a potential industrial source of uranium, then the recognition and regional depletion
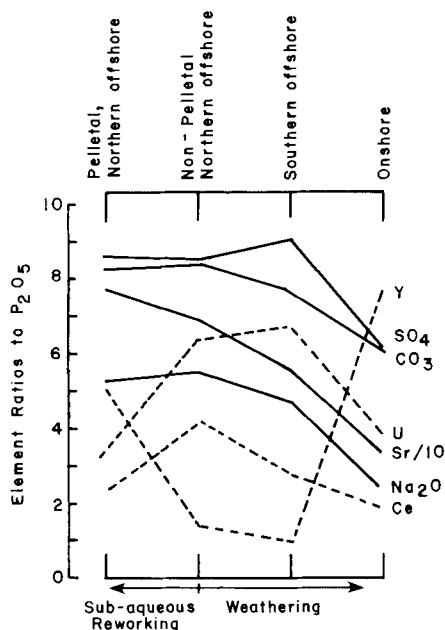
Fig. 203. Effects of reworking and weathering on element concentrations in Moroccan carbonate – apatite. (After McArthur, 1980.)

[1] This term refers to processes (e.g., brecciation) within the *depositional (syngenetic) environment* in contrast to processes operative *within a formation* (i.e., meaning *"intraformational per se"* or within a rock unit). These two settings are indeed very different – yet they seem to be covered by the same expression "intraformational"! These two cases can be separated by the two expressions "intra-environmental" (i.e., syngenetic – early diagenetic) and "intraformational" (i.e., early diagenetic – epigenetic to catagenetic – epigenetic) processes and products, respectively. In each setting, several different varieties of brecciations can take place.

of uranium in the phosphorites will become important. (b) More details are required on the collectively called "reworking" (mechanical, chemical, and biological) processes.

Aller/DeMaster (1984) estimated the reworking and particle flux along a deep-sea floor by using Th – U isotopic disequilibrium data.

Schulz (1983) considered, among others, the resedimentation of Pb – Zn ores in a pyrite – oncolite layer. Barrett/Fralick (1985) discussed the reworking and redeposition of an Archean iron formation.

– See also Remobilization.

RIVER ENVIRONMENTS

Durum/Haffty (1963) deliberated on the implication of minor element contents of some major streams in the world; Abdullah/Royle (1972) listed heavy-metal contents of some rivers and lakes (in Wales); and Meybeck (1982) discussed the N, C and P transport by world rivers and offered models of their cycles (see Cycles). Driel/Groot (1974) presented data on heavy metals in river sediments.

Hearn et al. (1983) undertook authigenic investigations of the Rhone River plume in the eastern Lake Geneva and considered the phosphorus content, among others.

Strakhov (1967, 1969, 1971) offered a large amount of data related to the transportation of particulates, colloids, ions, complexes, etc., of the world's exogenic systems.

Bernard/Samama (1976) outlined the French School's ideas on continental sources of metals.

– See also Sources, and Transportation.

SALINITY

Müller/Förstner (1973) studied the origin of Recent iron ore deposits in the African Lake Malawi, and demonstrated that, for example, oolitic limonite, silica, vivianite (P-mineral), and manganese deposits, often loosely referred to in regard to fossil sequences as of marine origin, can form in land-locked lakes.
   Note: (a) The "source factor", not the "salinity-classified" milieu, may be more (even most) fundamental in the present case, insofar as the quick influx of large amounts of hydrothermal fluids and gases can override and nullify any earlier-established syngenetic and diagenetic systems. An earlier-formed (pre-hydrothermal) pH – Eh stratification in the lake and/or in its sediments, however,

may have given rise to an euxinic, black-mud-type organic matter-rich zone, among others, with which the debouching hydrothermal solutions reacted.

Hanor (1979) discussed in his chapter on the "sedimentary genesis of hydrothermal" fluids (among numerous other aspects, see Hydrology; Hanor, 1979) the chemical composition and the temperature – salinity relations of the ore solutions, as based on fluid-inclusion studies (see Roedder, 1976, for example) of the Mississippi Valley-type sulfide and fluorite minerals. The bulk composition of the ore-forming solutions is very similar to that of sedimentary brines, although some significant differences do occur. For instance, although each basin has a unique trend of values (Fig. 204), the apparent enrichment of K with increasing Cl content (perhaps due to membrane-filtration or interaction with evaporites) is characteristic in general. Interesting, in the present context of diagenesis, is the fact that fluid-inclusion studies have revealed differences between early- and late-stage carbonates, fluorides, barites, etc. – both locally and regionally. Thus, both the paragenetic relations and zoning can be worked out. Also, Hanor stated (p. 161) that "these variations in water composition probably reflect selective distribution of source rocks or facies types that yield particular elements during diagenetic alteration and not portions of the crust unusually enriched or depleted in these sediments." The data in Fig. 205 give a general idea of the range of both the temperature and salinities of the fluids that produced Mississippi Valley-type ores in contrast to those of sedimentary waters (see also Hanor's figs. 4.3 and 4.7 in the original publication; also refer to the limitations or restrictions that apply to Fig. 204, discussed by Hanor, pp. 161 – 163).
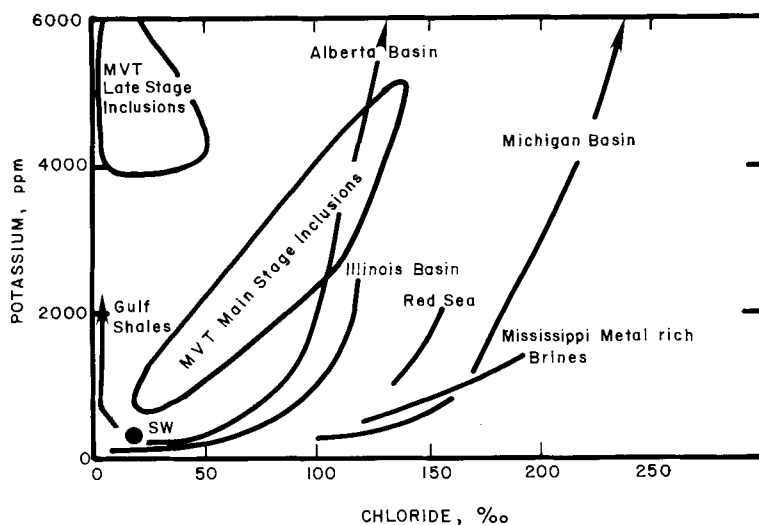
Fig. 204. Relation between potassium and chloride concentrations in Mississippi Valley-type fluid inclusions and various sedimentary brines. *SW* marks the position of seawater. (After Hanor, 1979; see for original data sources.)

Nicholson's (1979, 1980) study of sediment types and their syngenetic and diagenetic phases resulted in a model that explains the origin of base-metal lodes and U – Cu – Pb and Au deposits with the following features: (a) Tourmaline (B-rich) lenses were formed by hot seafloor brines in a paleotrough and are correlatable with economically interesting sedimentary tuffaceous hostrock zones: pyrrhotite – pyrite-rich, siliceous, and two base-metal-rich facies, which in turn pass into ferruginous shale as well as iron formations elsewhere. The latter is hosting Au-deposits. (b) The facies and mineralogy plus chemistry of the deposits suggest that the processes were similar to those in Lake Magadi, Kenya (Surdam/Eugster, 1976): restricted, perhaps evaporitive, environments led to the breakdown of the tuff and the mobilization and origin of silica and zeolites. Base-metals may thus have been released into surface and connate waters. (c) In the paleotrough, salinity stratification (see Fig. 206) caused by the influx of brines hampered water circulation and allowed a buildup of anoxic water at the bottom of the basin. Chalcopyrite and pyrite were precipitated where the brines encountered reducing conditions, whereas pyrrhotite, galena and sphalerite formed in deeper, more reducing water. Boron, silica and Fe-sulfides were
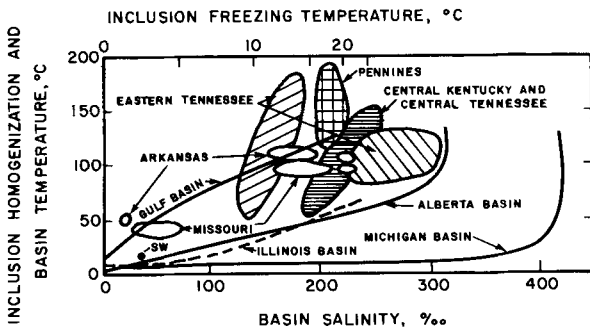
Fig. 205. Temperature – salinity relations in ore-forming fluids from Mississippi Valley-type districts (patterned areas), as deduced from fluid inclusion data and temperature – salinity relations for waters in the Illinois, Michigan, Alberta, and Mississippi Gulf basins, *SW* marks the position of surface seawater. (After Hanor, 1979; see for original data sources.)
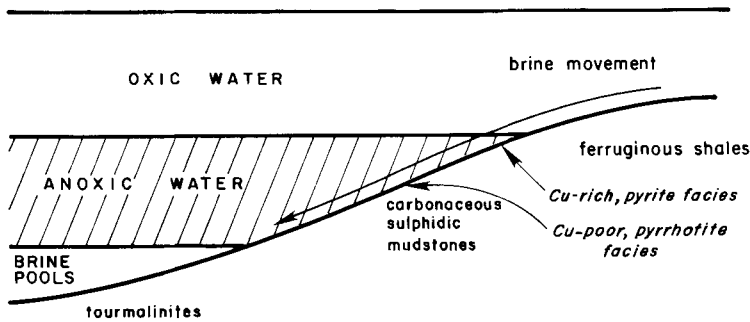
Fig. 206. Salinity – Eh zoning controlling metal and non-metal mineral distribution. (After Nicholson, 1979.)

deposited as the brines evolved in time and/or space. (d) The Au-deposits in the iron formations were probably precipitated also from the brines, as suggested by several criteria.

Coradossi et al. (1980) studied the geochemistry and depositonal environments of a clayey sedimentary complex, including the elemental (e.g., heavy metal) composition of an intra-evaporitic marl, permitting the delineation of three salinity supercycles. No metal enrichment above that of coeval marine sediments was noted, which is contrary to observations by other researchers. What is the reason for this discrepancy — could early diagenetic remobilization have depleted the metals?

Buchanan et al. (1981) examined fluid inclusions of a barite deposit and offered a temperature – salinity diagram of various deposits.

Sheu/Burkart (1982) inferred the paleosalinity and P-content of carbonate rocks from a cyclic evaporite – carbonate sequence.

Brass et al. (1982) dealt with warm saline bottom water in the ancient ocean, and Dodd/Crisp (1982) with non-linear salinity variations of Sr/Ca and Mg/Ca ratios in water and organisms as a possible indicator of paleosalinity.

SANDSTONES

Gustafson/Williams (1981) and Bjørlykke/Sangster (1981) described, respectively, the sediment-hosted stratiform Cu, Pb and Zn deposits, and the sandstone Pb-deposits and their relation to red-bed Cu and carbonate Pb – Zn concentrations; thus unequivocally demonstrating the importance of syngenesis, diagenesis, catagenesis and burial metamorphism in the origin of these types of ore accumulations. Many other publications too have dealt with such deposits, see for example the 14-volume Handbook edited by Wolf (1976, 1981, 1985, 1986). See also Zuffa (1985) and Bodard et al. (1984).
    Much data of the literature on general sandstone diagenesis ought to be applied eventually to ore hostrocks: Scholle/Schluger (1979) discussed diagenesis of all the sandstone-group lithologies, i.e., quartzites, arkoses, graywackes, volcanic/pyroclastic and volcaniclastic rocks. See also Bjørlykke (1983) for diagenetic reactions; Füchtbauer (1983) for facies controlling sandstone diagenesis; Hutcheon (1983) for siliciclastic diagenesis; and Longstoffe (1983) for stable isotopes as related to diagenesis of clastic rocks. McBride (1984) provided rules for sandstone diagenesis in regard to reservoir quality, and Hoholick et al. (1984) described the regional variations of porosity and cement of sandstone complexes.

Rickard et al. (1981) and Ncube et al. (1981) studied, respectively, the Pb- and S-isotopes of galena from a sandstone-hosted Pb – Zn deposit, whereas Ncube et al. discussed its genesis in more general terms. Bjørlykke/Thorpe (1982) considered the source of Pb in a sandstone lead deposit. Rasulova et al. (1982) examined the role

of country rocks in the origin of a layered-infiltration deposit in alluvial sandstones. This latter process has often been suggested for U-deposits of the roll type (= geochemical cell type).

Mader (1981) studied a sandstone complex's diagenesis in general, e.g., the heavy minerals and iron oxide. On the other hand, Land/Milliken (1981), Nwajide/Hoque (1982) and T.R. Walker (1984) considered selectively the feldspar diagenesis including albitization, in sandstones and mudrocks. Conca/Rossman (1982) concentrated on case hardening of sandstones.

Stonecipher/Bishop (1984) dealt with sorting and wave abrasion that controlled composition and diagenesis of a sandstone, i.e., the composition influenced diagenetic progression or evolution in both time and depth (space).

Dickinson/Valloni (1980) reviewed the plate-tectonic settings and provenances of sands in modern ocean basins. Since tectonism en toto controls the intermediate stages of sediment genesis of all types of deposits, including sandstones, and inasmuch as the composition influences directly the diagenesis, it is safe to state that tectonism manipulates any style of secondary alterations — not to forget its control on the hydrologic systems. See also Dickinson et al. (1983) for a relevant investigation and Klein/Lee (1984) for an assessment of geodynamic controls on environmental systems and sandstone diagenesis. The above-cited link of tectonism → environment + composition → diagenesis has as yet not been fully studied because either the first two or the last two variables were preferentially investigated, but not all four parameters in combination (with a few exceptions). (See Füchtbauer, 1983, for facies controls on diagenesis.)

— See also Environments, Facies, Multi-factorial, and Red-beds.

SILICIFICATION – SILICA – CHERT

Lovering (1972) and Lovering/Heyl (1980) offered a detailed study of several types of jasperoids, some indicative of the presence of ore.
    Note: Just as in the case of dolomite (and several other ore mineral-associated gangue minerals), more work ought to be done on the various types of silicification products to determine which varieties are indicative of mineralization. For example, the differences between diagenetic – sedimentary, diagenetic – hydrothermal or epigenetic – hydrothermal, and weathering/supergene-type silica deposits (e.g., Wolf, 1972) must be determined.

Yariv/Cross (1979) offered basic data on the colloid geochemistry of silica, whereas Goudie/Pye (1983), Ambrose/Flint (1981), Butt (1983) and Callen (1983) dealt with the silcrete-type silica deposits.

Pisciotto (1981) studied the diagenetic trends in a siliceous facies complex, whereas

Summerfield (1983) and Ross/Chiarenzelli (1985) outlined the paleoclimatic significance of silcretes (see also Climates).

Lovering (1981) examined various types of metal element-containing silica, including diagenetic types in sedimentary rocks. His emphasis, however, was on jasperoid float/stream cobbles as a geochemical exploration tool for hydrothermal ore deposits. As to the latter variety (volcanic, hydrothermal, etc.), see Rona et al. (1980) for hydrothermal quartz vugs from the Mid-Atlantic Ridge; Rimstidt/Cole (1983) for geothermal mineralization and associated siliceous sinter in comparison with sedimentary types; and Blankenburg/Schrön (1982) for trace-element content of volcanic agates (comparing volcanic with sedimentary and other types).

Zielinski (1982b) studied U-containing opal and its genesis and implications for exploration. How do we differentiate between syngenetic, diagenetic, various types of epigenetic, and supergene silica concentrations? See Wolf (1972) for supergene silicification.

Truscott/Shaw (1984) investigated B in chert and Precambrian BIFs, including diagenetic mobilization.

Disler (1984) and Williams et al. (1985) provided fundamental data on the subsurface silica-bearing solutions, as controlled by low and high temperatures, and on thermodynamics of silica diagenesis, such as the kinetic concepts involved, pressure – temperature, and pH influences.

Paris et al. (1985) compared various systems of silicification processes in explaining the origin of cherts in a greenstone belt, including submarine exhalative mechanisms.

SILVER

Boyle (1968) reviewed extensively the geochemistry and genesis of Ag and associated elements in a variety of deposits. Like his books on Au and U + Th ores, the summary of Ag offered a unique introduction into diagenesis, among many other topics.

Graybeal et al. (1986) provided a recent up-to-date summary of the Ag deposits – much of the data is useful to the researcher of diagenesis of sedimentary and volcanic rocks.

SOLUBILITY

Barton et al. (1963) discussed the "equilibrium in ore deposits" in general terms. Insofar as it is normally *assumed* that equilibrium has occurred during the formation of diagenetic minerals, their comments are pertinent.

362

Note: (a) Assuming equilibrium during initial diagenesis, how are the equilibrium conditions altered during later diagenesis and catagenesis? (b) What are the criteria of non-equilibrium and equilibrium of ore and gangue mineral assemblages and parageneses? What are the criteria to recognize non-equilibrium conditions that succeeded earlier equilibrium milieus? (c) It must be pointed out, however, that numerous researchers believe that in many cases an equilibrium was not attained.

Holland (in Barnes, 1967), plotted in his table 9.2 (p. 430) nine gangue minerals usually present in hydrothermal systems (e.g., quartz, calcite, dolomite, fluorite, anhydrite, barite) and discussed and compared the relative importance of several mechanisms of precipitation (i.e., simple cooling, SO_2-destruction, boiling, replacements, and ground- or connate-water mixing).

Note: A comparative/contrastive-type review of all precipitation mechanisms of most ore minerals and gangue minerals found in sedimentary – volcanic deposits is required, culminating in a list of uncertainties, lack and availability of data, and suggestions for future research. Are there certain ore and gangue mineral combinations or associations and parageneses that cannot occur in nature purely because certain minerals respond to different precipitation mechanisms (under otherwise identical conditions)? What are these associations?

Perel'man (1967): Although the book is on "epigenesis – pedogenesis", much of the information is related to solubility and other chemical variables that are generally applicable to syngenesis – diagenesis of ore deposits. Insofar as the temperature, for example, increases during early to late diagenesis and catagenesis/burial metamorphism, data like the one presented in Fig. 207 is of interest. On p. 152 and in his table 26, for instance, Perel'man lists the "migrational intensity" of numerous elements under different pH – Eh conditions.

Andrews-Jones (1968; see Levinson, 1980, fig. 3-19, p. 143) tabulated the "relative mobilities" of all major elements according to Eh – pH of the environment.
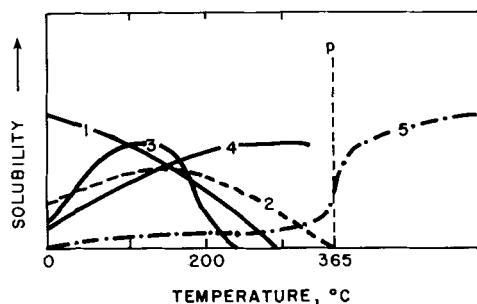
Fig. 207. Different types of solubilities of salts at constant pressure (about 1 – 5 atm) and rising temperature. *1* = $CaSO_4$ type; *2* = NaCl type; *3* = sulfate type; *4* = some halides; *5* = silicates. *P* is the critical point of water. (After Perel'man, 1967; see for original sources.)

Brooks et al. (1968) found that the observed concentrations of metals in interstitial water vary and that "predictions based on calculated solubilities can be misleading." Enrichment of Zn, Cd, Cu, and Co often occurs at the mud – water interface, and organic matter may be the source of these elements. Mobilization and transportation either to the surface or to a deeper layer may lead to localized concentrations.

Boyle (1968) described the eleven modes of occurrences of Ag in natural waters, i.e., in ionic form, as complexes, as colloids, as organic compounds, and adsorbed to various materials. This is followed by an outline of the nineteen modes of precipitation.

Note: This work represents fine examples of reviewing the mode of behaviour of one metal. Such data is usually disseminated in the literature. Similar summaries are needed for each element to assist geologists in offering plausible interpretations after having considered all possibilities and after explaining their preferentially selected processes.

Rashid/Leonard (1973) described sediment-associated humic acids and amino acids that effectively dissolved unusually large quantities of metals (up to 682 mg/g^{-1} of organic matter) from their insoluble salts. The presence of humic acids prevented the precipitation of metals as carbonates, hydroxides, or sulfides that would have resulted in the metal's immobilization. The organo-metal complexes thus formed should be able to migrate over considerable distances leading consequently to the enrichment of metals.

Crerar/Barnes (1974) described complex diagenetic deep-sea environment within sediments that controls physicochemical and biochemical mobility, precipitation, differentiation, remobilization and recycling, adsorption, bacterial fixation, cation substitution, and oxidation – reduction of Mn, Fe and trace elements. (See the geochemical profile in Fig. 208.)

Barnes (1975) provided data on the chemical order of deposition based on solubility data, among others, e.g., relative solubilities of sulfides in bisulfide complexes and in chloride complexes, predicted sequence of stabilities of bisulfide complexes, and relative ionic solubilities of sulfides. This data is then used to explain zoning (see Zoning), i.e., syngenetic – sedimentary, syngenetic – hydrothermal and epigenetic – hydrothermal zoning.

Crerar/Barnes (1976) provided information on solubilities of several copper minerals at higher temperatures. In addition, data at lower-temperature ranges is supplied that can be used in deciphering the origin of late diagenetic ore types.

Finlow-Bates/Stumpfl (1979, 1981) and Finlow-Bates/Stumpfl (1979/80) showed (Fig. 209) that a change of the metal solubility with falling temperature could lead to the lateral metal-facies zoning observed at Mount Isa, Australia.

Note: (a) Is a temperature fall the only way of changing solubility resulting in such
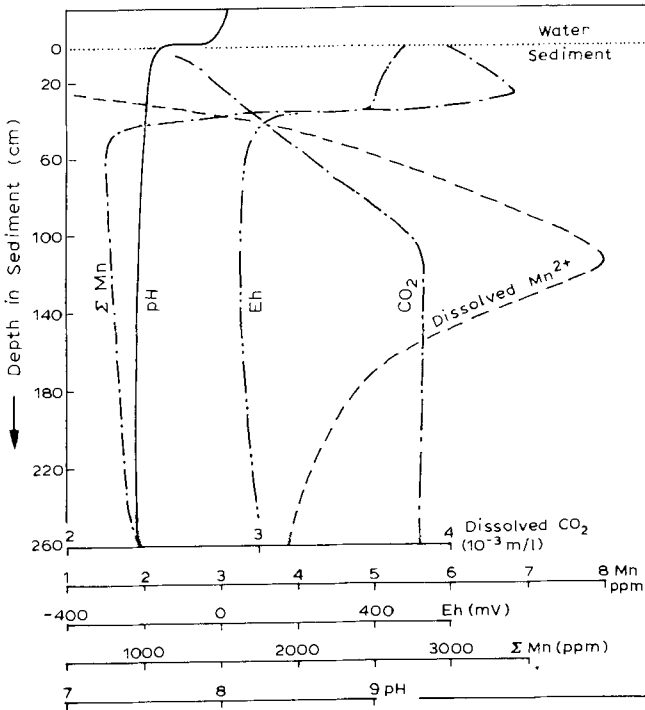
Fig. 208. Generalized geochemical profile on a marine sediment, showing vertical distribution of total Mn, dissolved Mn, Eh, pH and dissolved CO_2. (After Crerar/Barnes, 1974.)
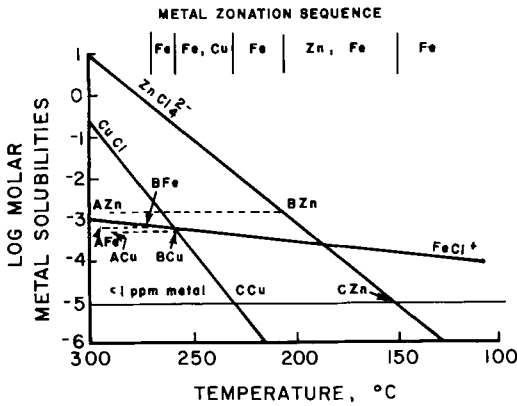
Fig. 209. Diagram showing how changing metal solubility with falling temperature could lead to the observed separation and composition of metal-bearing facies at Mt. Isa, Australia. A solution with a starting temperature of almost 300°C, pH = 4, S = 10^{-3} molar, pO_2 = 10^{-40} and initial metal contents at AZn, AFe and ACu has been assumed. Whereas change in any one of the assumed parameters will change the position of these curves, it will not change the gradients and the fundamental argument. (See for details Finlow-Bates, 1980.)

zoning? Have other possibilities been exhausted? (b) Once the metal has accumulated, what are the subsequent diagenetic – catagenetic (burial) geochemical conditions required to *preserve* the metal accumulations? (c) What conditions are required to remobilize them?

Finlow-Bates (1980), and many others, demonstrated the chemical and physical controls on the genesis of ore deposits. Much of the data on exhalative fluids may be applicable to other types of solutions, especially to mixed fluids. As a mere example, Figs. 210, 211 and 212 show the influence (or lack thereof) of pH and temperature

Fig. 210. Change in metal solubilities with change in pH for a solution at 250°C, S = 10^{-3}M, Σ Cl$^-$ = 1 M, and pO$_2$ = 10^{-48} atm. It can be seen that if pH was the dominant control on sulphide precipitation then orebodies would be zoned from Fe $\rightarrow$ Zn with Cu in all zones; pO$_2$ = oxygen fugacity (pressure). (After Finlow-Bates, 1980.)

Fig. 211. From the known zonation of orebodies, such as Mt. Isa (Australia) and the Kuroko deposits (Japan), the changes in metal solubility against the controlling variable should appear as above. The total reversal of the roles of Cu and Fe compared to Fig. 210 suggests that pH is not the main control on sulphide precipitation. (After Finlow-Bates, 1980.)
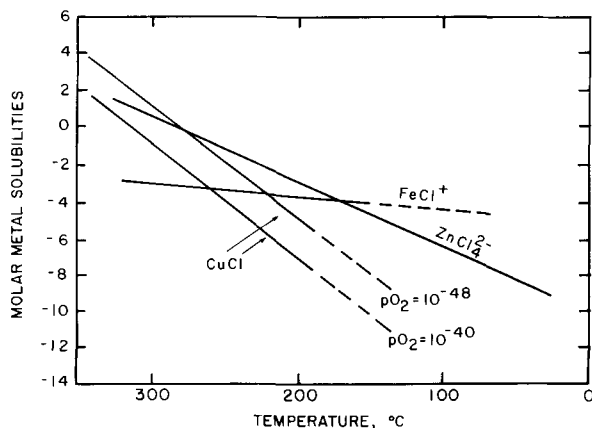
Fig. 212. Metal solubilities as chloride complexes against temperature (at 1 M NaCl, pH = 4). The effect on Cu solubilities by varying pO$_2$ is also shown. In the H$_2$Saq field the solubilities of Fe and Zn are not dependent on pO$_2$ (see figs. 11 – 13 in Finlow-Bates, 1980). The similarity of this diagram to Fig. 211 is quite striking. (After Finlow-Bates, 1980.)

on solubilities. Other data show the relationships between salinity and solubility of Cu, Fe, and Zn. The stability fields of Ca, Ba and Fe oxide, sulfate, and sulfide phases, are also presented by Finlow-Bates.

Wedepohl (1980) discussed the geochemistry of the Kupferschiefer deposits, comprising large horizontally and vertically zoned Zn, Pb, and Cu accumulations in the Upper Permian bituminous marl. The copper was concentrated in a restricted near-shore environment, whereas the Zn and Pb concentrated farther from shore. At 150 km from the former shoreline, the metal-rich sediments grade into bituminous marls (black shale facies) low in Zn, Pb, Cu, but still high in V, Mo, U, etc. The metal zoning, which is due to the low but increasing solubility of the sulfides in seawater, is in the order of Cu, Pb, Zn. Wedepohl discussed both syngenetic and diagenetic models and concluded that "a syngenetic and early diagenetic accumulation of metals in marls and shales . . . precipitated by bacterially produced sulfides, by organic residues and by carbonates from anoxic seawater mixed with continentally derived waters", is supported by all observations. Epigenetic processes caused only minor local remobilization (see Jung/Knitzschke, 1976).

Lippman (1980) provided phase diagrams of the aqueous solubility of binary systems (including $FeCO_3 - MnCO_3 - H_2O$).

Bilinski/Schindler (1982) and Mirona/Zotav (1980), respectively, offered data on the solubility and equilibrium constants of Pb in carbonate solutions and As^{3+} sulfide complexes (both at low-temperature conditions).

Jacobs/Emerson (1982) studied the trace-metal solubility in an anoxic fjord.

Mounin/Schott (1984) determined the solubility products of sodium carbonate minerals as applied to the origin of trona (an industrial mineral ore); and Jahnke (1984) discussed the synthesis and solubility of carbonate fluorapatite.

– See also Multi-factorial (e.g., Vaughan, 1976), Replacement, Solutions, and Zoning.

SOLUTIONS

Baas-Becking et al. (1960) published a classical paper on the pH – Eh limits of natural aqueous environments (e.g., see Figs. 81 and 213, and Table 70).
   Note: (a) Eventually, an attempt has to be made to (i) classify diagenesis according to Eh – pH and other simply to complexly related parameters; (ii) correlate (i) with all natural local and regional environments (e.g., see Fig. 213); and (iii) determine the secondary processes that under certain specific environmental settings can syngenetically to catagenetically concentrate or remobilize and reconcentrate metals and non-metals.
   (b) Investigations are beginning to establish the limits of natural conditions by us-
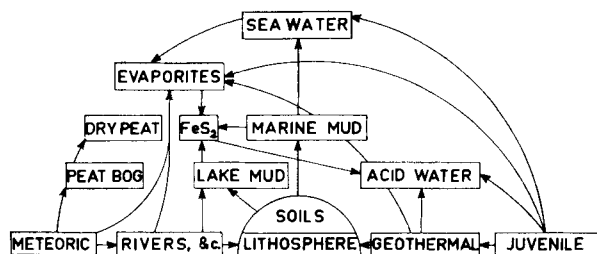
Fig. 213. Interrelations of the natural aqueous environments. (After Baas-Becking et al., 1960.)

ing more than two or three geochemical and geological variables. Especially the limitations of specific processes, for example, are not well understood as yet. Consequently, there is a lack of knowledge on the controls on metal zoning and subtle alterations (see Barnes, 1975).

(c) Curtis (1967) concluded that it is particularly difficult to equate certain diagenetic mineral assemblages with variations in the pH and Eh of the precipitating milieu(s), without considering all other influencing factors.

Strakhov (1967, 1969, 1971, in three volumes) provided considerable amount of data related to the migration of elements and complexes in solution and suspension, often controlled by climatic conditions. The form of migration of specific elements is given also, e.g., Fe: 94.8% in suspension versus 5.2% in solution: Mn: 87.1 vs. 12.9%; Ni: 94.9 vs. 5.1%; P: 84.3 vs. 15.7%; Co: 45.7 vs. 54.3%; Cu: 48.2 vs. 51.8%; and Sr: 44.3% in suspension vs. 55.7% in solution.

Note: (a) The above data must put certain constraints on the diagenetic behaviour of the elements, e.g., the mobility, distribution, differential separation, adsorption – desorption, diffusion, and precipitation patterns are all controlled. (b) The above quoted data are only a sample of the mass of information to be found in the three volumes by Strakhov.

Rickard (1970) supplied much data on the Cu-content of natural solutions, including subsurface waters (Table 71), factors controlling Cu-concentrations, and the geochemical cycle of Cu (see Cycles). Much of the information is directly applicable to syngenesis and diagenesis.

The following must be considered: (a) The connate thermal chloride-rich fluids contain the greatest amount of Cu; and (b) inasmuch as the "No. of analyses" are rather small, this data (and similar ones often provided in other publications) cannot be used to unequivocally prove which fluids, *in general,* are the real "ore-formers". *Exceptional* natural conditions provide the metal-carrying solutions – and 2 – 5 analyses most likely do not include potential exceptions. Additional data, therefore, is required.

Hitchon et al. (1971) investigated the composition of basinal, intraformational fluids, which are originally similar to seawater. Then they are altered as a result of

dilution by freshwater recharge and subsequently are concentrated by membrane-filtration and dissolution of evaporites to brines. Especially Mg, Ca, SO_4, Co_3, Sr, Br, and I were considered, but it was shown that Cu, Fe, Mn and Zn were all concentrated in formation waters. Their geochemical behavior, however, was not understood.

Rieke/Chilingarian (1974) in their book summarized many aspects of solutions. Interstitial solutions are either (i) syngenetic (formed at the same time as the enclosing rocks, or (ii) epigenetic (owe their origin to subsequent infiltration of meteoric and other waters into already formed rocks, or (iii) a combination of both. The main alteration processes affecting the chemistry of buried waters are: (a) physical (e.g., compaction), (b) chemical (reactions among rock minerals, organic matter, interstitial solutions, etc.), (c) physicochemical (filtration through clay membranes, adsorption/desorption, base exchange, etc.), (d) electrochemical, and (e) biochemical. The results may be: (i) concentration of dissolved solids, (ii) preferential increase or decrease of various dissolved minerals and organic matter, (iii) desalting of the water, and/or (iv) formation of saline fluids. Merely two additional

TABLE 71

Average copper concentrations in subsurface waters (calculations based on data in White et al., 1963; Rickard, 1970)

			No. of analyses	Average Cu (ppb)
Groundwaters			38	13
Waters with connate affilations	Oilfield waters[1]	NaCl type	2	170
		Na – Ca – Cl type	2	250
	Springs	NaCl type	4	28
		Na – Ca – Cl type	3	51
Waters with magmatic affiliations	Springs associated with volcanism	Geyser waters	5	4
		Non-geyser NaCl type	3	207
		Acid SO_4 – Cl type	2	95
		Acid SO_4 type	3	35
Waters with metamorphic affiliations	Springs	$NaHCO_3$-boron type	2	155
Miscellaneous waters	Springs associated epithermal deposits		9	13
	Springs depositing travertine		3	2

[1] Rittenhouse et al. (1969) analyzed the copper content of 823 oilfield waters from the United States. They found concentrations ranging from 1 ppb to 1 ppm, with mean concentrations of 10 – 100 ppb.

WATER ESCAPE CURVE
(Powers , 1959)
(Schematic)

WATER ESCAPE CURVE
(Burst)
(Schematic)

WATER CONTENT OF SHALES
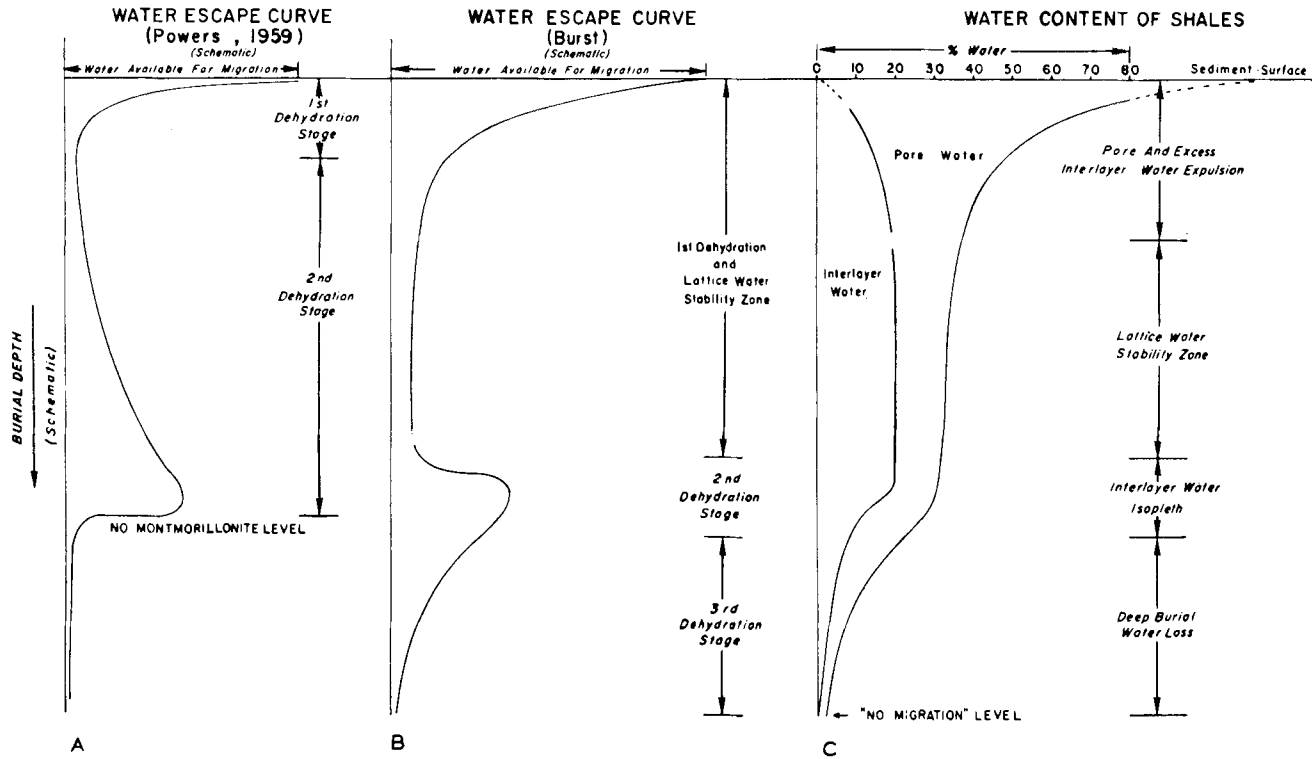
Fig. 214. Surface water redistribution. (A) Curve from Powers (1959) illustrating two-stage dehydration of montmorillonite sediments; (B) curve from Powers adjusted and reinterpreted as three-stage system; (C) water content (%) at various stages of dehydration. (After Burst, 1969, fig. 9, p. 86, in Rieke/Chilingarian, 1974, fig. 175; see for original data sources.)

370

aspects of interest are mentioned here: (a) During maturation of a clay-rich sedimentary pile, montmorillonite is dehydrated during two or three stages, with a large amount of fluids being released (Fig. 214). (b) The alteration of gypsum to anhydrite can also release water, in particular with an increase in temperature during burial of the sediments (Fig. 215). Little information is available as yet on the release or mobilization of metals during the production of the fluids from clays and evaporites, for example.

Bradley (1975) discussed the chemical effects of pore waters. According to him, the fluids in sandstones become more saline with increasing depth, but they may become fresher with depth in the *abnormally high-pressured* zones. (As observed by one of the writers, however, the water can become fresher with increasing depth in *normally pressured* formations; see Rieke/Chilingarian, 1974.) The shale water is fresher
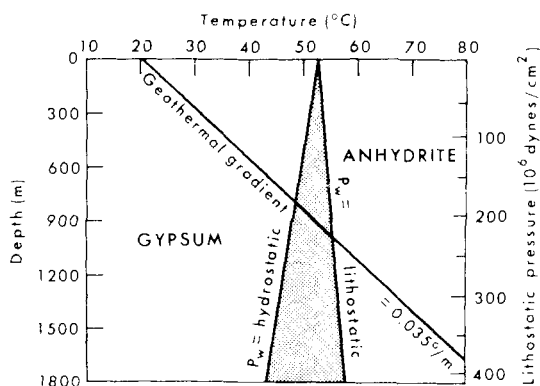
Fig. 215. Pressure – temperature relationship between gypsum and anhydrite where activity of H_2O = 0.93 ($\approx$ 2 M NaCl). (After Hanshaw/Bredehoeft, 1968, fig. 8, p. 1116, in Rieke/Chilingarian, 1974, fig. 174; see for original sources.)
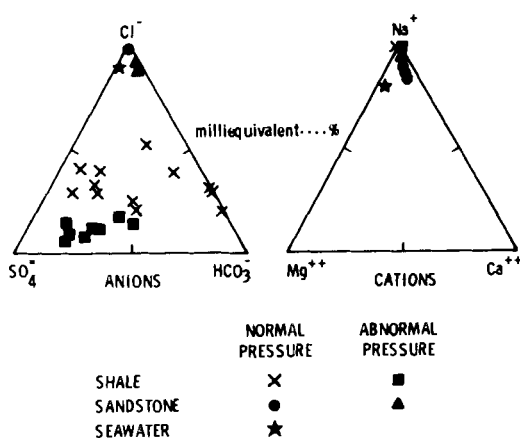
Fig. 216. Ion concentration in waters from sandstones and shales of Manchester field area, Louisiana, U.S.A. (After Bradley, 1975.)

than that in associated sandstones; water in undercompacted shales, however, is more saline than that in well-compacted shales. Individual ion-concentrations of water from shales differ radically from those in associated sands (Fig. 216). Many other aspects were discussed by Bradley, e.g., osmosis.

Engler/Patrick (1975) studied the stability of sulfides of several metallic elements in flooded and non-flooded soils, and Berner (1980a) discussed the dissolution of pyroxenes and amphiboles during weathering. Such studies of soils and weathering can offer data of interest to the diageneticists, e.g., see Berner's SEM observations of etching features which often are the product of an incipient diagenetic process, and Evan's (1964) work on the organic solubility of minerals in sediments (see Organic matter).

Back et al. (1976) outlined the geochemical evolution of ground water. An example is presented in Fig. 217. Similar evolutions of hydrologic systems in sedimentary basins are required to understand the origin of both oil and ore mineralization (see Schvartsev, 1976, below).

De Boer (1976) provided data on the changes in the chemistry of solutions as controlled by pressure and temperature through geologic time.

Schvartsev (1976) pointed out that the "transformation" or "evolutionary history" of the composition of water in the course of lithogenesis has not been investigated by many geochemists. "Subsurface-fluid synthesis and decomposition" occurs in all stages during basin development and rock genesis − from weathering, sedimentation or syngenesis, through diagenesis and epigenesis/catagenesis, to metamorphism.

White (1974) discussed thermal and mineral waters of different origins that formed "hydrothermal" ores. Some waters are contemporaneous, whereas others are "epigenetic" in relation to their hostrocks. The most useful data to deduce the origin of ore-forming fluids are: (i) fluid inclusions in ore and gangue minerals; (ii) isotopic analyses (but with numerous *assumptions and limitations* to be considered); (iii) results of studies of natural waters and active geothermal systems; and (iv) diagenetic features. White offered a classification of natural waters, and outlined problems for future research. He also referred to some important publications.

Barnes (1979) reviewed the "sedimentary genesis of hydrothermal fluids" during basin evolution, i.e., from early to late diagenesis and burial metamorphism. The various aspects of aqueous solutions in sedimentary basins were discussed: (1) sources, fluid volumes involved during burial/compaction, and porosity reduction; (2) influence of temperature, pressure, density, and viscosity; (3) salinity, dissolved species, Eh, pH; (4) controls on major-element geochemistry such as interaction with evaporites and membrane-filtration; (5) other mechanisms (Soret effect); (6) ore-forming components in sedimentary waters (S, Pb, Zn, Ba, Sr, F); (7) properties of some ore-forming fluids (isotopes, chemicals, temperature − salinity relations,

sites of ore precipitation); and (8) flow of subsurface brines during compaction, tectonic deformation, and evolution in thermal regions.

Goulevitch (1980) discussed in detail the low-temperature syngenetic origin of sulfide deposition, as based on the concepts by Barnes/Kullerud (1961), Helgeson (1969), Anderson (1975), Ryabinin/Bogaschuk (1977), and Turner/Gustafson (1978), who have dealt with the solution, transportation, and precipitation environments of hydrothermal systems, for example.

Note: (a) Much of the geochemical and geological data on "hydrothermal" solutions and conditions applies to the non-magmatic hot fluids ranging from diagenetic
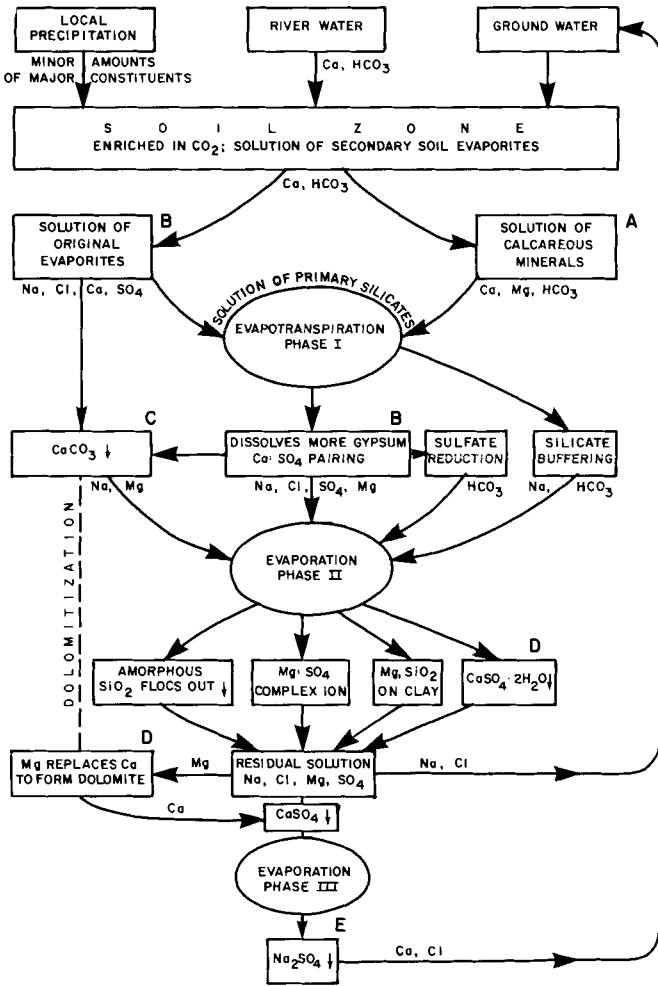
Fig. 217. Schematic diagram of the geochemical evolution of the groundwater of Rechna Doab. (After Back et al., 1976; see for details.)

to metamorphic types, including basinal compaction fluids. (b) Much experimental data of "hydrothermal" systems is at a relatively low temperature and pressure to be useful to those studying "warmer" basinal solutions.

Nakayama et al. (1981) examined the dissolved state of Cr in seawater. How does this state affect the coprecipitation of Cr in Mn-nodules and any possible diagenetic remobilization?

— See also numerous related topics, such as Eh, Fluid inclusions, Multi-factorial, pH and Solubility.

SOURCES

Morita (1955) studied the Cu- and Zn-distribution in various phases of the earth materials, but Fenton (1984) was more specific in his geochemical characterization of siliciclastic sedimentary rocks. The latter concluded that in source rock investigations one has to compare the elemental composition of sand with those of muds.

Wedepohl (1964) provided pertinent data and concepts related to syngenesis and diagenesis of the Kupferschiefer. He also discussed the sources of metals. Evidence is provided that several elements (V, Cr, Zn, Mo, etc.) are fixed by iron oxides of red-bed-type sandstones (Fig. 218). Through reduction of ferric iron, these elements may have passed into solution, i.e., they were mobilized/remobilized from the sandstones and transported into stagnant waters to be precipitated as "syngenetic" accumulations.

Note: A number of questions arise here such as: Is this an example of syngenetically accumulated metals adsorbed on iron oxide, diagenetically remobilized and transported to be in turn again "syngenetically" (re)precipitated?
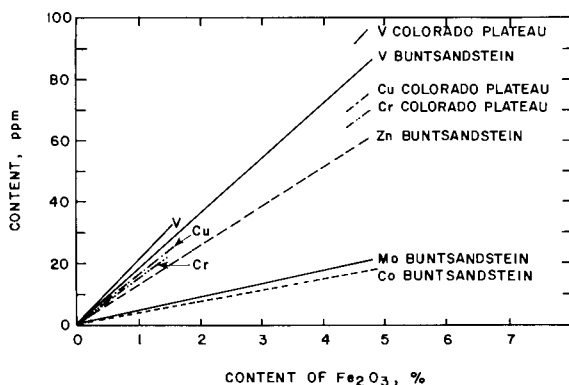
Fig. 218. Relationship between Fe_2O_3, and V, Cu, Cr, Zn and Co contents in red sandstones of the Triassic in Germany and of the Colorado Plateau, U.S.A. (After Wedepohl, 1964; see for original data sources.)

Curtis (1967): Inasmuch as the syngenetic (i.e., pre-diagenetic) clastic sediment contained Fe-containing minerals (such as chlorite and clays), during the study of diagenesis of iron minerals (siderite, pyrite, ankerite). Curtis differentiated between total, extracted, externally derived, original and diagenetically formed iron fractions and iron sources (Fig. 219).

Krauskopf (1967b, 1971), Smirnov (1968), and Laznicka (1985c) summarized the general aspects of metal sources, including sediments and volcanics. Some aspects bear directly on diagenesis.

Elliston (1969): By utilizing the theories of thixotropy and colloidal chemistry he proposed that the adsorbed metals in sediments can be released into interstitial (compaction?) fluids to be (re)precipitated elsewhere as gelatinous masses or nodules and as veins. His ideas bridge the syngenetic versus epigenetic controversy and consitute an important contribution (see Fig. 220).
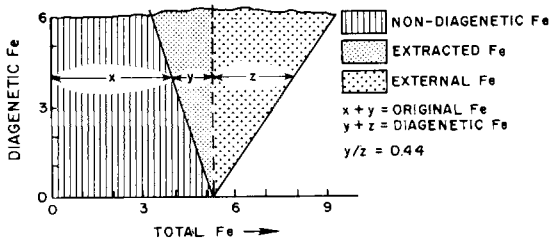
Fig. 219. Diagrammatic representation of iron distribution in the Mansfeld sediments, Germany (for details see Curtis, 1967.)
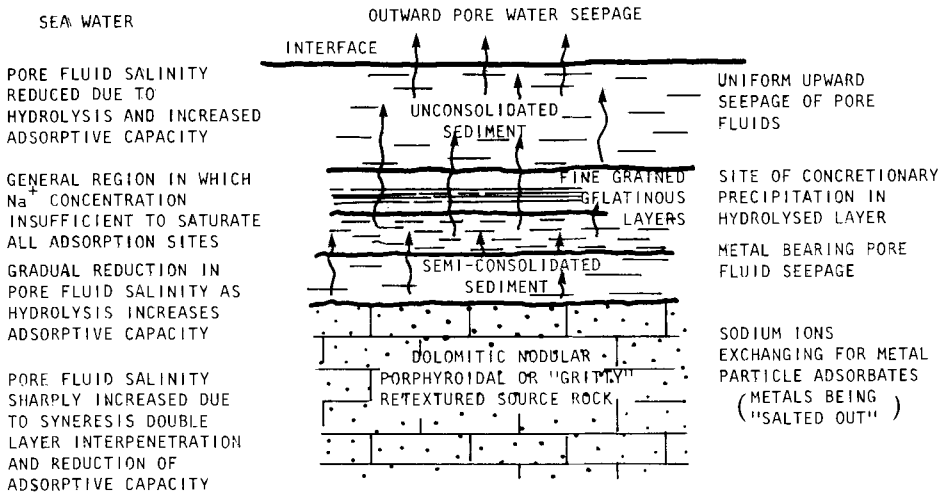
Fig. 220. Generalized scheme of syngenetic ore formation. (After Elliston, 1969.)

Vine/Tourtelot (1970) presented a comprehensive summary of the geochemistry of black shales. The elements are tied up in the detrital minerals, carbonates, and organic matter. The latter is particularly rich in "syngenetic – diagenetic" elements, and may provide a local sink for minor elements after burial. Thick units that include much organic matter and are exposed to hypersaline solutions may provide a source of mobile elements that are expelled and transported to adjacent more permeable rocks.

Robertson (1970) studied the Co-distribution in oceanic waters; Carignan/Kalff (1980) discussed the P-sources for aquatic weeds, attempting to determine whether the water or the sediments acted as the source; and Lisitsyn et al. (1982) investigated the relation between element influx from rivers (see River environments) and concentration in oceanic sediments. The source of many elements in the ocean water and sediments have as yet not been unequivocally determined insofar that hydrothermal, seawater and land-derived sources have been proposed.

Hirst (1971) compared the acid-soluble contents of Co, Ni, Cu and Pb of modern deposits with those of older consolidated sedimentary rocks. He found a considerably smaller amount in the older rocks. Hirst stated that "some of the differences in proportion of acid-soluble metal to total metal may be ascribed to removal of metal by connate brines expelled from sediments during consolidation", i.e., during the late-diagenetic to catagenetic stages. For example, recrystallization and clay-mineral neomorphism may have expelled adsorbed – absorbed metals.

Piper (1971) determined the distribution of Co, Cr, Cu, Fe, Mn, Ni and Zn in an anoxic fjord. The metal distribution was controlled by Eh, pH, H_2S, and organic matter.

Horvath (1972) and Mitchell (1972) (merely to mention two of many publications on soils) provided data on the trace elements of soils (e.g., Mn, Fe, Se, Ca, Co, Cu, Ni, Mo, Cr, etc.) and discussed mechanisms of metal transfer (e.g., diffusion, mobilization), for example.
   Note: (a) Insofar as interdisciplinary approaches have often made advancements, the concepts developed by pedologists ought to be critically reviewed to see which ideas can be applied to problems of the geochemistry of sedimentology, diagenesis of metals, alteration processes, halmyrolysis, etc. (b) Sorption – desorption processes in soils, the relations between organic matter and complexing, etc., may be easier to investigate in soils than in the oceanic milieus. Although the environments are quite different, certain fundamental mechanisms may be similar. Also, more data is required on the soils acting as potential sources of metals and non-metals.

Eargle/Weeks (1973) like others (see also Zielinski, 1981), advocated diagenetically altered tuffaceous sediments as the source for uranium. Interesting also are the four very different environments in which the ore was precipitated along the Texas coastal plain region: (a) nearshore sandstones, (b) sandstones interbedded with claystones along the sides of major paleo-stream-channel deposits, (c) sandstones

near faults along which natural gas containing H_2S has migrated; and (d) sand-stones situated above the sulfurous caprock of a salt dome. The oxygenated, alkaline groundwater carrying the uranium moved into various settings where reducing conditions were conducive for precipitation.

Samama (1973, 1976) and Bernard/Samama (1976) represented the school-of-thought that basement (granitic, etc.) rocks, and continental/terrigenous rocks in general, can supply metals. (See also Strakhov's three volumes on lithogenesis and ore genesis.) In particular the sandstone-type and red-bed type ores may have derived their metals from a land-mass. Alternative sources, however, have been suggested, e.g., leaching of associated volcanics and arkoses by saline solutions. The leaching may have occurred during the diagenetic or catagenetic/burial metamorphic phases.

The following topics were treated by the above-cited authors: (1) the heavy-metal distribution in terrigenous clastic phases; (2) the behaviour of metals during weathering (e.g., during allitization, monosiallitization, bisiallitization, podzolization); (3) regional examples of relations between weathering of a basement and the geochemistry of a sedimentary basin (e.g., differential balance sheets of elements, geochemical zonation related to zonal weathering processes: $U - Cu - Pb$); (4) pedological differentiation, and (5) sandstone-type ore deposits. Although Samama (1973, 1976) concentrated on studying weathering in the continental source area, he realized that once the metals reach the depositional environment, additional factors have to be considered in the origin of ores, namely, the mechanisms of syngenesis and diagenesis, such as concentration – precipitation and possible remobilization – (re)precipitation in several cycles.

Lindsey (1975) treated the diagenesis of tuffs during zeolitization, which resulted in the release of F, U and Mn, among others, and in the origin of uranium deposits and $Be - F$ concentrations.

Mimran (1977) described the deformation of limestone that consequented the large-scale migration of calcium carbonate, e.g., up to 90% by volume loss of limestone by compaction and pressure solution. In the present context of the chapter on diagenesis, this paper proves that the large volumes of carbonates and evaporites can be removed by dissolution during basinal evolution. As advocated by some researchers, the released metals can subsequently form ore deposits.

Nissenbaum (1977) revealed that minor and trace elements in the Dead Sea are (a) incorporated into diagenetic/authigenic carbonates and sulfides in the sediments (Sr, Zn, Cd, Fe); (b) involved in the formation of soluble salts or chloride complexes (Li, Mn, Pb); and (c) removed due to the reduction and origin of sparingly soluble compounds (U). The interstitial fluids are rich in Mn as part of inorganic complexes. Also, in the Dead Sea water, U and Fe are depleted, Cd and Mn are enriched, and Pb, Mn, Cu, Co, Ni are highly enriched.

Sonnenfeld et al. (1977) proposed that within a density-stratified evaporite pan, the

interface between surface waters and a hypersaline brine is being replaced by gypsum. Waters beneath the photozone are anaerobic and deposit only organic oozes. Major- and trace-element (including base metal) concentrations in the brines increase with depth (Fig. 221). Both the gypsum (Fig. 222) and organic matter (Fig. 223) extract significant quantities of the metals. The system provides a model for base-metal concentration in a euxinic-shale shallow-water milieu. (See also Fig. 224; Routhier, 1980.)

McEwen (1978) discussed the diffusional mass-transfer processes during pressure solution, which resulted in the reduction of mobile elements (e.g., Ca, Ba, Sr) and the concentration of immobile elements (e.g., Mg, Al, Fe, Mn, Ti). Similar studies must be conducted on the dissolution of limestones (e.g., during widespread stylolitization) as a mode of metal-element-mobilization mechanism.
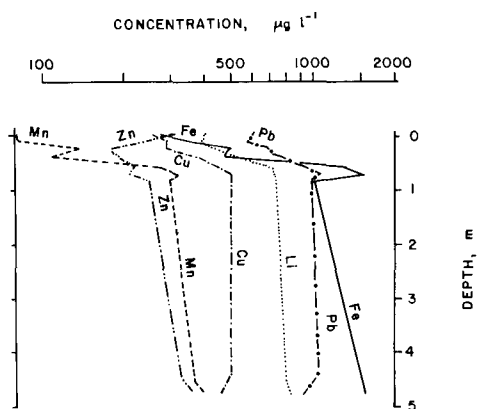
Fig. 221. Trace-element concentration in waters of Lago Pueblo, 145 km north of Caracas, Venezuela. (After Sonnenfeld et al., 1977.)
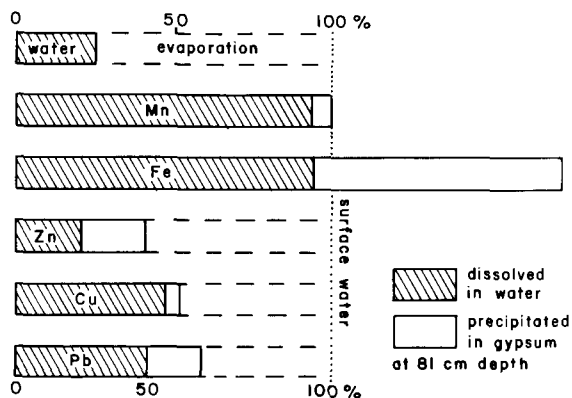
Fig. 222. Trace-metals balance in water at the level of gypsum precipitation. Top bar represents degree of concentration of brine, relative to seawater. (After Sonnenfeld et al., 1977.)
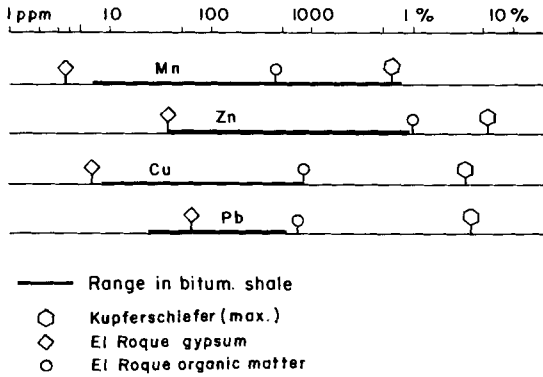
Fig. 223. Lago Pueblo samples compared to bituminous shales. (After Sonnenfeld et al., 1977; see for original data sources.)
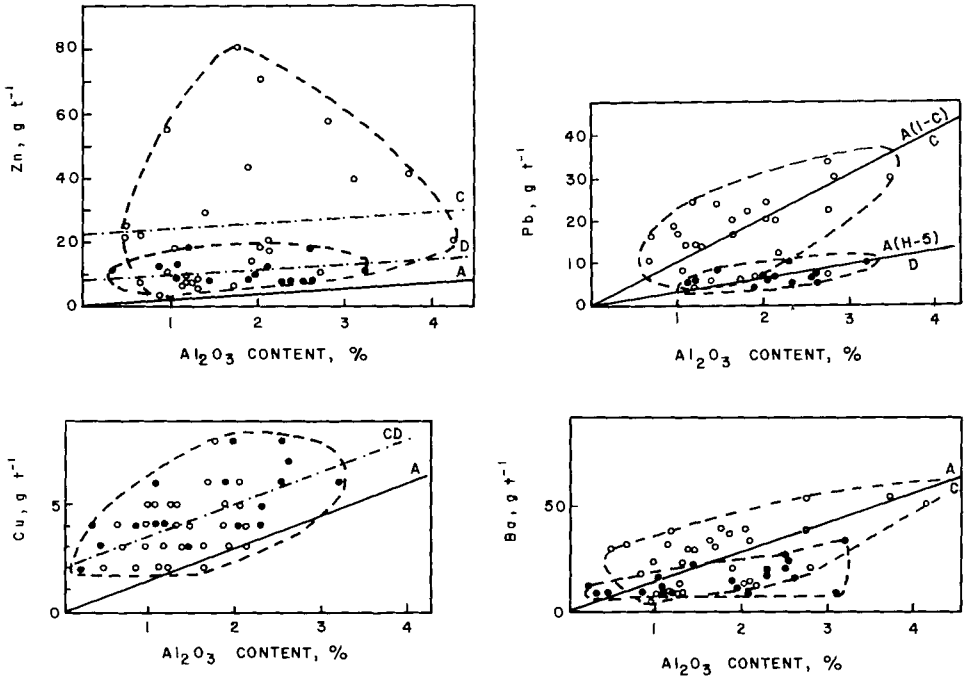
Fig. 224. Dolomitization and expulsion of metals. (After Routhier, 1980, fig. 82, p. 333.)
Correlation metal (Zn, Pb, Cu, Ba) vs. Al_2O_3 in limestones and secondary dolomites; Trèves (France). By Macquar, unpublished.
   Common legend. Empty circles: limestones; black circles: dolomitic facies. A (straight line) = correlation metal/Al_2O_3 in argillaceous facies; generally well defined by one elliptical flat cluster, not shown on diagrams, case of Pb excepted. For Pb two lines must be drawn depending on stratigraphic level: A(H-S) for Hettangian and Sinemurian, A(L-C) for Lotharingian and Carixian. C or D (straight lines) = correlation metal/Al_2O_3 in limestones (C) or dolomites (D), defined from a cluster of white or black circles. C and D can be superposed or fall in with A (e.g., Pb and Ba).

Fig. 226. Migration of elements in the "exosphere" and metallic provinces permanency; idealized section. *M* is any metal or other chemical element. This sketch illustrates two models: direct deposition in marginal environment or way down to a basin and later up towards the shore. (After Routhier, 1980, fig. 77, p. 324; see text therein.)

Lebedev/Nagaytsev (1980) studied the minor elements in metamorphic rocks as an ore source set free by remobilization. Preat et al. (1983) investigated the features of Pb – Zn – Ba – F veins formed by lateral-secretion origin rather than by a long-distance supply of the metals, as provided by geochemical data collected by these reasearchers.

Barsukov/Ryabchikov (1980) and Krivtsovo (1983), in addition to Laznicka's (1985c) excellent review, offered general comprehensive summaries of the metal sources of ore deposits, whereas Brown (1984) dealt specifically with those of the stratiform Cu-deposits, and Bubnoy (1983) of the source of the Sn-deposits in geosynclinal regions. What is the diagenetic – burial metamorphic behaviour of Sn, for example? Calvert/Piper (1984) examined the multiple diagenetic sources of metals in the Mn-nodules in the deep oceans.

Heath (1981), as many others before him, discussed numerous aspects of diagenesis during the origin of deep-sea ferromanganese nodules, especially related to the source of the metals and the concentration mechanisms resulting in the absorption of the metals in the concretions. There are four sources: (1) dissolved metals in rivers flowing to the sea, (2) leaching of newly formed oceanic crust by seawater hydrothermal systems at mid-ocean spreading centers, (3) anoxic diagenesis of hemipelagic sediments, and (4) oxic diagenesis of pelagic sediments. Eight basic concentration processes have been invoked to account for the availability of transition metals for incorporation into ferromanganese nodules: (1) Vertical (biological) transport; (2) by settling particles, precipitation from waters; (3) upward diffusion of metals dissolved in pore fluids by both anoxic and oxic diagenetic reactions; (4)

authigenic reactions in surficial sediments; (5) bacterial activity in surface sediments and on nodules; (6) activity of epibenthic microfauna on nodules; (7) preferential incorporation of dissolved metals in specific Fe – Mn oxyhydroxide minerals; and (8) local seafloor volcanism.

The recent ocean and lake systems offer an environment par excellence for all aspects of diagenetic studies, including ore genesis.

Zielinski (1981), Steven et al. (1981), and Henry/Duex (1981) studied experimentally the leaching of volcanic glass as the source of uranium. Pervasive devitrification and zeolitization are significant processes that lead to the mobilization of uranium either directly into groundwater or to sites that make the uranium available for dissolution and removal in the hydrologic regime to be precipitated and concentrated elsewhere. Much of the released uranium may be adsorbed by iron hydroxides before significant migration. Mitchell et al. (1981) demonstrated that if carbonates are present, the organic matter and pyrite in limestones, for example, furnish reducing conditions that precipitate the uranium (see Karst). The identification and detailed study (including the diagenetic history) of the metal-source rocks *as part of an exploration program* is especially noteworthy. Is this confined to the exploration for uranium? In oil exploration, the recognition of the source beds has always been paramount.

Goodell/Waters (1981), Walton et al. (1981), Robinson/Spooner (1982), and Zielinski (1983) all treated at some length the possible sources of uranium from volcanic, volcaniclastic, volcanic glass, and tuffaceous sedimentary rocks. Robinson/Spooner discussed the U-sources of the conglomerate-hosted deposits at Elliot Lake. Zielinski proved that alteration of rhyolite glass is a highly efficient way to (re)mobilize U, but more advanced alteration is required. Many more studies on U-mobilization are required inasmuch as contradictory information has been published.

Rickard (1981) deliberated on the isotopic constraints on the source of Pb in a sandstone-hosted Pb – Zn deposit.

Förstner (1982) studied the differentiation/fractionation of the major chemical forms of metals in Recent aquatic deposits (e.g., limnic sediments, pelagic Fe/Mn-rich deposits, and coastal marine sediments). The effects of autochthonous phases on the enrichment or reduction of heavy metals in lacustrine sediments, for example, is given in Table 72. (See also Coprecipitation.)

Glassley (1983) deliberated the deep-crustal carbonates as CO_2-fluid sources as evidenced by metasomatic reaction zones. Can such data eventually be extended to catagenetic – diagenetic – surface-exhalative studies?

Koma et al. (1983) examined the total S-content and sedimentary environment of a geologic complex and discussed the S-sources.

Laznicka (1985d) discussed the metal sources of ore deposits and his contribution is strongly recommended to both theoreticians and explorationists.

Dill (1984) studied the hydraulic system of ascending and descending ore-forming fluids (Fig. 227), the relation between heat source and hostrock's preconcentration of U; and modeled the sediment-hosted and igneous-derived elements and vein-type deposits (Fig. 228). This is a neat study combining numerous variables, including sources and (re)mobilization, ranging from syngenesis – diagenesis to epigenesis of various types.

Miller/O'Nions (1985) investigated the source of Precambrian chemical and clastic sediments by examining the geochemistry of the BIFs, for example. In this context they discussed the burial and diagenetic mobility of trace elements.

TABLE 72

Effects of autochthonous phases on the enrichment or reduction of heavy metals in lacustrine sediments (after Förstner, 1982, p. 193)

	Source[1]		Lake examples	Enrichment $(+, ++)$ Reduction $(-, --)$
	Endogenic	Authigenic		
Silicates				
Opaline silica	x		Lake Malawi[2]	$--$ HM (heavy metals) $-$ Cu
Nontronite		x	Lake Malawi[2]	$\pm$ HM; $+$ Co, Mn
Carbonate				
Aragonite	x		Van Gölü (Turkey)[2]	$+$ Mn; $\pm$ Zn; $--$ HM
Mg-calcite	x		Balaton (Hungary)[2]	$\pm$ Mn, $-$ Fe, Cu, Zn
Ca-dolomite		x	Lake Neusiedl (Austria)[2]	$--$ Cu, Co, Ni
Siderite		x	Birket Ram (Israel)[3]	no effect
Sulphate				
Gypsum	x		Lake Hart (Australia)[2]	$--$ all HM
Alunite	x		Lake Brown (Australia)[2]	$--$ Fe, Mn, Zn, Cr; $-$ Ni, Cu; $\pm$ Pb
Sulphide				
Pyrite		x	Black Sea[4]	$+$ Cu, Ni; $\pm$ Zn, Cr
Hydrotroilite	x	x	Lake Constance[5]	$+$ Co, Cu, Cr, Ni; $\pm$ Pb, Zn, Mn
Organic substances	x		Lakes in Norway[6] Perch Lake, Ontario[7]	$+$ to $++$

[1] Jones and Bowser, 1978; [2] Förstner, 1978; [3] Singer and Navrot, 1978; [4] Volkov and Fomina, 1974; [5] Förstner, 1981; [6] Tobschall et al., 1978; [7] Jonasson, 1976.

Laznicka (1985e) and Valkovic (1983), respectively, reviewed the geological association of coal and metallic ores, and trace elements in coal. Can elemental remobilization from the coal supply ore-forming metal-bearing fluids?

Gordeev (1984), Boyle et al. (1985) and Kremling (1985) provided data on the sources of metals in three environments, namely documented by river discharge into oceans, trace-metal enrichments in the Mediterranean Sea (five sources were recognized, of which the anthropogenic – pollutional source is difficult to differentiate from naturally derived inputs by using flux-balance calculations), and the metal (Cd, Cu, Ni, Mn, Al) distribution in some shelf and open-ocean surface waters. The latter investigation discussed eolian and biological cycles and the relation between salinity and metal contents, among others.

– See also Multi-factorial, Remobilization (e.g., several papers on uranium sources from tuffs), and Volcanic – exhalative (e.g., Valette, 1973).
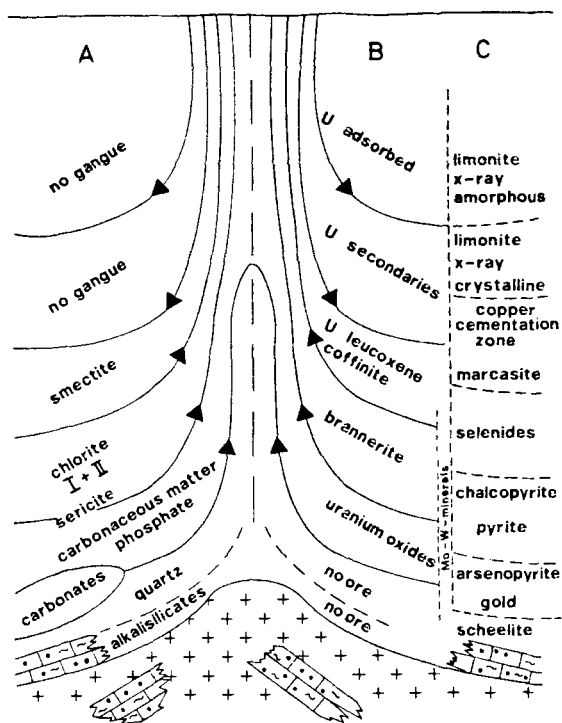
Fig. 227. Schematic diagram of Höhensteinweg ore mineralization showing the ascending (arrows) and descending fluids. The lower half was taken to represent the relation (idealized) between heat source and hostrocks' preconcentrating uranium. (After Dill, 1984.)

SPECIALIZATION

Zakrutkin (1980) described geochemical specialization of sedimentary basins, including particular environments such as lakes, seas, oceans, etc. More geological (lithological, mineralogical, etc.), geochemical, and geophysical "specialization" studies ought to be attempted which could result in geochemical/geological classification schemes of ore-forming environments as well as of their syngenetic – diagenetic – metamorphic processes and settings.

Fenton (1984) studied the geochemical characterization of clastic sedimentary rocks. Similar approaches are required in metal source-rock studies to establish the elemental compositions of mud- and sand-enriched lithologies, for instance.

STRUCTURES – STRUCTURAL CONTROLS

McClay (1979) interpreted folds and associated structures of the Ag – Pb – Zn orebodies of Mount Isa as the result of tectonic deformation. These folds were thought earlier to be "sedimentary" syngenetic – diagenetic in origin by some
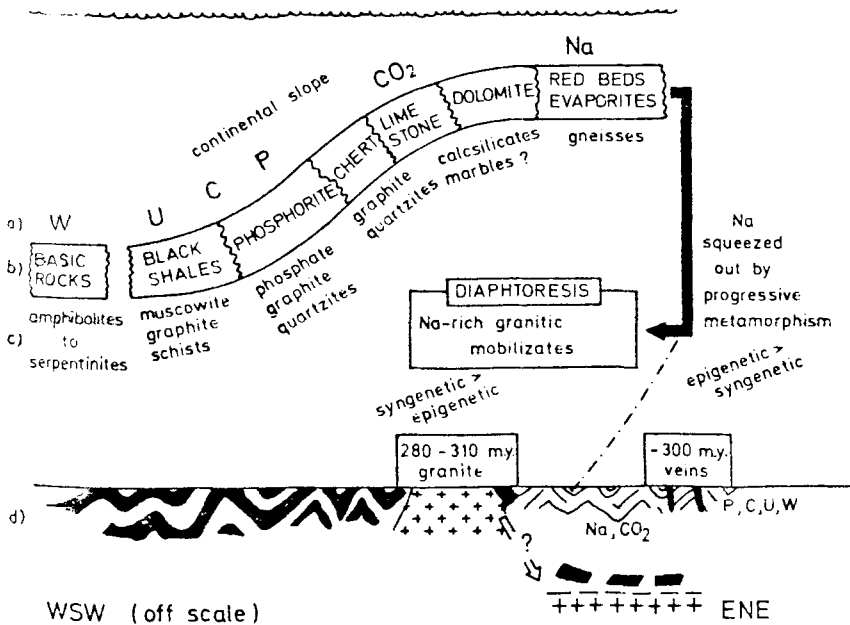
Fig. 228. Schematic representation of sedimentary-hosted and igneous-derived elements and vein-type deposition. (a) Elements to be found in source rocks and veins; (b) continental slope and lithology modified as to igneous source rocks; (c) metamorphic rocks cropping out in the area under study in NE Bavaria (principal types of rocks); (d) cross-section through the area under study (WSW – ENE, off-scale). (After Dill, 1984.)

researchers and as of "diagenetic-crystallization" origin by others. Many problems remain in differentiating the numerous textures – fabrics – structures of primary and secondary derivation, i.e., of sedimentary-depositional, soft-sediment- and lithified-sediment-diagenetic, tectonic, volcanic, and igneous origins.

Brookins (1980) opined that all unconformity-associated vein-like uranium deposits have conventionally been explained by hydrothermal processes (± tectonic control), metamorphism of original syngenetic/diagenetic or early epigenetic sedimentary deposits, mechanical accumulation, supergene processes, or some combination of these mechanisms. Exploration is usually restricted to the basin edges where the distance to the unconformities is minimal. Thus, the interiors of the basins have not been intensively explored. The unconformities, however, are not necessarily the primary control for ore localization. By using an example from Oklo, it was suggested that the deposits are similar to Phanerozoic syngenetic/diagenetic/ early catagenetic sandstone-type ore concentrations.

Cloud/Lajoie (1980) studied "defluidization" structures in littoral sands; Postma (1983) examined the "water-escape" structures; and Boulter (1983) the post-lithification deformation of sandstone dikes as possible criteria for "tectonic dewatering". Much more data is needed to establish field and laboratory guides and criteria that can assist in the recognition of paleofluid movements and in the reconstruction of the paleohydrologic evolution of sedimentary sequences (e.g. see also Compaction, Hydrology, Evolution, and Multi-stages).

Dzulynski/Sass-Gustkiewicz (1980, 1985) attempted to provide evidence for a "hydrothermal – epigenetic" origin of the Cracow-Silesian (CS), Eastern Alpine (EA), and some Mississippi Valley (MV) types of Pb – Zn deposits, in contrast to the sedimentary (syngenetic – diagenetic and/or diagenetic – epigenetic), exhalative – sedimentary (exhalative syngenetic – diagenetic and/or exhalative diagenetic – epigenetic), and meteoric-karst-type of epigenetic genesis. Dzulynski/Sass-Gustkiewicz concentrated on the mechanisms of ore emplacement as seen by the spatial position of the ore, centered around selected structures that are either controversial or diagnostic. These structures range from micro- to macroscopic types.

Note: These are interesting contributions insofar as these authors re-interpreted structures commonly considered as being indicative of syngenetic – diagenetic origin, to be in fact late-stage epigenetic features, with the ore formed by ascending hot (= hydrothermal) solutions. These structures are, for example: internal sediments, various types of breccias, karst features, solution structures, depositional – sedimentary structures such as cross-lamination, graded-bedding and cavity fillings – all of which can form in a large dissolution cavity system within a carbonate hostrock. The vertical distribution pattern of metasomatic ore, starting with fissure veins and vein breccias at the bottom to karst ores at the top, suggests that the ore-forming solutions were ascending epigenetic hydrothermal in nature. These authors concluded that in one system an association (or a paragenesis) of several generations of epigenetic, diagenetic, and syngenetic ores can form.

Bubela (1981b) examined banded sulfide ores in sediments formed from flowing liquids, whereas Solov'yev (1981) described Mn-rich stalactites and stalagmites in ore deposits.

Acharya et al. (1982) discussed evidence for sedimentary – diagenetic crystallization and migration in BIF deposits (see also Textures; e.g., the paper by Dimroth).

Einsele/Seilacher (1982) provided some details on the origin of syndiagenetic cyclic ore deposits event stratification, and the source (black organic-rich) and host (carbonate) rocks, e.g., Kupferschiefer.

Hagni (1982) discussed the influence of the original hostrock character upon the alteration and mineralization of the Mississippi Valley-type ore deposits. The sizes, cross-sectional shapes, arcuate map patterns, and other features of the dolomite "cores" in the mining areas are suggestive of bioherms, which are easier to recognize elsewhere where they are not altered by dolomitization, silicification, and mineralization. Fracturing, folding and dissolution controlled the localization of the ore.

  Note: (a) As pointed by Hagni, the original depositional structures have been ignored in the study of ore localization, which ought to be corrected. (b) Fracturing, folding and dissolution can occur very early in the history of "reef-to-basin" sedimentary complexes. These features can be of diagenetic origin within the reef that has been *lithified very early,* while the unconsolidated basin sediments are *still compacting,* as mentioned by Wolf (1976a).

Kim (1982) offered data on the structures and textures, among others, of the manganese nodules. These included megascopic concentric layers, core structures, unconformity and fissure-filling structures, in addition to microscopic colloform, fragmental, and diagenetic features. In Fig. 229, he classified the colloform textures/microstructures, which are composed of three basic units: banded, cuspate, and globular. Each one of these three basic textural units reflects a different mode of nodule growth controlled by physical and chemical environments.

Lehne/Amstutz (1982) described "megascopic textures" (= structures) of sedimentary and diagenetic origin in and around $Cu - Pb - Zn - Ag$ ore deposits, such as stratification types, geopetal and slump structures. These suggest a synsedimentary – syndiagenetic origin (as to time!), but the source may have been volcanic – exhalative. A distinction was made between timing and source in choosing the term; hence, the deposit can be referred to as a "volcanic – exhalative syndiagenetic" deposit.

Schulz (1982) listed features in the $Zn - Pb$ carbonate hostrocks that suggest the origin of the ore within a paleokarst system. These textures/fabrics are not necessarily indicative of a "post-diagenetic – hydrothermal replacement" origin (as proposed earlier), but could equally well reflect an "extrusive – sedimentary" mechanism. Therefore, it is important to search for the *few decisive* field and

TEXTURAL UNITS	SHAPE OF BASE			TEXTURES OF AGGREGATE	COMBINED TEXTURES	
	FLAT	CONVEX	CONCAVE			
BANDED				BANDED(B) LAMINATED(L)	CUSPATE BANDED(Bc)	
CUSPATE SHORT				CUSPATE(C) SHORT CUSPATE(Cs)	BANDED CUSPATE(Cb)	
MEDIUM				MEDIUM CUSPATE(Cm)		
LONG				LONG CUSPATE(Cl)	GLOBULAR CUSPATE(Cg)	
GLOBULAR				GLOBULAR(G)	BANDED GLOBULAR(Gb)	

Fig. 229. Classification of primary colloform textures and structures in manganese nodules. Symbol for each type given in parentheses. (After Kim, 1982.)

laboratory features that unequivocally demonstrate a specific process, with no alternative interpretation being possible. Thus, Wolf (1981) suggested that one should always, wherever convenient, *state the assumptions, limitations, and alternatives.*

Zimmermann (1982) described depositional and soft-sediment deformational structures that prove an early diagenetic origin of a turbidite barite sequence.

Currie (1982) discussed the origin of fracture porosity as controlled by cyclical basinal subsidence or burial, diagenesis/lithification/cementation, uplift, and erosional unloading. Similar studies ought to be attempted to comprehend the genesis of vein-type systems, for example.

Beach (1982) investigated chemical deformational processes at low-T/P (pressure solution and hydraulic fracturing), and Woodland (1982) studied the gradational origin of slaty cleavage (including diagenesis). Especially hydraulic mechanisms have been mentioned frequently in the origin of veins, which may be of the early to late diagenetic varieties (see Mills, 1983, and Magara, 1981).

McClay (1982, 1984) discussed the tectonic and sedimentary structures in sulfides, especially in stratiform Pb – Zn and related types of deposits, including the fabric and textural differences between sedimentary (depositional) and tectonic (deformational) structures, comprising also those of diagenetic origin.

Holland/Schidlowski (1982) provided a diagram that depicts the structure (= stratification) within BIFs as dependent on scale (Fig. 230). The diagenetic products, their cyclicity, regional variation, etc., are reflected in the microbands, mesobands, cyclothems, macrobands and associated features due to secondary mobilization, for instance.

Mills (1983) reviewed the genesis and diagnostic value of soft-sediment deformation structures; Elliott/Lapido (1981) described synsedimentary gravity slides; and Magara (1981) the mechanisms of natural fracturing in a sedimentary basin.

Kropacheva/Ponomarev (1983) offered a table outlining the characteristics of the principal structural types of sulfate rocks and correlated these with genetic (environmental) conditions (Table 73).

Seilacher (1984) investigated sedimentary structures tentatively attributed to seismic events (earthquakes). In an indirect fashion, these events also control diagenesis via fluid mobilization, sudden compaction due to grain settling, changing thixotropy, etc.

Plimer (1984b) in a mineralogical – historical reconstruction of the Brocken Hill lode discussed textures and structures and their development/evolution as part of a submarine – exhalative deposit.

Laznicka (1985e) discussed concordant versus discordant ore deposits and ore transformation – a most stimulating contribution.

Füchtbauer et al. (1984) described neptunic dikes and their relation to hydrodynamic circulation of submarine hydrothermal systems (see Hydrothermal).

Ritger (1985) believed that dewatering formed vein structures in slope deposits of modern accretionary prisms in sediments: this is an example of synsedimentary – early diagenetic joints that may be filled to form veins resembling late-tectonic types.
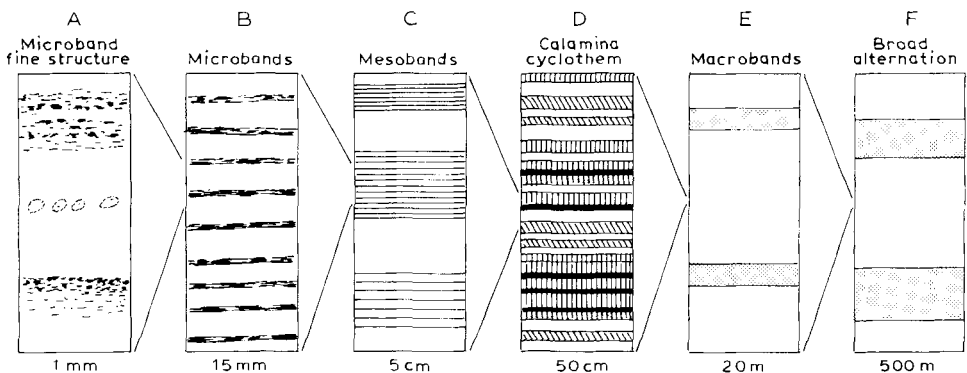

Fig. 230. Summary of stratification scales within BIF's of the Hamersley Basin, Western Australia (A) shows fine structure within the microbands, defined by iron-rich minerals, shown in (B). In (C), microbanded chert mesobands of different microband interval are represented, separated by chert-matrix (blank). (D) shows a regular cyclicity of different chert types which occurs within the larger cyclicities shown in E and F. (After Holland/Schidlowski, 1982.)

TABLE 73

Characteristics of the principal genetic types of rock in the sulfate bed of the Tirass Suite (after Kropacheva/Ponomarev, 1983)

Structural type and variety	Characteristics	Average[1] content of insoluble residue (%)	Formation conditions
I. Stratified 1. Horizontally bedded mono-sulfatic (laminites)	Thin layers of sulfates from 0.5 – 2 mm to 1 cm thick, distinguished from one another either by grain size alone or separated by thin clay films. Bedding consistent, horizontal	1.2	Subaqueous, below the zone of photo-synthesis
2. Clay – anhydrite rhythmites	Little layers of sulfates, not exceeding 2 – 3 mm in thickness, separated by comparable or twice as thin laminae of dark, bituminous, sometimes carbonate clays	6.3	The same
3. Carbonate – sulfate, wavy bedded	Thin layers of sulfates from several millimeters thick to 1 – 1.5 cm, separated by twice as thin calcareous or clay – calcareous wavy laminae rich in organics. Bedding uneven: thickness of the layers not maintained	4.1	Subaqueous, in the zone of photosynthesis (nearshore portion of halide basin, salt lakes on tidal flats)
II. Carbonate – sulfate porphyritic	Bedding absent or indistinct. Inclusions of sulfates in the form of crystals or aggregates are scattered in calcareous or clay – calcareous material, which forms the main framework of the rock. The surrounding material is of sedimentary origin; sulfate inclusions are expanded subaerially	3.7 – 8.25	Subaerial, paleosabkha facies
1. Microdisseminated	Externally uniform, massive, reminiscent of limestones or marls. Scattered crystallites of sulfate less than 0.5 mm in size are recognizable only under magnification		The same
2. Finely disseminated	Sulfate crystals and their aggregates are well noted in the surrounding carbonate framework, oriented along the bedding. Pockets and disseminates of sulfate attain an area of several square millimeters		The same
3. Nodular	Accumulations of closely connected, oval nodules (small concretions) of sulfate with a size of 0.1 mm to 1 – 1.5 cm across. The enclosing material is the same. Sometimes indistinct bedding is observed, along which nodules are oriented		The same

TABLE 73 *(continued)*

Structural type and variety	Characteristics	Average[1] content of insoluble residue (%)	Formation conditions
III. Stromatolite-like	The structure corresponds to that of columnar – stratal stromatolites. Thin wavy little layers are compressed or wedge out in very short areas. Nodularity is formed in rock chips	1.7	Subaerial, formed by means of sulfatization of still slightly lithified stromatolies
IV. Coarse crystalline gypsums	Coarse columnar crystals, often bladed, from several centimeters to 1 – 3 m in length, oriented subvertically to the bedding plane; twins of the "dovetail" type are characteristic		Subaqueous
1. Coarsely bedded, monomineralic	Layers of coarse-crystalline gypsum up to 10 – 20 cm thick alternate with fine-grained sulfates (anhydrite, secondary alabaster gypsum)	1.9	Subaqueous
2. With impurity of sedimentary carbonates	Areas of solid carbonates or of clay – carbonate material, occasionally with fine inclusions of sulfate; gypsum crystals are separated out. Bedding is absent	4.5	Subaqueous in the zone of photosynthesis and subaerial (paleosabkha facies)

[1] Based on the data from chemical analyses for rocks of the sulfate bed in the southeastern part of the Transcarpathian sulfur-bearing basin (authigenic minerals excluded).

Bogush (1985) examined discontinuities in volcanic – sedimentary ore genesis, which include exhalative – sedimentary – diagenetic varieties and their characteristic (?) structures – stratigraphy – cycles/rhythms. The sources for the ore was both exogenic and endogenic in nature.

– See also Karst, Tectonism, Textures, and Unconformities.

SUSPENSATE (-TYPE DIAGENESIS)

Hartmann (1973) published a very interesting paper on the "suspended material" (= suspensate[1]) in the hydrothermal brines of the Red Sea Atlantis-II Deep. His

[1] Although *The Shorter Oxford English Dictionary* (2 vols., 1973) does not define the word "suspensate", it is to be found in the *Glossary of Geology* (2nd ed.) edited by Bates and Jackson, American Geological Institute, 1980: "suspensate" equals "suspended load". Any diagenesis occurring in the suspensate state before settling to the bottom has been called by the senior author (Wolf, 1973, unpublished) "suspensate diagenesis" (see Table 10).

and the observations of others permitted the reconstruction of a schematic vertical geochemical profile of the hydrothermal solutions, which has three zones, called the 60°C-zone, 50°C-zone and the transition zone, the latter being between the brines and normal Red Sea water. The ten parameters measured are depicted in Fig. 231. The following results were obtained: (a) Metal concentrations in suspended form were lower by $10^{-1} - 10^{-5}$ in contrast to the dissolved concentrations of the brines; (b) suspended Cu and Zn were enriched particularly in the deeper brine zone (60°C zone); (c) Fe, Cu and Zn in the deeper zone (and occasionally also in the 50°C brine zone) were present as sulfide suspensate; (d) in the transition zone of the 50° − 60°C brine, highly concentrated iron hydroxides were recorded; (e) Mn-suspensate was found only within the transition zone as Mn-hydroxides; and (f) in the past, an increase of thermal activity was accompanied by an increase in reducing conditions within the brines, apparently caused by the increase in discharge of higher amounts of sulfides into the basins. A concurrent increased precipitation of heavy-metal sulfides was also recorded. (Compare with Figs. 126 and 127.)

The interpretation of the chemical reactions between the three zones of the brines are of particular interest in the context of diagenesis. No details can be offered here (see Hartmann's original paper) − suffice it to say that: (a) Diagenetic (secondary) reactions take place between the three zones, and between the high-temperature lower zone and the bottom sediments and volcanic rocks, as depicted in Fig. 232; (b) insofar as the system, shown in Fig. 232, represents one particular stage of an everchanging cyclic or evolutionary system, it seems reasonable to assume that with an increase and decrease of hydrothermal activity, the rate and type of diagenetic
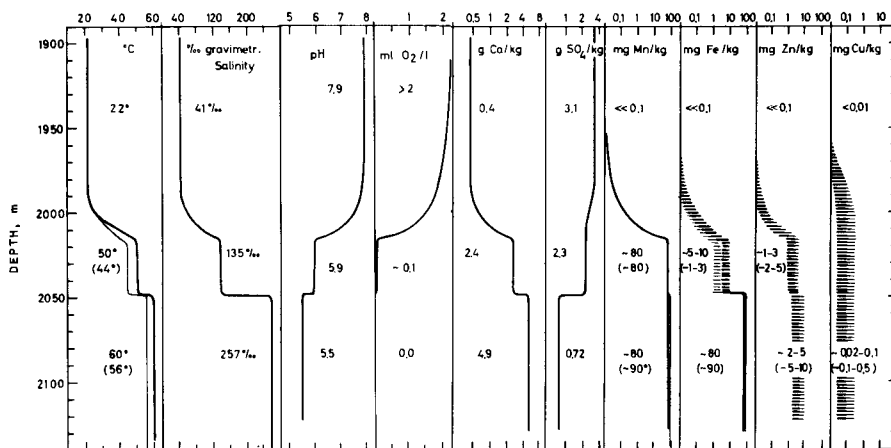

Fig. 231. Schematic vertical profiles of the Atlantis-II Deep, with temperature, salinity, pH, and O_2, as measured on board of "Valdivia" by researchers of Preussag AG. Additional profiles provide the contents of solutes based on laboratory analyses. Thin lines and values in brackets are the corresponding values of 1966. (No dissolved H_2S was found.) (After Hartmann, 1973; see for original data sources.) (See also Figs. 126 and 127.)

processes will alter accordingly; (c) it is necessary to know such changes in order to reconstruct horizontal and vertical zoning as well as to comprehend the origins of laminations in sedimentary ore deposits; (d) once the suspensate settles to the bottom, what types of sediment – water interface diagenetic mechanisms will affect it?; (e) when the hydrothermal system has terminated, further diagenetic changes are to be expected; (f) thus, one can speak of a new type of diagenesis that has been largely ignored and understandingly so, because little was known about it: the diagenetic reactions between suspended material and the circumjacent fluids in the sea, lake, etc., could be termed "suspensate diagenesis" (Wolf, 1973, unpublished, see Table 10); and (g) Degens et al. (1972) discussed the origin of microcrystalline sphalerite in resin globules suspended in the East African Lake Kivu.

TECTONISM

Kunzendorf et al. (1984/85) discussed the metal variations in divergent plate-boundary sediments; the metals were of hydrothermal origin and concentrated in sedimentary rocks. Several books are available dealing with the metallogeny in the context of plate tectonics. Syngenesis – diagenesis is merely one of many processes controlling metal distribution. (See also Hydrothermalism.)
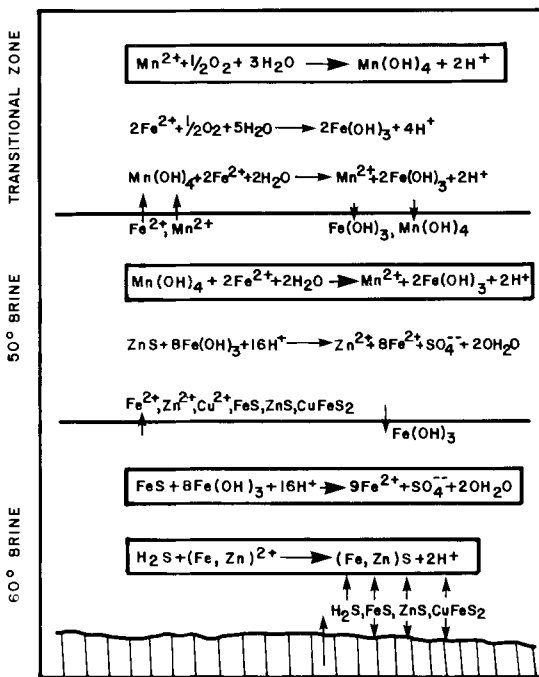

Fig. 232. Assumed (interpreted), partly simplified, chemical reactions in different zones of hydrothermal solutions of the Atlantis-II Deep. (After Hartmann, 1973.)

Riddler (1982) dealt with "basin inversion/tectonic inversion" which had an influence on diagenetic to catagenetic mineralogical changes in sandstones, ironstones, clays and sphalerite, for example. These alterations, in part of high diagenetic rank, have led to the development of economic and low-grade concentrations. (See also Iron.)

Raybould (1980) outlined the tectonic controls on Proterozoic stratiform mineralization, e.g., on sedimentary diagenetic and various epigenetic processes; and Boyce et al. (1983a) discussed the rapid subsidence that influenced the genesis of base metal deposits, e.g., tectonism determined the localization of surface brine-filling pools or topographic lows and metal dispersion halos.

Watson (1984) described continental crustal regimes as factors in sedimentary ore genesis and metallogeny.

Annels (1984b) studied the geotectonic environment of the Zambian Cu – Co ores.

Larue (1981) provided evidence for sedimentation on a Precambrian platform and basinal pre-iron formation of siliciclastic sediments (that then set the stage for the Fe-ore deposition). Gross (1983) outlined the tectonic systems for the precipitation of iron formations. Pfeufer (1983) described the origin of oceanic ore muds and the geotectonic setting of iron ore and massive sulfide ore deposits.

Hesse/Ogunyomi (1980) investigated the pre-orogenic subsidence depth and orogenesis in controlling diagenesis – burial metamorphism along continental margins; Shanmugam/Walker (1980) described the sedimentation, subsidence and evolution of a fore-deep basin, including all factors determining dewatering, increase in geothermal heat and, therefore, diagenesis – catagenesis – metamorphism; Brunet (1984) studied the subsidence history from special "subsidence curves"; Bond/Kominz (1984) constructed similar tectonic subsidence curves to unravel the mechanisms involved in basin evolution, age of break-up and crustal thinning (he also employed "delithification curves"); Cloetinghi/Wortel (1982) offered "finite element models" to study passive continental margins; and Oncken (1982) used "coalification curves" to recapture the history of geosynclines. Westbrook et al. (1982) described extensive underthrusting of undeformed sediments: the deformation increased the porewater pressure with consequent control of secondary processes within the sedimentary pile.

Bois et al. (1982) reconstructed the global geologic history and distribution of hydrocarbon reserves. His geotectonic classification should be combined with that of sediment-hosted ores in an attempt to recognize hydrocarbon – ore relationships (see also Oil – ore relationships). Harding (1983) discussed graben hydrocarbon plays and structural styles.

Worsley et al. (1984) retraced the global tectonic and eustasy over the past 2 billion years; Sleep (1984) discussed the contraction or stretching of basins; Hay et al.

(1981) the global sedimentation pattern in context of continental drift; and Ronov (1981) described the composition and evolution of sediments in major continental structural zones (e.g. by contrasting numerous metal concentrations in clays and organic matter from platform and geosynclinal sediments).

Read (1982) described the types, characteristics and evolution of carbonate platforms of passive (extensional) continental margins, i.e., tectonics controlled carbonate lithogenesis, but only the large-scale factors were considered. Eventually, the hydrologic system's evolution, and through it the diagenetic development, ought to be studied. Can such approaches be applied to M.V.-type ore districts (see M.V.-type ores)? Forti/Postpischl (1984) dealt with "seismotectonic" and paleoseismic analyses using karst sediments, e.g. they investigated the growth patterns of stalagmites and stalactites (see Karst).

Engelder (1985) described four different joint types (i.e., tectonic, hydraulic, unloading and release) that can originate during a tectonic cycle. During burial and tectonic compaction phases, joints do not form within the shallow portion of the stratigraphic/sedimentary sequence. How do diagenetic – burial joint types fit into the fracture systems that could form ore veins?

– See also Environments, Multi-factorial, Structures, and Textures.

TEMPERATURE

Barnes (1975) made an excellent, important contribution on metal zoning. The main controlling variable is solubility – not temperature (p. 307).

Bradley (1975) showed that temperature could determine "abnormal pressures" in sediments. The temperature, in turn, is controlled by numerous factors.

Dunsmore/Shearman (1977) demonstrated that the range of temperature over which the Pb – Zn Mississippi Valley-type ores are formed is essentially the same as that over which crude oil seems to be generated and preserved. This range is of interest because it lies within the temperature limits where the rates of both bacterial and non-bacterial (chemical) reduction of sulfate should be at their lowest (Fig. 233). This might be the most favorable condition for ore genesis, because there must be an optimum rate of flow of the brine that would permit an economic concentration of metals. If the sulfide ion production is too fast, sulfide would go to waste. Also, the fuel of the reaction (the oil) could be consumed before even a fraction of the metalliferous brine had been processed. Thus, to precipitate a maximum amount of ore, a steady supply of sulfide ions is required throughout the time over which the brine was migrating through the site of potential ore precipitation.

Sharp (1978) and Sharp/Domenico (1976) discussed the hydrology and energy re-

quirements related to the lateral-secretion origin of Pb – Zn ore deposits. Factors controlling the temperature in sedimentary basins are listed in Table 74.

Roedder (1979) and Blatt (1979), among many others, discussed the influence of temperature in sedimentary piles and its control on diagenesis, including the origin of Mississippi Valley-type ores. Figures 234 and 235 are examples of the relatively high temperatures reached at comparatively shallow depth-of-burial.

Note: In such cases, the basinal fluids may be non-magmatic hydrothermal fluids as a result of a steep geothermal gradient.
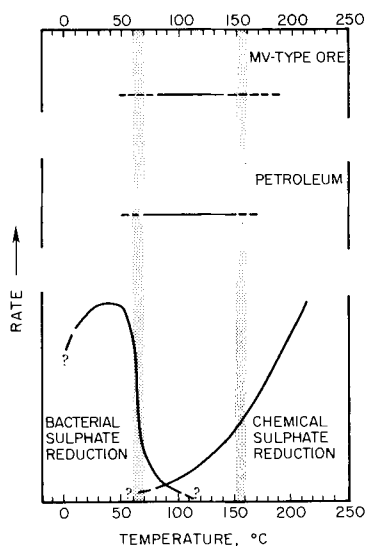

Fig. 233. Interrelationship among temperature, Mississippi Valley-type ore formation, petroleum preservation and rates of sulphate reduction. (After Dunsmore and Shearman, 1977.)

Temperatures at 3050 m
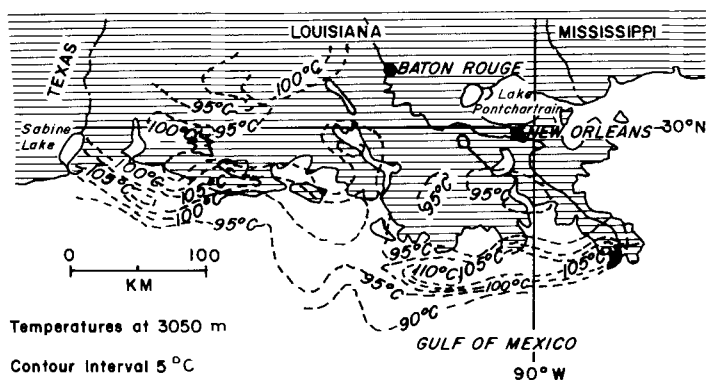
Contour Interval 5 °C

Fig. 234. Temperature in south Louisiana at a depth of 3050 m illustrating the irregular isotherms characteristic of this type of map. (After Jam et al., 1969, in Wolf/Chilingarian, 1976; see for original data sources.)

Nekrasov/Besmen (1979) studied the pyrite – pyrrhotite geothermometry and the distribution of Co, Ni and Sn and compared low-temperature with high-temperature types; Weninger (1981) dealt with the microthermometry of the East Alpine ore deposits and offered interesting data on fluid inclusions that was plotted as temperature vs. fluid composition and temperature vs. paleopressures; Piperov et al. (1981) also used fluid inclusions from hydrothermal fluorites obtained from seven localities within one ore field, each fluorite exhibiting a different crystal habit, and they also determined the acidity, pressure and the pH of the original hydrothermal fluid system. The acidity was plotted vs. pressure.

Brookins (1980) stated that the commonly accepted hypothesis of the origin of

TABLE 74

Factors controlling temperature and excess pore-fluid pressures in sedimentary basins (after Sharp, 1978, table 1)

Excess pore-fluid pressure
  Buildup mechanisms
  1. Increasing rates of sediment accumulation
  2. Hydraulic diffusivity decrease by
     a. Consolidation
     b. Increasingly finer sediments
     c. Diagenesis
     d. Mineral precipitation
  3. Aquathermal pressuring
  4. Phase changes
  Dissipative mechanisms
  1. Fluid release over time
  2. Hydraulic diffusivity increase by
     a. Faulting and hydraulic fracturing
     b. Increasingly coarser sediments
  3. Human actions (petroleum exploration, dewatering)

Temperature
  Interface variations
  1. Long-term
  2. Periodic
  Heat transport mechanisms
  1. Conduction and dispersion
  2. Convection
     a. Forced
        i.   Fluid movement
        ii. Diapirism
        iii. Moving boundary effects
     b. Free or natural
  3. Chemical reactions

Heat sources
  1. Basement heat flux
  2. Magmatic intrusions
  3. Work done on sediment – water system

unconformity-type uranium deposits is that they were formed from "hydrother-mal" solutions, although fluid inclusion and other data argue for a wide range in temperature of solutions. Thus, the deposits can be interpreted alternatively to have formed from fluids that range from groundwater, through basinal hydrothermal to metamorphic and igneous – hydrothermal types. He proposed a syngenetic – dia-genetic mode of origin.
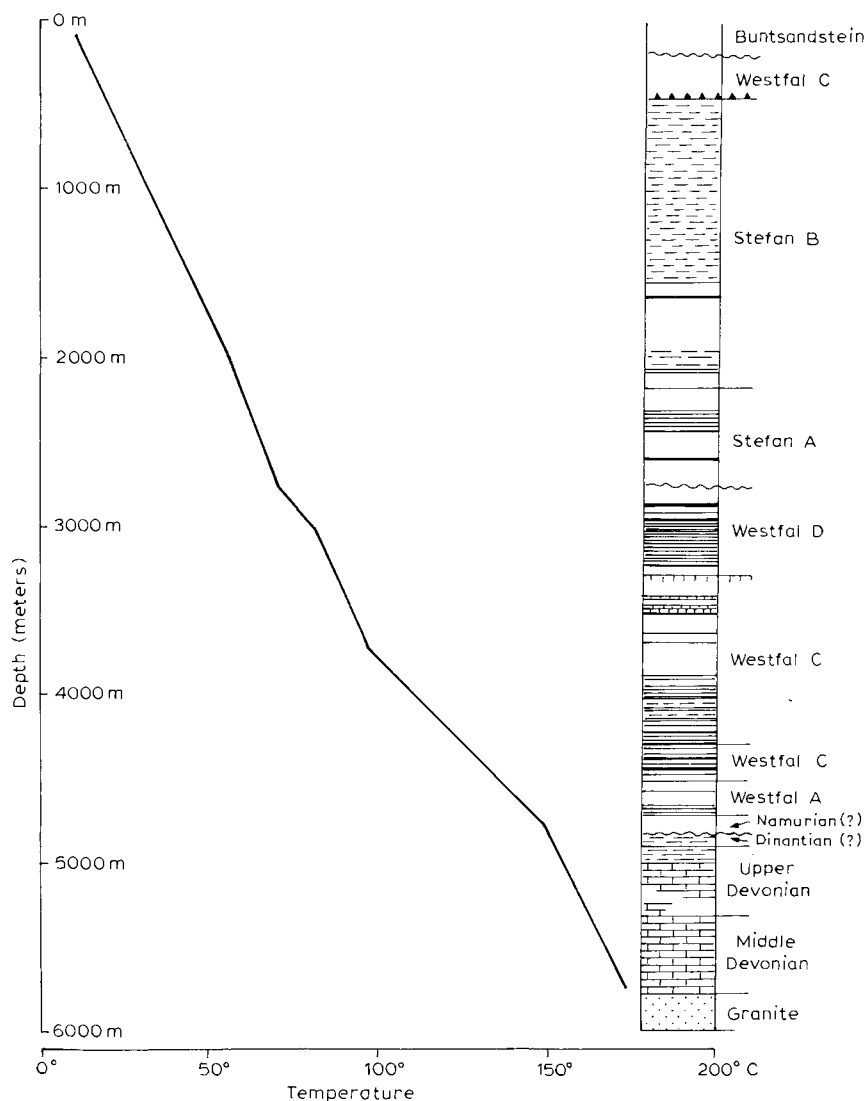

Fig. 235. Extrapolated temperature profile of well Saar 1 in southwest Germany. (After Tissot/Welte, 1978, p. 262; see for original data source.)

McDowell/Elders (1980, 1983) studied the authigenic/allogenic layer silicates from a geothermal borehole. They concluded that the increase in temperature affected the sandstone through intense calcite and dolomite/ankerite cementation, which was preserved as a suite of allogenic biotite – chlorite – muscovite, followed by decementation which caused "delayed" reactions.

Russell et al. (1981) discussed the time – temperature contrasts between volcanic- and sediment-rock-hosted exhalative ore deposits (Fig. 236).

Giggenbach (1981) dealt with the geothermal mineral equilibria offering a model ranging from 50° to 300°C, thus comprising also early diagenetic and burial-diagenetic conditions.

Barton (1981) discussed among others the influence of temperature on ore genesis, and depicted the types of mineralization on a scale (Fig. 237). Note the *range* of temperature of formation. "Diagenetic" types (early to late) may reach as high as 200°C; even higher depending on various natural circumstances and on the human-imposed definition of diagenesis! (See also Thermodynamics, Time and rate, and Temperature.)

Stetter (1982), Walsby (1983) and Baross/Deming (1983) studied bacteria and other organisms existing under higher-temperature conditions, e.g., in submarine volcanic and hydrothermal systems up to 250°C (see Bacteria).

Francis (1982) examined thermal expansion effects in deep-sea sediments, and Kastner/Siever (1983) investigated the effect of high thermal gradients on the diagenesis of Recent siliceous sediments.

Perry/Gillott (1982) discussed the mineralogical transformations as indicators of combustion zone temperatures during in-situ burning. How can these data be used to differentiate man-induced processes from several types of natural higher-grade diagenetic products? Aoyagi/Asakawa (1984) studied the paleo-temperatures of authigenic minerals and their application to petroleum exploration.
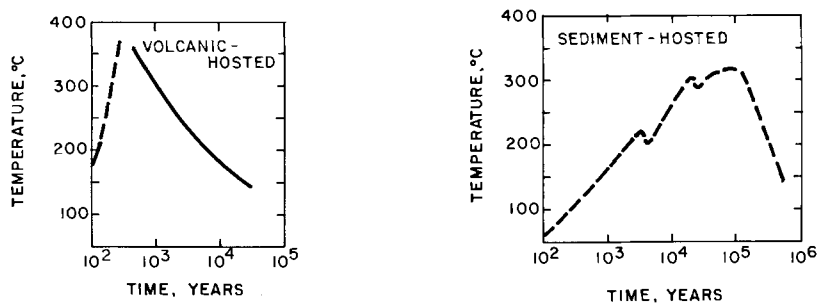

Fig. 236. Time – temperature contrast between volcanic-hosted and sediment-hosted exhalative sulphide deposits. The latter curve is a sketch only. (After Russell et al., 1981; see for original data source.)

Franke/Ghobarkar (1982) studied the morphology of hydrothermally grown K-feldspar: the size of faces depends on temperature and on neutral vs. weak alkaline environments, i.e. the textures depended on both temperature and pH. This information should be compared to that of diagenetic feldspars.

Skirrow/Coleman (1982) investigated the origin of S and geothermometry of hydrothermal sulfides from a Recent rift zone, and Cole (1983) studied the O-
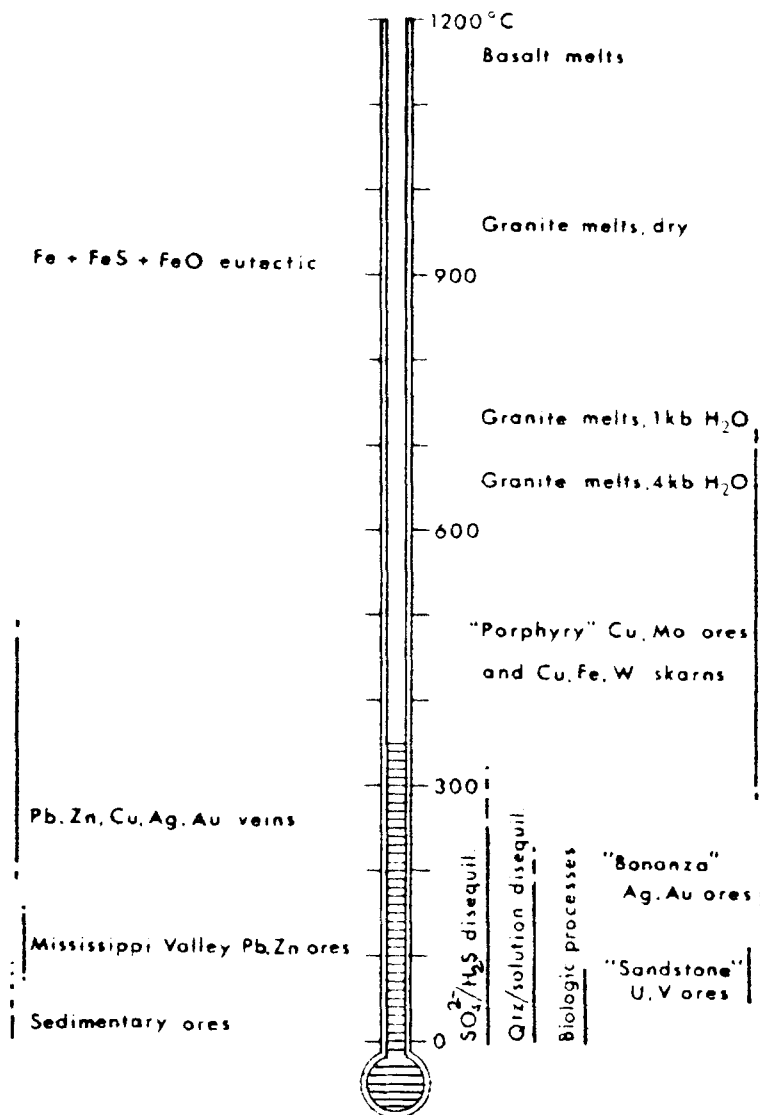

Fig. 237. Relative temperatures of some typical hydrothermal processes. (After Barton, 1981.)

isotope geothermometry and origin of smectites in a Red Sea Deep, and offered data on numerous syngenetic and diagenetic facies with a model on fractionation.

Tarasov/Aplonov (1982) examined the temperature conditions of sulfate mineral genesis associated with sulfide; Hanus (1982) estimated the temperature of formation by interpreting sulfide textures; and Bancroft/Jean (1982) studied Au-precipitation at low temperature on sulfide minerals.

Isprapilov/Abdurakhmanov (1984) deliberated on the origin of thermal anomalies in sedimentary basins, whereas Lerche et al. (1984) unraveled the paleoheat from vitrinite reflectance.

Butuzova (1984) depicted in Fig. 238 the temperature and Cl distribution in a contemporary ocean environment, delineating three "solution layers". How do these layers affect diagenesis of particles in suspension in the ocean waters; that is, what are the changes *before* the particles have settled on the ocean floor? (Remember that in some of the East African rift lakes metalliferous particles are formed within the water column and undergo "suspension-diagenetic" changes before accumulating at the bottom.) (See also Hydrothermalism, and Suspensate.)

Dangic (1985) used minor-element distribution between galena and sphalerite as a geothermometer; the low-temperature sulfides can be distinguished from the higher-temperature sulfides. Can minerals of different paragenetic systems/associations be distinguished? Should one analyze isotopic *and* elemental compositions and *compare* the results?

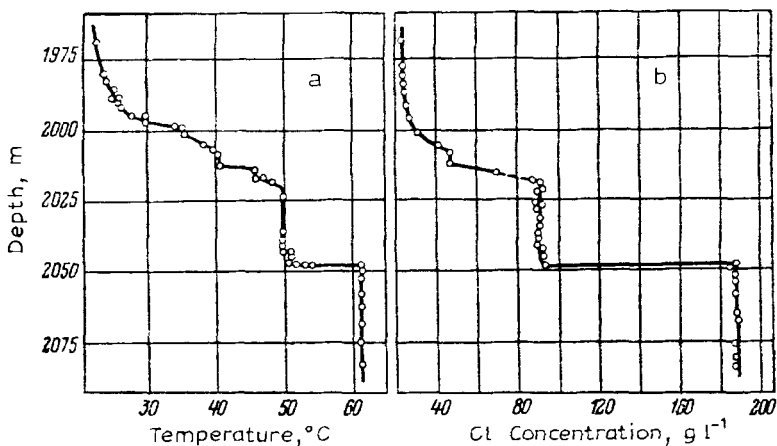– See also Depth, Hydrothermalism, Multi-factorial, and Pressure.

Fig. 238. Temperature distribution (a) and Cl distribution (b) in solution layer. (After Butuzova, 1984, pt. II.)

TEXTURES – MICROSTRUCTURES – FABRICS

Teodorovich (1961) offered in a book on authigenesis and diagenesis of minerals a list of textural and microstructural criteria that are helpful in reconstructing the history of sedimentary rocks. It seems that an up-dated version of this book ought to be written with an incorporation of ideas from the English-language literature, for example.

Amstutz et al. (1964) reviewed certain aspects of the "diagenetic behavior of sulfides", such as (1) the shallow-water patterns of iron sulfide distribution (e.g., congruent and non-congruent patterns); (2) galena localization in late diagenetic fissures in algal carbonate rocks; (3) generations of diagenetic crystallization of a Cu – Pb – Co – Ni deposit (e.g., geopetal, concretionary, and paragenetic features); (4) paragenetic relationships of sphalerite – fluorite – galena with an oolitic hostrock; (5) differential localization of sulfides in fossil wood; and (6) criteria for diagenetic crystallization and deformation in the Mt. Isa sulfide beds (e.g., geometric features).

Schmidt (1965) illustrated how detailed textural studies of carbonate and non-carbonate minerals (including "ore" minerals) can unravel the diagenetic – paragenetic history of carbonate oil reservoir or carbonate hostrocks. Similar studies must be performed for ore hostrocks.

Love/Amstutz (1966) reviewed comprehensively the origin of "microscopic pyrite" and concluded that the framboidal pyrite spherules are of early diagenetic origin, as supported by the framboids in recent anoxic sediments, even along the sediment – water interface. Park (1967) then used this conclusion to prove that the sphalerite of the Southern Illinois fluospar district is of early diagenetic origin because of its association with framboidal pyrite. See also Honjo/Fischer (1965) who used framboids in shells as geopetal criteria.

Note: (a) The question arises here as to where is the *limit* of "early diagenesis". Can the framboids form only within a few centimeters from the water – sediment interface, or can they originate at a depth of 100 m within the sediments? Or perhaps even at a greater depth of, say, 500 – 1000 m? Is its origin independent of the depth of burial, but is controlled by other geochemical – geological factors, such as degree of (un)consolidation, presence of organic matter and bacteria, and flow of fluids (i.e., is an *open* diagenetic system required)? Can framboids form during *late* diagenesis? The observations that framboids form along the surface of Recent sediments does not conclusively prove their confinement to the near-surface environment and the subsurface must be checked. (b) Framboid-like pyrite has also been formed in a volcanic rock, but the significance of this does not seem to have been fully evaluated. Are they genuine framboids, or do they constitute a different variety? If there are different types of framboids, then their proper identification is needed before plausible genetic interpretations become possible. (c) Has any framboidal pyrite been replaced by galena, sphalerite, etc., in sediment-hosted ores? Why can framboidal pyrite co-exist with other ore minerals in one deposit, but

pyrite is replaced in others? It has been stated that base metals will replace earlier-formed pyrite when the latter is in its semi-colloidal state. Once the pyrite (in whatever form, either cubic or framboidal) is crystallized, is it more resistant to replacement under diagenetic conditions?

Amstutz/Bubenicek (1967) reviewed the "fabric changes during diagenesis of sedimentary mineral deposits". They offered a classification, discussed paragenetic sequences, compared/contrasted syngenetic – epigenetic and supergene – hypogene types, outlined gravity – density features, and described motion and disruption features. This was followed by geochemical considerations and a list of publications on the diagenesis of different deposits. Finally, they provided a case study based on the role of diagenesis in the origin of oolitic iron deposits.

Amstutz/Park (1967) offered a descriptive and megascopic classification of stylolites as based on field and microscopic observations. The stylolites formed during various stages of diagenesis (early-, intermediate-, and late-(burial) diagenesis), with carbonate, silica, fluorite and sphalerite occurring near or along the seams. Recrystallization, dissolution, grain growth, grain orientation, pressure-twinning, fracturing, and residual accumulation of these minerals were observed along stylolites. A paragenetic sequence of ore and hostrock minerals has been established by these authors (Fig. 239).

Bernard/Samama (1968) described regional variation (zoning?) of cements. For example, along the basin margin the cement in red-bed-type clastic rocks changes from the deeper to the shallower parts of the basin from argillite, SiO_2, PbS, ZnS, (Ca, Mg)CO_3, and (Ba,Sr)SO_4, to $CaCO_3$ and $MgCO_3 + CaSO_4$.
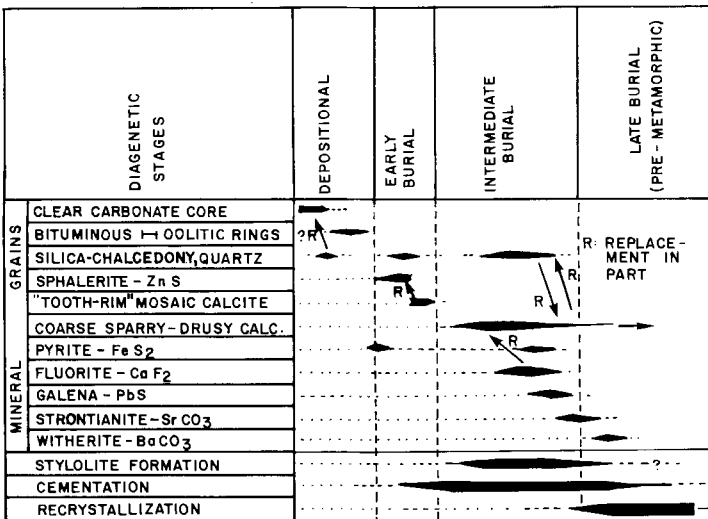

Fig. 239. Diagenetic crystallization sequence of some oolitic country rocks in area studied by Amstutz/Park (1967).

silicagel

iron oxide
hydrate

siderite
mud

precursor
silicate

hematite dust

micro-granular
siderite

compaction

cementation

primo-
crystalline
quartz

quartzine
chalcedony

specularite

magnetite

recrystallized
siderite

minnesotaite

styolites

micropolygonal
quartz

specularite

magnetite

recrystallized
siderite

reaction with
Al-silicates

recrystallized
quartz

reticulated
magnetite

stilpnomelane

recrystallized
quartz

specularite

magnetite

recrystallized
siderite

?

riebeckite

?

recrystallized
silicates

recrystallized
quartz

specularite

maghemite
and
martite

magnetite

"limonite"

powdery
hematite

hematite

"limonite"

dissolution

EARLY DIAGENETIC (pre-primocrystalline)

LATE DIAGENETIC (post-primo-crystalline)
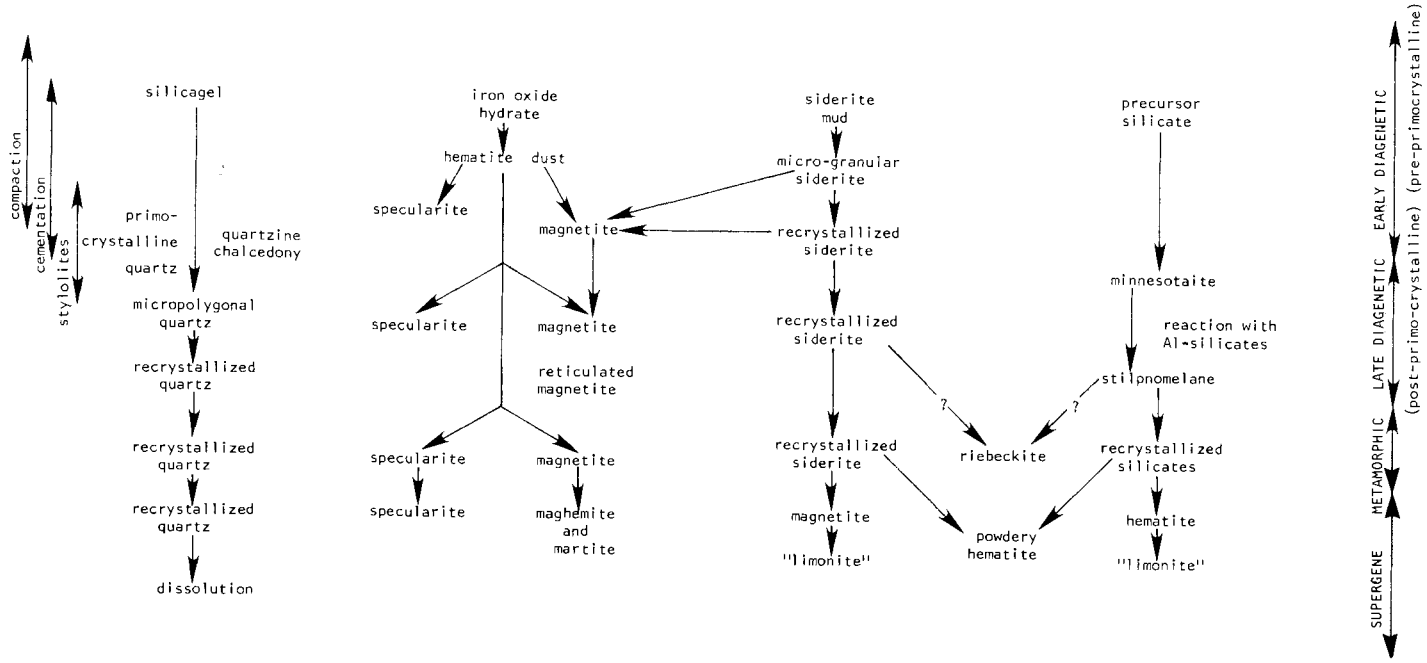
METAMORPHIC

SUPERGENE

Fig. 240. Epigenetic processes in the Precambrian Sokoman Iron Formation, Labrador Trough, Quebec, Canada. (After Dimroth/Chauvel, 1972, 1973. See also Dimroth, 1976.)

Note: (a) Whether early or late diagenetic in origin, any cement occupies the open spaces of an earlier-formed sedimentary framework, either a clastic or a carbonate rock. Thus, this type of ore-mineral cement is one of the best examples of dia-epigenetic origin. (b) The zoning of this cement ought to be contrasted with other types of ore zoning, e.g., of strictly syngenetic zoning. Would a hydrothermal source in contrast to a basinal compactional fluid cause a difference in paragenesis and zoning? (See also Gustafson/Williams, 1981; and Bjørlykke/Sangster, 1981.) (c) Eventually a comparative study of the sandstone-, volcanic- and carbonate-hosted ores will be required. Ore-forming diagenesis in each is different.

Dimroth (1968, 1976) and Dimroth/Chauvel (1973) presented excellent examples of the use of sedimentary microscopic petrology of cherty iron formations. The well-known limestone classification by Folk was successfully modified for the iron ores. Many of the textures of grain types, matrixes, and cements of the sedimentary carbonate rocks are present also in the iron ore deposits. Numerous diagenetic features were illustrated by these authors and flow-chart-like models summarized the paragenesis from early to late diagenesis, through metamorphism, to supergenesis (see Figs. 240 – 242).

The limestone classification has also been adopted to the investigation of phosphorites.

Amstutz/Park (1971) discussed the paragenetic sequence of the minerals and various sedimentary structures formed during several diagenetic stages of ore deposits.

Štrucl (1971) discussed syngenetic and diagenetic textures, fabrics, and microstructures. He also compared diagenesis with epigenesis. The dolomite- and limestone-hosted ores are of several types: (a) stratabound sill type, (b) stratabound vein type, (c) reef-bound ores in reef zone and in reef breccia plus lagoonal dolomite, and (d)
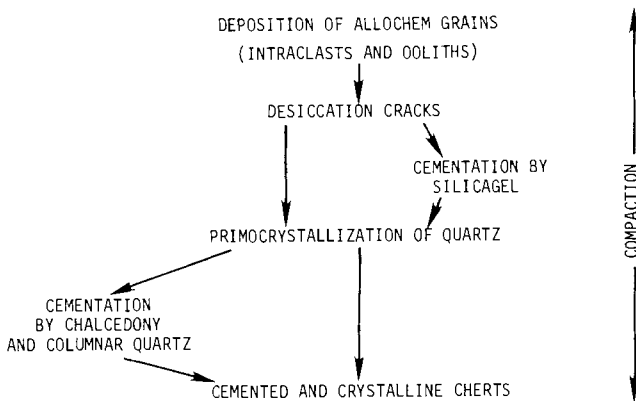

Fig. 241. Lithification of Sokoman Iron Formation, Labrador Trough, Canada. (After Dimroth/ Chauvel, 1972; see also Dimroth, 1976.)
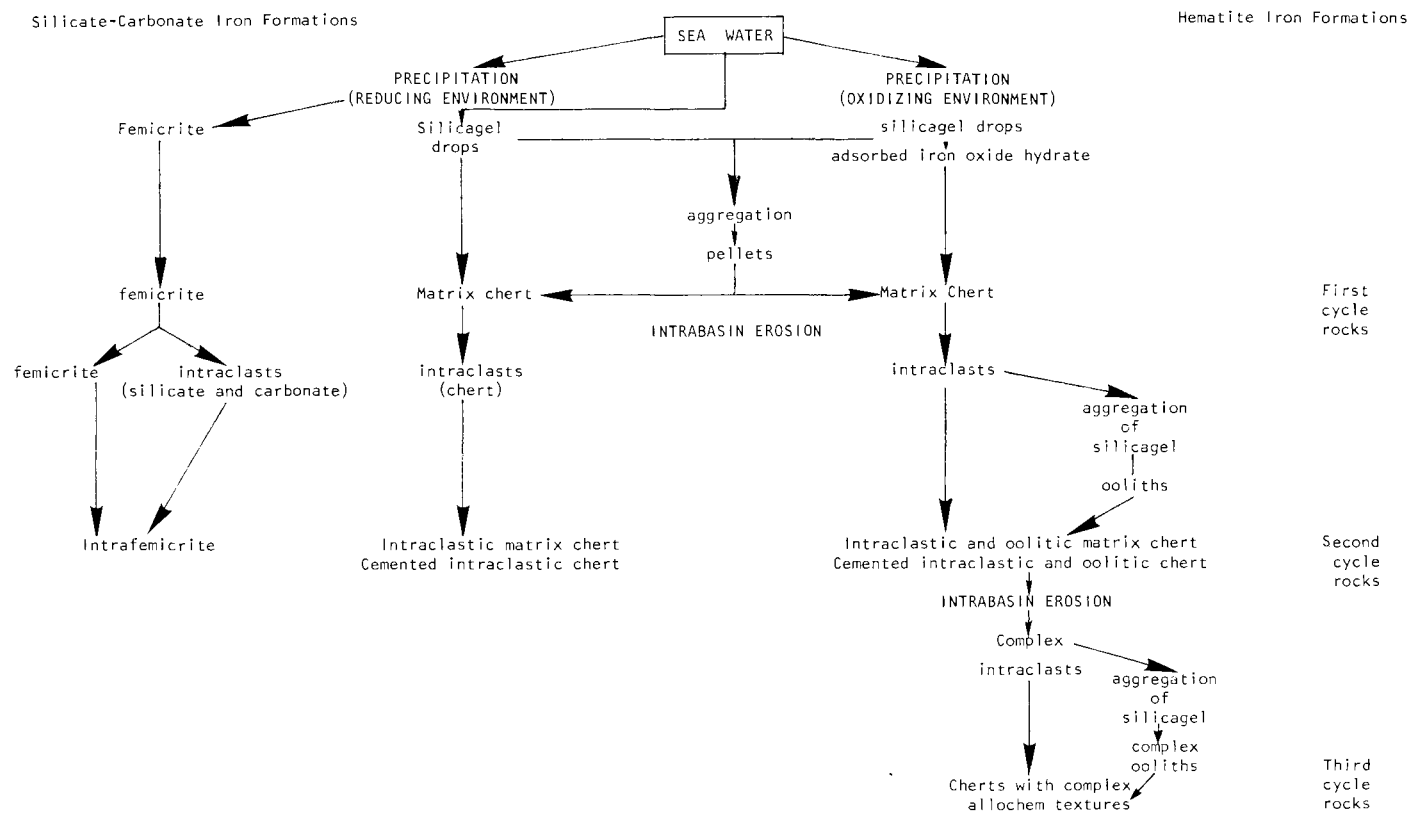
Silicate-Carbonate Iron Formations

Hematite Iron Formations

SEA WATER

PRECIPITATION
(REDUCING ENVIRONMENT)

PRECIPITATION
(OXIDIZING ENVIRONMENT)

Femicrite

Silicagel
drops

silicagel drops

adsorbed iron oxide hydrate

aggregation

pellets

femicrite

Matrix chert

Matrix Chert

First
cycle
rocks

INTRABASIN EROSION

femicrite   intraclasts
(silicate and carbonate)

intraclasts
(chert)

intraclasts

aggregation
of
silicagel

ooliths

Intrafemicrite

Intraclastic matrix chert
Cemented intraclastic chert

Intraclastic and oolitic matrix chert
Cemented intraclastic and oolitic chert

Second
cycle
rocks

INTRABASIN EROSION

Complex

intraclasts   aggregation
of
silicagel

complex
ooliths

Cherts with complex
allochem textures

Third
cycle
rocks

Fig. 242. Deposition of the Sokoman Iron Formation, Labrador Trough, Canada. (After Dimroth/Chauvel, 1972; see also Dimroth, 1976.)

ores bound to post-fault systems. Each is described in detail because many have been interpreted previously as of hydrothermal – epigenetic – metasomatic – replacement types. However, the newly accumulated data suggests a syngenetic and/or diagenetic origin. There is also a possibility that they are diagenetic in origin with epigenetic characteristics.

Amstutz (1972) presented an interesting paper outlining criteria for the classification of Mississippi Valley – Bleiberg – Silesia type of Pb – Zn – F – Ba (Cu – Co – Ni) ores in carbonate hostrocks. The reasons for combining these three classes of ores are: (a) The environment of these deposits with many sedimentary diagenetic features is not restricted to continental platforms; (b) they vary in age and occur on most continents; (c) in certain environments they grade into Kupferschiefer or red-bed types of deposits, or even into massive sulfide deposits; (d) they range all the way from absent to positive volcanic – exhalative affiliation; and (e) they occur in undisturbed as well as in metamorphosed and folded terrains. Studies range from the regional, through the local/district and outcrop scale, to the handspecimen and microscopic scale. Insofar as diagenesis is usually studied on the handspecimen and microscopic scale, it is emphasized that the diagenetic data ought to be supplemented by the information obtained from the larger-scale investigations.

Croxford/Jephcott (1972) discussed textures and structures, among others that indicate a syngenetic – diagenetic ("sedimentary") origin of the Australian McArthur Pb – Zn – Ag deposit. The source is volcanic – exhalative.

Arnold et al. (1973) showed that the pyrite of the Almadén mercury mine provides an excellent record of the early diagenetic history of the host sediments. The pyrite crystals are built up of a macromosaic nucleus circumcrusted by a diagenetic cortex. Framboids of the nucleus display frequently a mutual orientation, and the cortices display different growth types (i.e., zonal, fibrous, and sectorial). Cinnabar and pyrrhotite appear only within the nucleus and never in the cortex. Thus the Hg-mineral precipitated under equilibrium conditions between pyrite and pyrrhotite. The Hg was present prior to the addition of the diagenetic pyrite because it is trapped in the nuclei.

Bartholomé et al. (1973) described the diagenetic ore-forming processes of two stratiform Cu – Co-sulfide deposits in unmetamorphosed dolostone, chert, and shale hostrocks. The mineralized sedimentary rocks are probably of tidal-flat origin. They have undergone a complex sequence of diagenetic transformations and neomorphisms. Several authigenetic minerals have crystallized: dolomite, perhaps in part from hydromagnesite and $CaCO_3$; magnesite from the remaining hydromagnesite; quartz; chlorite and other phyllosilicates; colorless tourmaline; pyrite; and other sulfides (chalcopyrite, bornite, digenite, chalcocite, carrolite, etc.). New evidence showed that this diagenesis occurred at first in an environment devoid of Cu and Co, and then proceeded while the metals were brought-in from an outside source. One possible explanation: hypersaline brine (with a high pH and a high Eh) passed through the lower part of the rocks and a modified connate water (reducing

and less alkaline because of abundant organic matter) was present in the upper section.

Lambert (1973) examined textures and microstructures of sulfide minerals that could only have formed after the deposition (syngenetic) of the enclosing sediments through diagenetic and metamorphic recrystallization/remobilization. Experimental data supports the concept that the release of sulfur from organic matter and from pyrite combined with metals made available by concomitant processes can form diagenetic/metamorphic sulfide minerals.

Lemoalle/Dupont (1973) described iron-bearing oolites presently forming in Lake Chad (Africa). Colloidal or adsorbed iron from the solid load of the incoming rivers (94,000 t of reactive Fe in 1970–71) is separated from kaolinite, which becomes unstable in the lake, and forms a coprecipitate with silica. The oolitic structure is the result of agitation during concentration at shallow water depth and warm temperature. Eventually one should examine the incoming iron for adsorbed metals (Cu, Pb, Zn, etc.) and, if present, their fate within the lacustrine system should be established. Can iron-rich sediments, in general, be the source of metals?

Atkinson (1974) deformed experimentally polycrystalline galena, chalcopyrite, and pyrrhotite under conditions that could occur in sedimentary – volcanic piles undergoing late diagenetic – catagenetic – metamorphic processes (i.e., from as low as 20°C temperature and 1 bar confining pressure to up to 200°C and 3500 bars.)
   Note: (a) Little natural observational and experimental data is available in comparative summary form to the practicing geologist to distinguish between syngenetic, diagenetic, epigenetic, cataclastic, tectonic – deformational, etc., textures and microstructures of the ore minerals and hostrock constituents for useful genetic interpretations of handspecimen and drill-core work, let alone, for thin- and polished-section studies. The petroleum industry, on the contrary, has obtained a far better understanding of the sedimentary textures to fulfill their needs (although numerous problems are yet to be tackled). (b) There is a definite lack of data: Can any reader cite a publication that offers a comprehensive critical evaluative review of all possible breccias of all hostrock and ore types? What are the differences and similarities of tectonic, sedimentary, volcanic, plutonic, and metamorphic breccias? Each one has dozens of sub-types and there are only few criteria or guides to discriminate between them! (c) A similar lack of comparative/contrastive-type investigations exists for textures – fabrics – microstructures. Not even the known data has been properly summarized for the field- and laboratory-oriented geologist. Consequently many "sedimentary" deposits have been misinterpreted as "epigenetic" types or vice versa. A fault breccia in limestones may become a reef breccia; or a diagenetic dissolution breccia becomes a tectonic breccia, although internal sediments (even with syngenetic sulfide) would have provided a conclusive criteria (Wolf, 1982, unpublished observation).
   Suggestion: (a) As part of university theses, more comprehensive evaluative reviews of specific topics could (or ought to) be prepared. For example, when during a regional study a number of breccias are encountered, why not prepare a com-

parative/contrastive-type synopsis of *all* breccia types as a foundation to plausibly differentiate those breccias on hand? Why not attempt to put the local particular breccia types into the context of a generally applicable synoptic classificatory scheme, which lists criteria and guides to differentiate between the varieties? How else would one propose that *all* possible breccia types have been considered so that no misinterpretations could occur? The axiom ought to be: "No comprehensive all-inclusive summary − thus, no overall comparison − thus only a limited approach". The same argument applies to many other textural and structural problems; indeed, to most geological − geochemical − geophysical problems!

Deelman (1975, 1976) examined textures indicating pressure solution, plastic deformation, and force of crystallization.

  Note: Criteria and guides to discriminate between the many types of "primary" and "secondary" textures and microstructures are required. Also required are guidelines as to their proper interpretations. What conditions do specific textures indicate? What "primary" features are preserved within "secondary" textures and microstructures? Can paragenetic textural evolutions be established from the primary through slightly altered, to highly altered textures? One must find answers to these questions.

Cook (1976) recognized in his comparison of the geosynclinal (West Coast) and platform (East Coast) types of phosphate deposits, several textures: nodules, "grains", pellets (several varieties), ooliths, etc.

Glasby/Read (1976) and Callender/Bowser (1976), among many others, described the hypotheses advanced to explain the origin of marine and freshwater (lacustrine) manganese nodules, crusts, coatings, and dispersions.

Levin/Amstutz (1976) discussed difference between depositional time-dependent rhythmites and diagenetic-crystallization rhythmites. A classification of diagenetic textures was also offered.

Logan/Semeniuk (1976) offered a new, unique, and controversial interpretation of many late diagenetic to so-called metamorphic textures and structures. Anyone working on carbonate hostrock petrology ought to read this stimulating book.

Schulz (1976), Hagni (1976), Hoagland (1976), Zimmermann (1976), and Kyle (1981), among many others, represent some well-illustrated publications on the textures − fabrics − microstructures of Mississippi Valley-type ores of syngenetic − diagenetic − "epigenetic" origins: rhythmites, geopetal features, breccias, compaction features, and nodules.

Oehler/Logan (1977) found within the McArthur (HYC) mineralized sequence several laterally discontinuous layers of fragmented and globular black chert, which possibly formed from colloidal silica that precipitated onto the seafloor or within the sediment during early diagenesis. The chert fragments and blebs are rimmed by

sphalerite; less commonly, they are partially or completely rimmed by galena. The ore textures are related to the chert textures, suggesting that the silica-ore deposition occurred over a prolonged period of time prior to final lithification of the sediments.

Walker et al. (1977), like Neudert/Russell (1981), found evidence of evaporitic conditions in the Proterozoic, as indicated by numerous pseudomorphs after halite, gypsum and anhydrite. These textures occur over a vast area (at least 5000 km^2) within relatively thick stratigraphic sections, and indicate the following: (a) The McArthur Group rocks were deposited in a marginal evaporitic environment; (b) the evaporites are similar to Recent coastal sabkha deposits in terms of chemistry, crystallographic habit, etc., and probably owe their origin to brines; (c) the Persian Gulf sabkha model is not applicable to all of the McArthur Group evaporites, some of which have a stronger resemblance to certain lacustrine gypsum deposits; and (d) the results show conclusively that the giant HYC (= McArthur) stratiform Pb – Zn – Ag deposit is yet another example of the widespread association of base metal sulfide deposits with sulphate evaporite sediments. Inasmuch as the McArthur ore is within a large evaporite-bearing basin, the possibility exists that metal-rich brines of the kind forming today in evaporite-bearing basins (rather than from volcanically derived hydrothermal – exhalative solutions) formed this metalliferous deposit.
   Note: This is an excellent example of how a detailed study of the hostrocks assists in the reconstruction of the ore genesis. Too many investigations have preferentially concentrated on the ore mineralization at the expense of the hostrocks.

Purser (1978) described early diagenetic cementation/lithification of carbonate reservoir rocks and source of carbonate for cementation. He also discussed occlusion and preservation of porosity, among others. More studies are required on the relationships between cementation and diagenetic ores in carbonate hostrocks.

Halls et al. (1979) discussed the "conceptual bridge to link syngenetic and epigenetic phenomena in the same deposit" exemplified by the Pb – Zn ores of Ireland. The syndiagenetic emplacement of the ore is indicated by the mineralizing fluids percolating into a connected system of stromatactis cavities in the limestone hostrock by the progressive diagenetic geopetal crustification by sulfides. Diagenetic dissolution of the limestone along stylolites resulted in the concentration of disrupted sulfide cavity fillings. Also present is geopetally laminated sulfide with numerous depositional/sedimentary features that include grading, load and cast structures, slumping, penecontemporaneous folding, and sulfide mud as a matrix in breccia. The conduit for the hydrothermal ore-forming fluids were faults – a "seismic pumping mechanism" is evidenced by some of the textures associated with brecciation of the hostrock.
   More such studies are required, e.g., on unequivocal geopetal features in ores, which indicate forceful injection of ore-forming fluids, suggesting "seismic pumping" by movement along fault.

Ostwald/England (1979) described the relationship between framboidal and euhedral pyrite in base-metal sulfide ores; Love et al. (1984) studied the mineral and organic material in matrixes and coatings of framboidal pyrite; and G.R. Taylor (1983a) discussed framboid formation in a volcanic – exhalative sediment. More investigations are required on framboidal minerals and textures inasmuch as several different environmental controls appear to be operative of which some are diagenetic. Since some framboids seem to have originated under higher-temperature volcanic settings, not all framboids are indicative of diagenesis.

Brown (1980) discussed syndiagenetic pyrite formation before Cu – Co mineralization as suggested by textural evidence.

Note: What are the textural and geochemical methods required to recognize pre-ore pyrite that was later replaced by ore minerals? (See Brown's paper for references on textures.)

Birch (1980) classified "sedimentary" phosphates into "diagenetic" and "authigenic" types (Table 75) as based on their mode of origin (Figs. 243 and 244). The genesis, in turn, is reflected in a number of features, especially in the textures, microstructures, larger-scaled structures, stratigraphy, and distributions.

Fontboté/Amstutz (1980) described stratabound F – Pb – Zn deposits in shallow-water, dolomitic carbonates which exhibit diagenetic crystallization rhythmites, associated with synsedimentary and intra-environmental (misnamed "intraformational") diagenetic breccia.

Fontboté/Amstutz (1982): Geochemical and microscopic data of sphalerite rhythmites are described from a stratabound Pb + Zn district. These rhythmites are

TABLE 75

Types of phosphate deposits in a modern environment (after Birch, 1980)

Diagenetic phosphates
1. Arenaceous:
   (a) Foraminiferal lime packstones (AI)
   (b) Glauconite/quartz packstones (AII)
   (c) Goethite-rich lime packstones (AIII)
2. Conglomeratic:
   (a) Glauconitic packstones with enclosed foraminiferal pebbles (CI)
   (b) Goethite-rich limestones containing abundant macrofossils and bone (CII)

Authigenic phosphates
1. Pellets:
   (a) Oolitic (PI)
   (b) Nucleated (PII)
   (c) Structureless (PIII)
2. Quartzitic packstone (Q)
3. Layered (L)

QUARTZ AND PHOSPATE PELLETS

AUTHIGENIC PHOSPHATE-RICH PACKSTONE

NON-PHOSPHATIC BEACH SAND

LAYERED AUTHIGENIC PHOSPHATE-RICH ROCK

AUTHIGENIC PHOSPHATE PELLETS

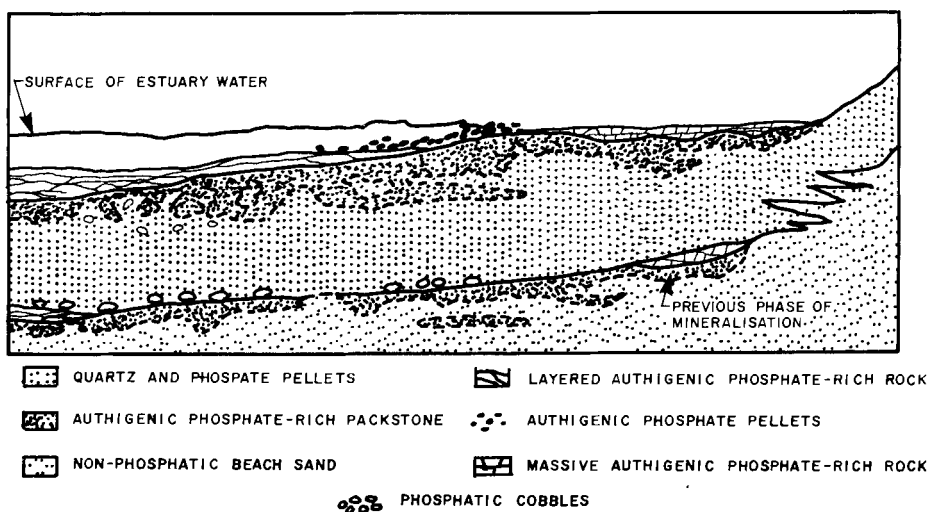MASSIVE AUTHIGENIC PHOSPHATE-RICH ROCK

PHOSPHATIC COBBLES

Fig. 243. The mode of formation envisaged for the massive and layered phosphatic rocks as well as for the phosphate pellets and phosphate-rich packstones from Saldanha Bay. (After Birch, 1980.)
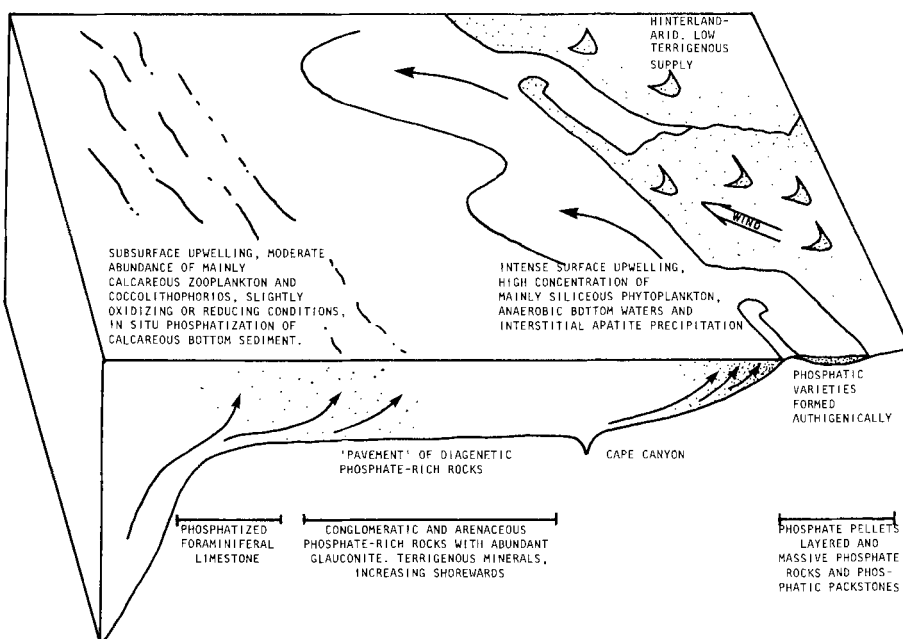

Fig. 244. A schematic diagram depicting the penecontemporaneous formation of phosphate-rich rocks and pellets by authigenic and diagenetic mechanisms from the southwest margin of South Africa. (After Birch, 1980.)

of diagenetic crystallization origin formed in shallow-water carbonates and are not of epigenetic origin.

Natale (1980) has written (in Italian mostly) numerous papers on the textural/microstructual characteristics of pyrites from several exhalative – sedimentary deposits and recognized differences that allow them to be distinguished from other (e.g., purely sedimentary) types of pyrites.

Note: In conjunction with trace-element, isotope and paragenetic studies, i.e., comparing/contrasting pre-ore, syn-ore and post-ore gangue and ore minerals, eventually it will be possible to establish several genetic groups of pyrites, including metamorphic and igneous-rock associated varieties.

Odin/Letolle (1980) outlined the evolutionary scheme of pelletal glauconite (Fig. 245).

Ramsay (1980) discussed the crack-seal mechanism of rock deformation which results in mineral-filled (non-ore) extension veins and pressure solution features in, for example, pisolitic ironstone, oolitic limestone, and oolitic chamosite rock.

Note: Many of the features resemble those of late diagenetic textures/microstructures. It is necessary to establish criteria to differentiate, say, early diagenetic pressure-solution phenomena from late-stage tectonic types.

Routhier (1980) presented information on textures and parageneses, among numerous other topics. One example is provided in Fig. 246, which is self-explanatory because of its detailed subscript.
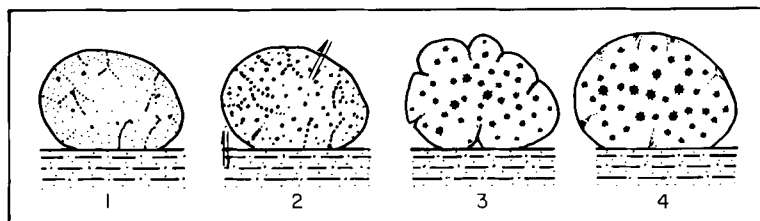

Fig. 245. Evolutionary scheme of pelletal glaucony. *Step 1* – An initial framework of variable mineralogical nature is altered on the bottom of the ocean ($\cdot - \cdot - \cdot$). Porosity is created and a semi-confined micro-environment results. *Step 2* – The initial framework rejects inherited ions to the sea while ions from the bottom water are trapped and feed the crystal growth of glauconitic smectites (**). *Step 3* – Glauconitic smectites are rearranged by recrystallization into more closed minerals. Surficial cracks appear as the result of faster crystal growth in the center than on the periphery of the framework. *Step 4* – A new generation of less evolved glauconitic minerals appears and surrounds the glauconitic pellet where glauconitic micas are born through new recrystallization (**). The pelletal nature of this glaucony is the result of the pelletal nature of the initial framework and of the selectivity of the process here described: pellets of $100 - 500 \ \mu m$ are especially favorable. This evolution may stop at any moment either through burial or through alteration. (After Odin/Lecolle, 1980.)
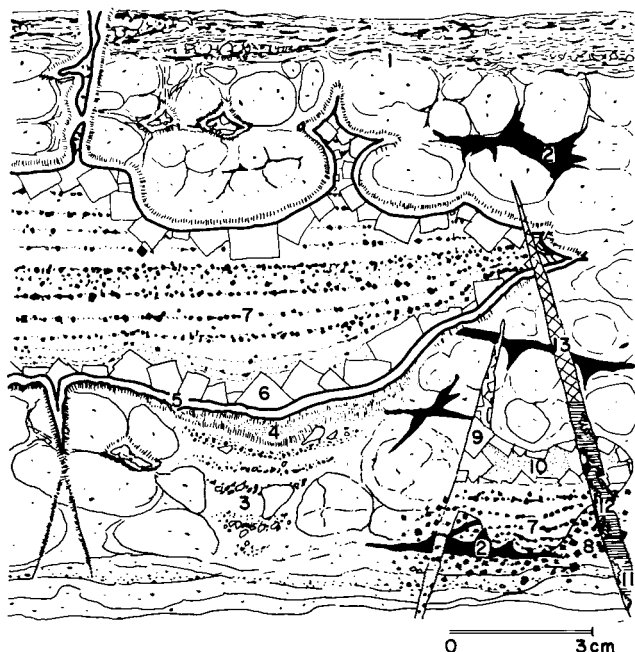
Fig. 246. Mineral succession in Asturias fluorite western district, France; general scheme. Dissolution cavities and deposition in these cavities (see text by Routhier, 1980, for details). This is an example of "microkarstification" on a basin margin. By Thibieroz (unpublished). *1* = Host rock: Triassic limestone; the nodular structure is of pedogenic origin and the laminated encrusting horizon (top) is to be compared with a calcrete; *2* = chert; *3* = on the bottom of a dissolution cavity, sediment made of limestone fragments and calcarenitic matrix; *4* = prismatic calcite; *5* = double edge, a violet-brown one (iron oxides) on the cavity bottom, a brick-red one coating the entire cavity surface; *6* = geodic fluorite (white, pink or yellowish); *7* = sediments with small fluorite crystals, intensely silicified; *8* (bottom right) = neoformed fluorite cubes on a small cavity border; in this cavity, *9* = geodic fluorite (yellow) and *10* = very fine-grained sediment. In a veinlet, *11* = crested barite (pink); *12* = calcitic sediment with fragments of yellow fluorite and pink barite; *13* = white and blond calcite. (After Routhier, 1980, fig. 86, p. 340; see also Thibiéroz, 1982.)

Lett/Fletcher (1980) modeled the possible diagenetic origin of pyrite framboids and chalcopyrite – covellite grains in a Cu – rich bog (Fig. 247); the model may well apply also to those textures seen in ore deposits. G.R. Taylor (1983a) described a mechanism of framboid formation under volcanic – exhalative conditions, this supplementing his earlier (1982) study (Fig. 248). These and other studies indicate that there is a whole spectrum of transitional – gradational – overlapping sedimentary and volcanic diagenetic milieus, processes and products, some of the latter may be identical or similar and are indistinguishable at present.

Möller et al. (1980) identified three textural types (with two sub-varieties; thus a total of five types) of fluorite (Table 76) reflecting five types of mineralizations (see their model of ore-forming brines).
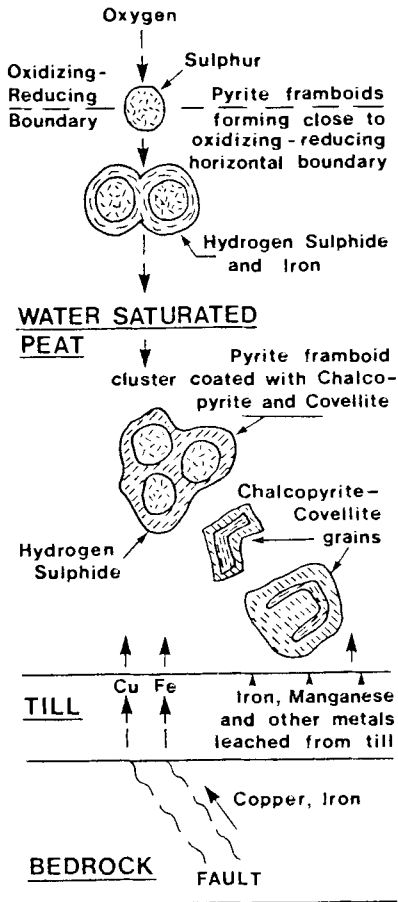
414

Fig. 247. Model for possible formation of framboidal pyrite and chalcopyrite – covellite grains in a typical bog profile. (After Lett/Fletcher, 1980.)

McClay (1980) described sheared galena, its textures and micro-structures, and compared diagenetic with deformational features. Subsequently (1983), he studied fabrics of deformed sulfides. Basu et al. (1984) deliberated on the significance of transformation textures in fahl ores from a polymetallic deposit. A lot remains to be done on establishing guides/criteria to discriminate between primary and secondary textures, microstructures, and structures (and their inter-relationships) on any scale (i.e., sedimentary vs. metamorphic vs. deformational features).

Utter (1980) described the rounding of ore particles from the Witwatersrand Au – U deposits as indicators of detrital/clastic origin. Several types of rounding must be differentiated: chemical vs. physical rounding, diagenetic vs. depositional, and transportational vs. in-situ corrosional styles of rounding, for example. (Many of these mechanisms overlap — the terminology has to be refined also!)
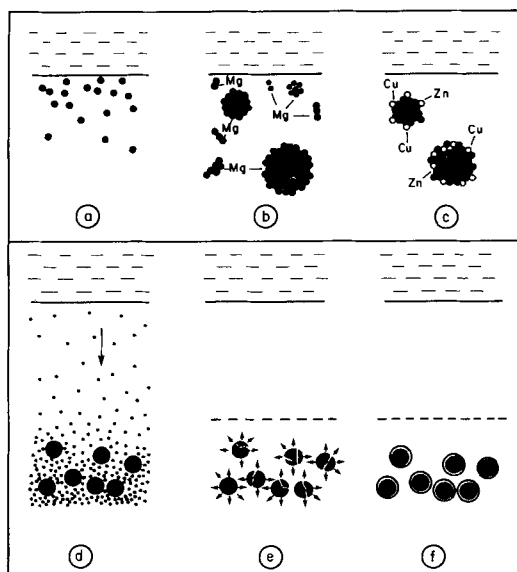
Fig. 248. Proposed mechanism for magnesioferrite spheroid formation. (a) Precipitation of ferroso-ferric hydroxide at exhalative fluid/seawater interface; (b) coagulation of magnesium stabilized hydroxide globules into spheroids; (c) adsorption of base metal ions within a composite gel spheroid; (d) entrapment of spheroid in silica gel; (e) diagenesis, water expulsion, syneresis fractures; (f) diagenetic reaction to form smectite shell. (After Taylor, 1983.)

Riedel (1980b) examined electron-microscopically the sphaeroids from an Irish Pb – Zn ore deposit and suggested that they may be similar to the sphalerite globules suspended in water as described by Degens et al. (1972) from Lake Kivu, East Africa. Lange/Elby (1981) described Cu – Ag-bearing oolitic deposits from the Precambrian.

Wilkins/Bird (1980) characterized the healed fractures in fluorite by etching and proton irradiation. Such studies can also be performed on M.V.-type ores, e.g., to reveal the last stage of ore development in the form of healed fractures and to establish the effect on fluid inclusions. Some of the fractures are invisible to the naked eye.

Wallace/Roper (1981) and Roper/Wallace (1981) mentioned almost inadvertently framboidal pyrite without providing more discussions: "Where footwall uranium is present, late veinlets of montmorillonite and framboidal pyrite cut the kaolinized and silicified rocks associated with the earlier mercury mineralization", being present in at least two *lavas*. Also, "scanning electron photomicrographs by Wallace show intermixed uraninite and coffinite (?) occurring as extremely fine-grained (< 1 μm) coatings around and between framboidal pyrite . . .".

416

TABLE 76

Classification of fluorite mineralizations (modified from Möller et al., 1980)

Type	Characterization of fluorite mineralization	Hostrock (ground mass)	Name of borehole or outcrop
I	Irregular distribution of impregnated fluorite; mostly of low contents; particle size of fluorite; particle size of ground mass	dolomite dolomite	Dalum Z Kalle
Ia	Irregular distributed fluorite, bounded to ooids or onkoids; fluorite often centered	dolomite dolomite	Neuenkirchen Eschwege
II	Streaked formed fluorite concentrating; particle size of fluorite; particle size of ground mass	limestone dolomite limestone/ dolomite limestone	Hoya Z Adorf Z Neuenkirchen Staffhorst Z
IIa	"Grains" of fluorite are essentially greater than the ground mass, partly with sharp-edged grain boundaries; sometimes elongated external form of fluorite aggregates	dolomite dolomite limestone limestone dolomite	Horstedt Z Neuenkirchen Staffhorst Z Hoya Z Eschwege
III	Veined mineralization of fluorite exclusively or in connection with other minerals. The veins take an approximately vertical course to bedding; width of the veins max. 2 mm	limestone limestone limestone dolomite dolomite dolomite	Verden Z Hoya Z Holthusen Hohes Moor Z Neuenkirchen Eschwege

Leitch (1981) reconstructed "inferred stages" in the recrystallization of original colloidal and framboidal pyrite (see his figs. 3 and 4 for four textural phases). His fig. 1 depicts their vertical distribution in a massive sulfide deposit of diagenetic-to-hydrothermal exhalative origin as outlined by the lower, middle and upper zone textures.

Friedman et al. (1981) studied carbonate deformation mechanisms in the world's deepest (approximately 9 km) well and compared shallow- with deepest-well specimens. How can such textural studies be applied to the hostrocks of M.V.-type deposits?

Stanistreet et al. (1981) deliberated on accretionary spheroids of graded units as possible environmental indicator.

Shadlun (1982) described the ore textures as indicators of formational conditions, including parageneses of three different stratiform Pb − Zn deposits: (a) hydrothermal − sedimentary ores in carbonate − sandy − argillaceous rocks; (b) hydrothermal ores in interlayer breccia in carbonate rocks; and (c) metamorphosed hydrothermal − sedimentary in schists (with or without relict features). These three
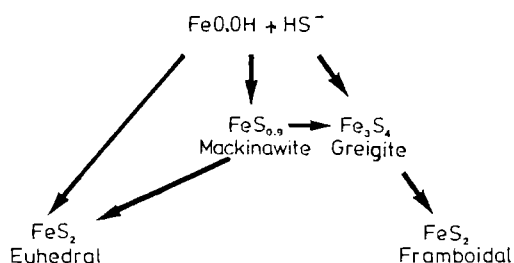
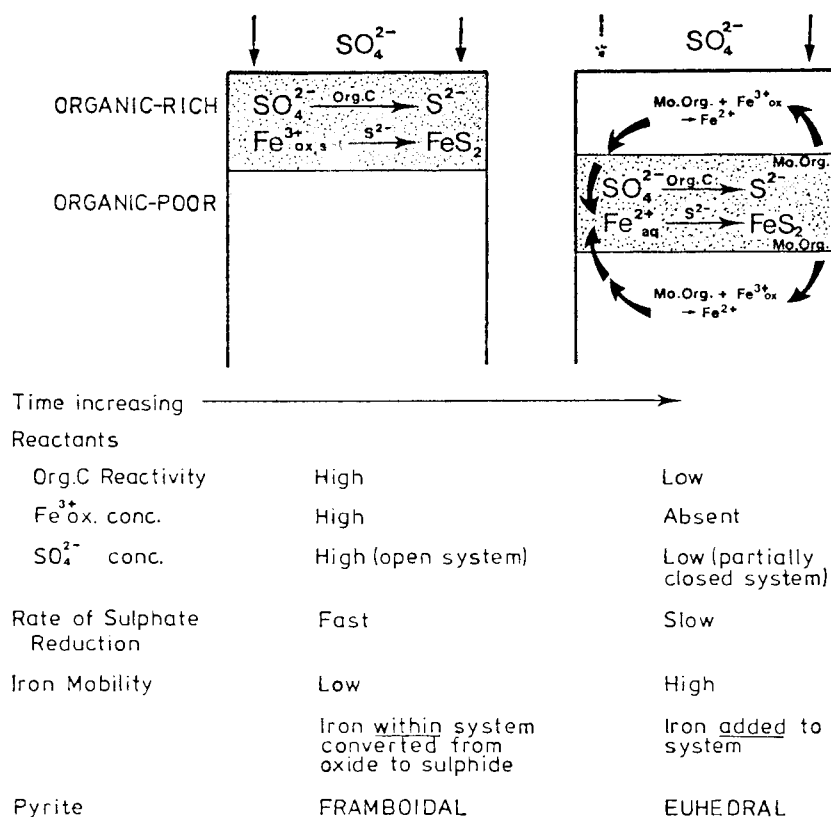Fig. 249. Possible reaction pathways to framboidal and euhedral pyrite. (After Raiswell, 1982.)

Reactants		
Org.C Reactivity	High	Low
Fe^{3+}ox. conc.	High	Absent
SO_4^{2-} conc.	High (open system)	Low (partially closed system)
Rate of Sulphate Reduction	Fast	Slow
Iron Mobility	Low	High
	Iron within system converted from oxide to sulphide	Iron added to system
Pyrite	FRAMBOIDAL	EUHEDRAL

Fig. 250. Relationship between pyrite texture and sediment chemistry. Organic matter reactivity is initially high, and the rapid production and precipitation of sulfide occurs, using the high concentrations of in situ, reactive iron and ultimately giving framboidal pyrite. Other reduced and dissolved products of bacterial decay (mobile organics or Mo.Org.) diffuse into adjacent sediments from which iron is solubilized for continued sulfide precipitation and the formation of euhedral pyrite. (After Raiswell, 1982.)
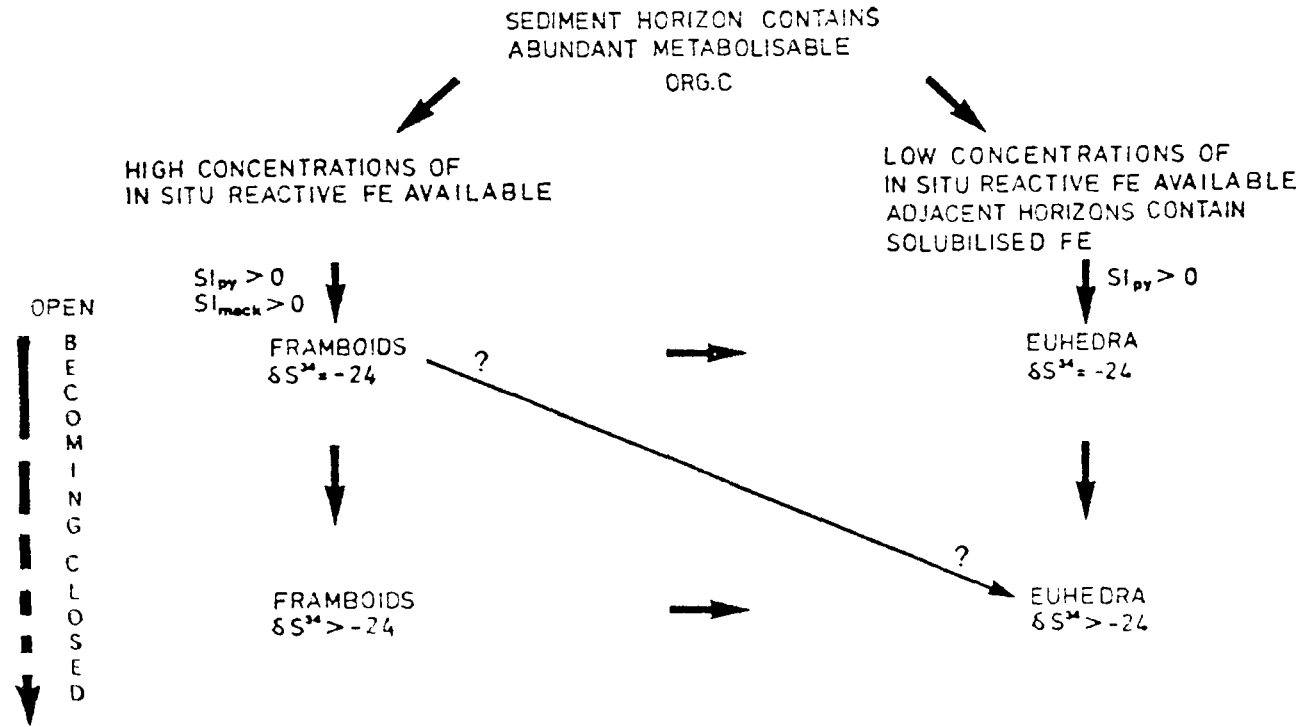
Fig. 251. Paragenetic relationships between pyrites of different texture and isotopic composition. Sulfate reduction in the presence of high concentrations of reactive iron gives oversaturation with respect to mackinawite and pyrite ($SI_{mack.}$, $SI_{py} > 0$) and ultimately framboidal pyrite. Where iron can be solubilized from adjacent horizons (either by in-situ formation of a reducing agent or diffusion of a reducing agent from the organic-rich horizon), lower degrees of sulfide saturation result in the formation of euhedral pyrite. (After Raiswell, 1982.)

"types" were used as "standards" in textural – structural comparative/contrastive-type studies. Many diagenetic textures are present in type No. 1 deposit.

Dubinchuck et al. (1982) used the electronmicroscope to investigate textures of stratal-infiltration-type uranium mineralization.

Raiswell (1982) offered three models (Figs. 249 – 251) depicting, respectively, the reaction pathways of framboidal – euhedral pyrite, relation between pyrite texture and sediment chemistry, and the paragenesis between pyrites of different textures and isotopic composition.

Swett/Crowder (1982) described the diagenetic paragenesis, textures, chemical elemental correlation matrix, cell parameter of apatite vs. CO_3/PO_4 ratio, diagenesis/weathering reactivity/solubility and consolidation of crustal structure of phosphorite nodules and associated glauconite sands. They also examined the oolitic structures. Many papers deal with Fe-rich oolites – ooids – concretions, such as those by Nahon et al. (1980) of laterite, weathering-type ferruginous ooids; Van Houten/Karasek (1981) studied a sedimentary oolitic iron formation; Riezebos et al. (1981) dealt with iron concretions; and Bhattacharyya/Kakimoto (1982) examined the microfeatures of ironstone and bauxite ooids/pisolites. What are the similarities and differences of and gradations between these numerous genetic types of coated grains (Peryt, 1983)? Marchig/Halbach (1982) studied the internal structures of Mn-nodules and related them to the conditions of sedimentation.

McClay/Ellis (1983) offered an excellent study of the deformation and recrystalliza-
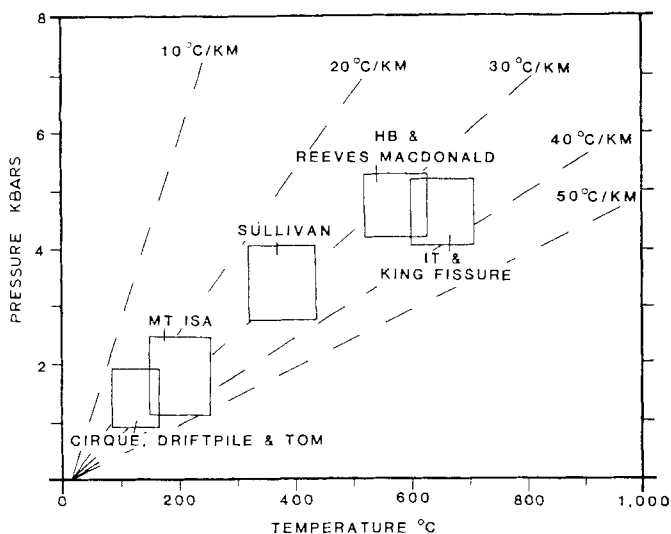

Fig. 252. Approximate pressure – temperature fields for the metamorphism of the sulphide deposits discussed by McClay/Ellis, 1983. (For details, see original publication.)

tion textures of pyrite of eleven ore deposits. In Fig. 252 he outlined the pressure – temperature fields of metamorphosed sulfides and in Fig. 253 the increasing metamorphic grade vs. grain-size fields. The latter shows three major groups, including the primary (also sedimentary – diagenetic) textural varieties. See also their figs. 3 and 7 and table 11, where diagenetic and metamorphic pyrites are compared and different deformation mechanisms are treated. It has been known for some time that diagenetic pyrite can act as nuclei for the precipitation or replacement of copper, for example. Consequently, it is of utmost importance in genetic investigation to distinguish between the numerous stages of pyrite formation.

Craig (1983) outlined metamorphic features in massive sulfides, including the textures. Are any primary structures preserved?

Merino et al. (1983) examined the pressure – solution seams formed during late diagenesis and discussed the stylolites, pore-fluid concentration, and differential solubility.

Fontboté/Amstutz (1983) studied the facies and paragenesis of diagenetic crystallization rhythmites in stratabound Pb – Zn(Bs – F) deposits of Europe, including the textures, cyclicity, differentiation/fractionation, external vs. internal factors, and others.

Sandecki (1984) studied the textures of several sulfide minerals from Sweden;
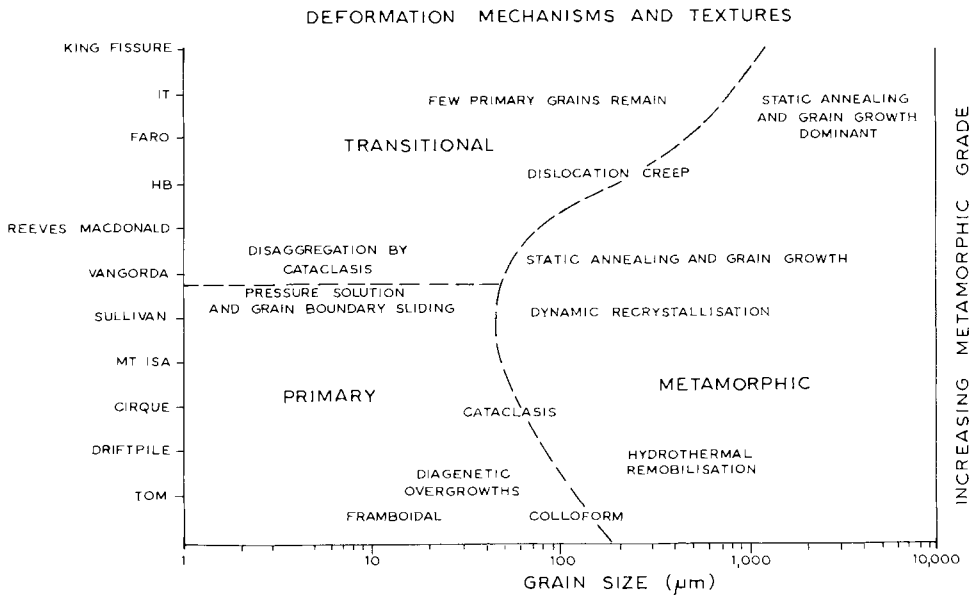

Fig. 253. Summary of the deformation textures and mechanisms as described by McClay/Ellis, 1983. The boundaries are transitional. Also note that the vertical axis is not to scale.

Reimer (1980) examined the diagenetic textures of Archean sedimentary barite; Boast et al. (1981) studied the textures and isotopic evidence of an Irish base-metal deposit. Durazzo/Taylor (1982) utilized experimental exsolution textures as a criteria for ore genesis; and Bellanca et al. (1984) investigated the textural – chemical – isotopic variations induced by hydrothermal fluids on Mesozoic limestones (the data ought to be applied to M.V.-type ores of diagenetic origin).

Swager's (1985) microstructural study of the syndepositional carbonate-replacement-type Mt. Isa copper mineralization enabled him to separate the epigenetic silica – dolomite – copper ore from the adjacent syngenetic – diagenetic stratiform Ag – Zn – Pb ores.

Frater (1985) examined premetamorphic textures of opaque ore minerals, including the depositional (primary) and various secondary diagenetic, metamorphic and deformational textures. See his excellent models.

– See also Multi-factorial, Paragenesis, Replacement and Temperature.

THERMODYNAMICS

Froese (1981) applied thermodynamics in the study of mineral deposits (e.g. see model on Kupferschiefer zoning and the hypothesis of the M.V.-type ores); Saxena (1983) used kinetics and equilibrium data in numerous mineral reaction studies (including in deciphering the paleoenvironment of rock genesis, thermal history, diagenetic-equilibrium data, among others); Hazen/Finger (1983) compared the crystal chemistry in the study of temperature, pressure, composition and the variation of crystal structures; and Grassmann (1984) wrote on the thermodynamics of life and energy involved, including on the biological energy of life processes. How does the energy of life processes affect those needed in physicochemical diagenetic mechanisms?

Kalogeropoulos (1983a) discussed FeS in sphalerite coexisting with pyrite as an indicator of the fugacity of S; Zhil'tsova et al. (1982) studied the physicochemical conditions of carnotite ore mineralization (see also Uranium); and Timofeyev (1984) examined the energetics of supergene processes (see Weathering).

Bischoff (1980) mentioned the physical limits of the geothermal fluid system and the role of adiabatic expansion in a geothermal system; Ohmoto/Lasaga (1982) discussed the kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems; Henley et al. (1984) summarized the fluid – mineral equilibria under hydrothermal conditions; and Hardie (1983) described the origin of $CaCl_2$ brines by basalt – seawater interactions as based on simple mass-balance calculations. What are the precise thermodynamic similarities and differences (as well as transi-

tions and overlaps) of low-temperature hydrothermal – exhalative conditions in contrast to "normal" diagenetic/halmyrolytic processes, and the differences between all those in deep-water (high pressure) and shallow-water (low-pressure) environments?

Pyzik/Sommer (1981) studied the kinetics and mechanisms of sedimentary Femonosulfides; Fox/Wofsy (1983) examined the kinetics of the removal of Fe-colloids from estuaries; and Ruppert (1984) discussed the physicochemical aspects of a Cretaceous iron ore deposit.

Savenko/Baturin (1981) modeled thermodynamically the Mn-precipitation from seawater in connection with Mn – Fe concretions; whereas Balzer (1982) discussed the thermodynamic and kinetic controls on the distribution of Fe and Mn at the sediment/water interface.

Baes/Mesmer (1983) outlined the thermodynamics of cation hydrolysis, including the transport of metallic elements from 25°C to high-temperature conditions.

Krainov/Ryzhenko (1981) modeled physicochemically the interactions of water – rock systems applied also to hydrodynamic and hydrochemical processes.

Lippman (1982) discussed the thermodynamic status of clay minerals, e.g., by comparing sedimentary, diagenetic, hydrothermal and other metamorphic clays, and deliberated also on the temperature – pressure controls, exogenic vs. endogenic reactions, miscibility gap, stability vs. instability, equilibria, and kinetic inhibitions.
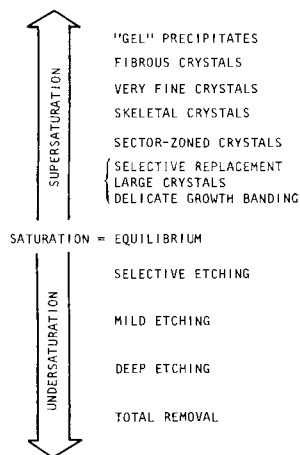

Fig. 254. Features indicative of the degree of saturation. Time is also an important variable, especially in the undersaturated region, for a slight undersaturation over a long time can completely remove a mineral. (After Barton, 1981.)

Siever (1983) reported on the burial history and diagenetic reaction kinetics in general (excellent on multi-factorial problems). (See also Metamorphism.)

Deelman (1980a) described "monolayer drying" as a new mechanism of crystal growth and he also outlined (1980b) the laboratory equipment for the study of irreversible geochemical reactions. See references to his investigations of dolomites, for instance.

Habashi (1983) wrote on the dissolution of minerals and hydrometallurgical processes. How much is applicable to natural systems?

Barton (1981) discussed, among many other variables, the "degree of saturation" (Fig. 254), which is partly controlled by *time*. Numerous processes and/or products are directly related to this saturation parameter, e.g., type of precipitation, textures/fabrics, replacement, etching, and removal. (See also Time, and Temperature.)
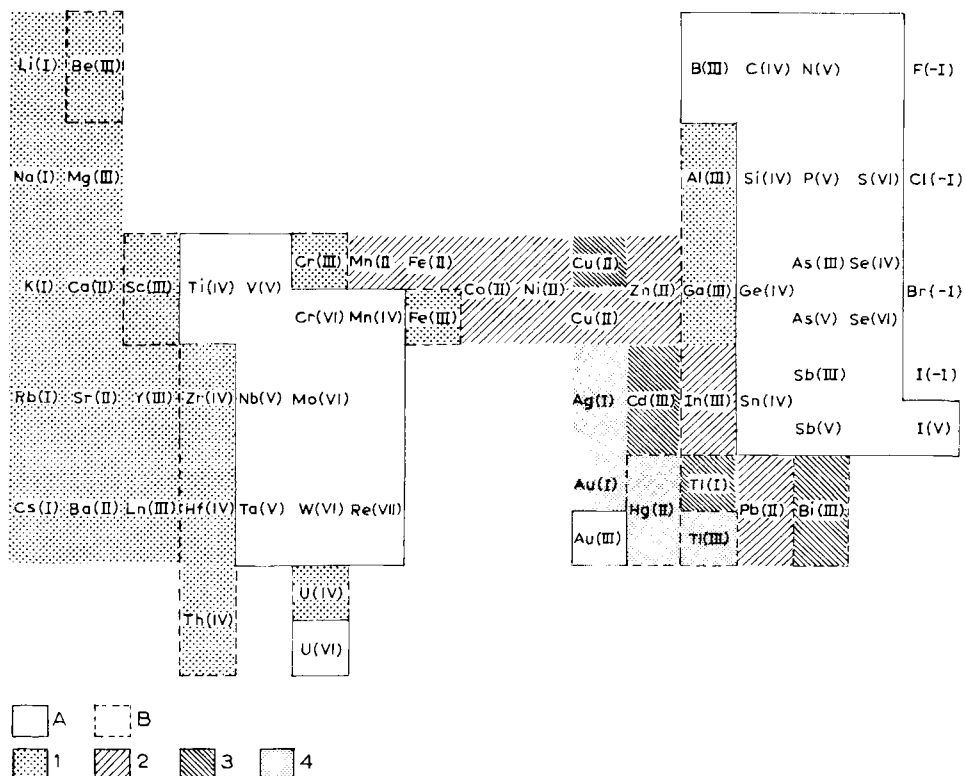

Fig. 255. Periodic table showing the classification of the elements. The symbol Ln represents the lanthanide series. A = fully hydrolyzed oxidation states; B = oxidation states in the transition zone of the Born plot (see fig. 3 by Turner et al., 1981); *1* = (a) cations; *2* = (a)' cations; *3* = (b)' cations; *4* = (b) cations.

Turner et al. (1981) offered an excellent summary of the equilibrium speciation of dissolved elements — much of the data is applicable to low-temperature and low-pressure diagenetic systems (see also pH, and Complexing sections). In Fig. 255, the periodic table shows the elements divided into several types of ionic groups.

Sverjensky (1985) examined the thermodynamics of the distribution of divalent trace elements between sulfides, silicates, and hydrothermal solutions. Similar approaches are to be used for lower temperature/pressure systems.

— See also Heat, Multi-factorial, Pressure, and Temperature.

THIXOTROPY

Elliston (in Carey, 1963; Elliston, 1963a,b,c, 1984, 1985; see also Hunter, 1963) rightly pointed out that the theories of rheology, thixotropy, and colloid chemistry have been largely neglected by geologists in the study of diagenesis and ore genesis, among others. Sediment mobility and remobilization, water outflow, accretion, syneresis, shearing, unmixing, crystallization, accretion and concretion, desorption, many diagenetic changes, and, therefore, metal mobilization and ore genesis are related to the thixotropic properties of unconsolidated sediments (see also Boswell, 1963). Elliston described many textures and structures indicative of these conditions.

Elliston (1966) applied his unique ideas of the diagenesis of mobile sediments to the origin of the Peko orebody, based on rheological and colloidal theories. Remobilization of thick pasty (i.e., unlithified or unconsolidated) sediments during diagenesis is an essential feature in the concentration of metals dispersed in the sediments. He provided many details on Van der Waals' attraction – coulombic repulsion, adsorption – desorption, accretion, dehydration, peptization, nucleation, concretion, gelatinous precipitation, and thixotropic reliquification. Elliston's concepts are useful in diagenetic studies and are thought-provoking.

Note: (a) Apparent difficulties between syngenetic, diagenetic and epigenetic hypotheses can be resolved by applying Elliston's concepts based on "rheological – thixotropic diagenesis". (b) Although his ideas were published 25 years ago, little attention has been paid to them. They definitely deserve a closer scrutiny and application.

Zimmermann/Amstutz (1973) described the intergrowth and crystallization features in a Cambrian "mud volcano", very similar to those in Recent mud volcanoes. Semiconsolidated sediments intruded into adjacent and overlying, more consolidated beds. The sediments contained pyrite/marcasite, sphalerite, galena and chalcopyrite. Numerous textures exist that allow the reconstruction of the paragenesis ranging from pre-brecciation to syn- and post-brecciation origin of the sulfides and other constituents. The concepts of Elliston's (1963a,b,c, 1966, 1984, 1985, see above) ought to be applied in this and similar situations.

Yariv/Cross (1979) offered a handbook of the geochemistry of colloid systems summarizing the basic principles needed in the study of thixotropy and related phenomena. (See also Eitel, 1964, 1975.)

TIME – RATE – RESIDENCE TIME

Turekian/Schutz (1965) and Turekian (1967) established that the rates of trace-element accumulation (Cr, Pb, Ni, Co, Fe, Sn, Mn) are related to the rates of clay deposition (e.g., see Fig. 256). They offered four alternative models explaining this phenomenon (see their pp. 57 – 58).

Lerman (1971) studied the time required to achieve chemical steady-states in lakes and oceans. How does the data influence reconstructions of diagenetic systems?

H.H. Wilson (1975) discussed the time of hydrocarbon expulsion during the evolution of sedimentary basins.
    Note: If it is factual that metals adsorbed on clays and organic matter, for example, are released during burial metamorphism-cum-late diagenesis and catagenesis into connate/compaction fluids, and these fluids constitute ore-forming solutions, then studies of "expulsion" as done by the oil geologists ought to be carried out also by the ore petrologists and geochemists.

Bowen (1975) discussed the residence time of heavy metals in the environment and Li (1982b) investigated the "mean oceanic residence time" of elements (including metals and non-metals), concluding that many factors control the systems, including those related to diagenesis. Varnavas/Papaioannou (1983) studied the metal ac-
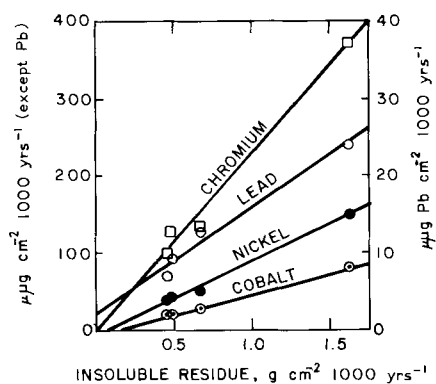

Fig. 256. Relationship of trace element accumulation rate (R_{yj}) to clay ("insoluble residue") accumulation rate (R_j). The intercept on the trace element axis gives a value of R_y* which statistically cannot be differentiated from R_y* = 0 as seen from the information (table 1) supplied by Turekian/Schutz (1965).

cumulation rates in oceanic rise metalliferous sediments; whereas Thomson et al. (1984) considered these rates for pelagic sediments.

De Boer (1976) provided data on (a) porosity versus geologic time (the porosity is controlled by pressure solution); (b) solubility increase caused by external load; (c) porosity versus load pressure; and (d) porosity versus temperature of solutions.

Pačes (1976) discussed various types of short-, intermediate- and long-time (temporal) changes in the chemical composition of natural waters. He also presented evidence of Precambrian to Recent changes that are due to and/or may have affected the composition of natural waters. It is important to determine how such changes affected diagenesis throughout geologic time. Additional questions that arise here are (a) What are the effects on ore-forming solutions in sedimentary basins? (b) Are they overridden by more influential exhalative processes?

Curtis (1977) discussed the links between sediment mineralogy and burial rate in marine sediments, which controlled the origin of clays, various carbonate species, phosphate, oil and gas, and the preservation of carbon (Table 77). The preservation of carbon is important in the subsequent genesis of ore deposits.

Finlow-Bates/Stumpfl (1979, 1981) and Finlow-Bates/Stumpfl (1979/80) stated that if one accepted the proposition that the exhalations of hydrothermal fluids onto the seafloor control certain diagenetic processes (as well as the supply of metals and quantities and types thereof) and the zoning of metalliferous precipitation (see their fig. 6), then the rate of hydrothermalism will also control diagenesis. A relatively rapid burst in metal supply and precipitation was proposed.

Lydon (1978a,b) discussed the possible effects of degeneration rate and flow rate of hydrothermal solutions on the crystal size, degree of dispersal, and the degree of zonation of ore minerals (Fig. 257). A similar concept must be developed and applied with regard to mineralization due to precipitation from different types of solutions.

Beales et al. (1980) timed the ore mineralization of Mississippi Valley-type ore deposits by measuring the (paleo-)magnetic remnance imprinted on the ore.

Maynard (1980) studied the rate of sedimentation that, in turn, influenced the S-isotopic composition of iron sulfides.

Meyer (1981), Anhaeusser (1981), Nash et al. (1981), Lambert/Groves (1981), among many others, have provided information on the evolution or development of ore-forming processes from the Archean and Proterozoic, through the Phanerozoic, to the Recent. Although many of these studies are confined to specific time periods (i.e., either to the Precambrian or the Proterozoic or shorter periods thereof), others attempted to reconstruct the whole Earth's history by not only considering the changes of the ore deposits but also by examining a whole spectrum of

environments and their deposits. This included (1) the evolution of the crust, continents, atmosphere, and oceans; (2) the development of life and its control on the geochemical or rock cycles; (3) the lithologic evolution from the Precambrian to the Recent (e.g., the ratios and certain properties of limestones, primary and secondary dolomites, evaporites, shales, various sandstone types, cherts, and volcanic and plutonic rocks); and (4) tectonism and continental drift/plate tectonics.

Note: (a) To put the above into context with diagenesis (from the data in the above-cited publications, with some of the information being even semi-quantitative to quantitative), one can only surmise by extrapolation (using one's common sense and by reading between the lines of the writer's discussions) that the numerous *diagenetic* physicochemical – biochemical – mechanical processes and products must also have evolved through geologic time. This was due to the development of (1) the atmosphere (O_2), (2) the oceans' composition and with it the composition of related fluids (e.g., connate waters and basinal compaction fluids), (3) life (bacteria, fungi, and carbonate-formers), (4) the Earth crust (influencing and controlled by tectonism, plate movements, platforms versus geosynclines), and (5) lithologies (the diagenesis within platform carbonate – evaporite environments is certainly different in general and in detail from the diagenesis in sandstone/shale basins, volcanic-rich milieus, and red-bed-type intramontane clastic basins. (Possibly this is also indicated by the associated different styles of ore mineralizations.)

(b) The study of the evolution of diagenesis has to consider the changes due to *world-wide* causes in contrast to those confined to *specific* localities or *particular* basins, because they may be controlled by fundamentally different parameters. For example, the universal diagenetic evolution may be unidirectional and irreversible versus the local or basin-confined change that is multidirectional, cyclic, and repeatable.
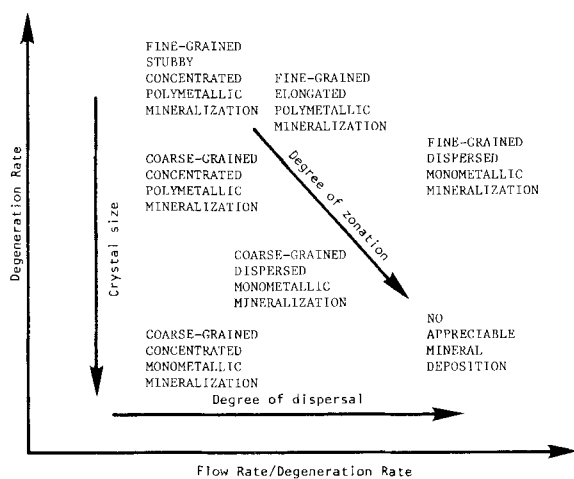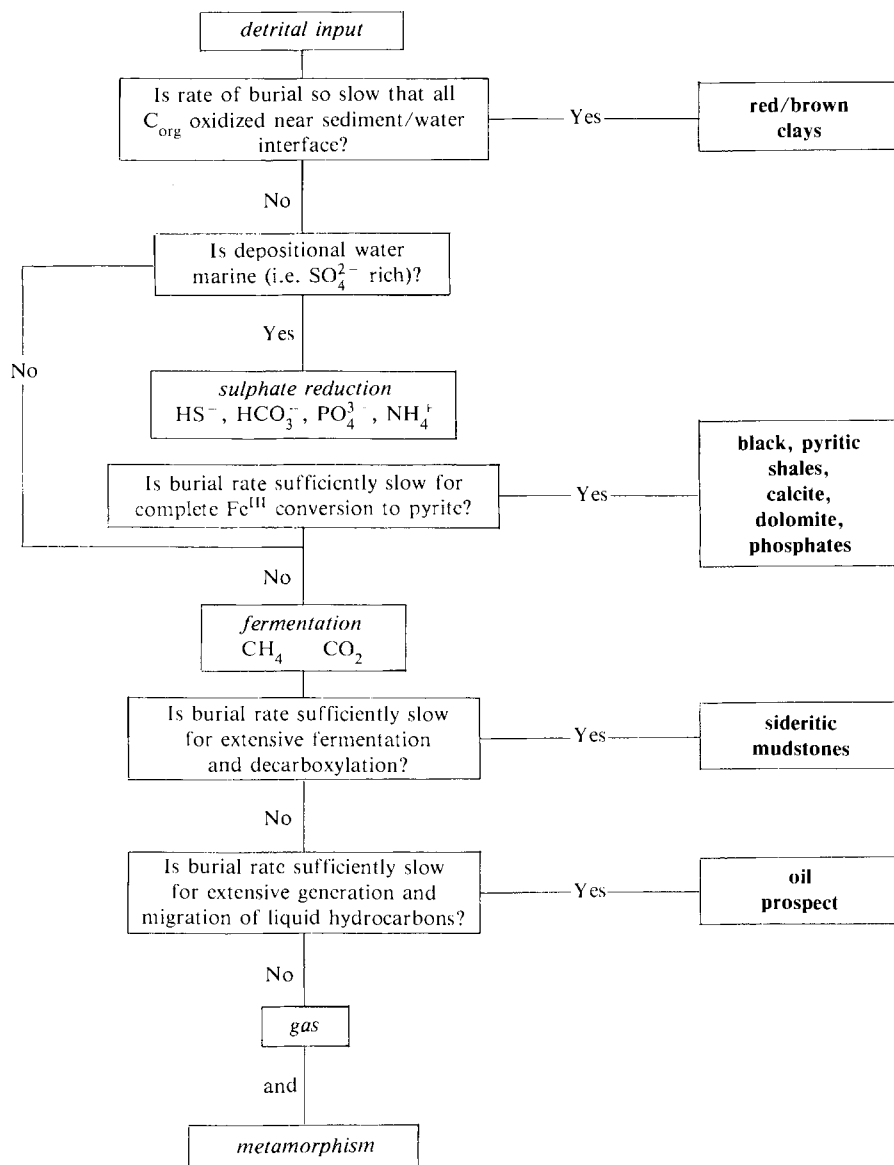

Fig. 257. Possible effects of the degeneration rate and flow rate of a hydrothermal solution on the grain size, degree of chemical dispersal, and degree of chemical zonation of the precipitate. (After Lydon, 1978.)

TABLE 77

Links between sediment mineralogy and burial rate in marine muds (after Curtis, 1977, in Leeder, 1981)

---

detrital input

Is rate of burial so slow that all C_{org} oxidized near sediment/water interface? —— Yes —— **red/brown clays**

No

Is depositional water marine (i.e. SO_4^{2-} rich)?

Yes

sulphate reduction
HS^-, HCO_3^-, PO_4^{3-}, NH_4^+

No

Is burial rate sufficiently slow for complete Fe^{III} conversion to pyrite? —— Yes —— **black, pyritic shales, calcite, dolomite, phosphates**

No

fermentation
CH_4 CO_2

Is burial rate sufficiently slow for extensive fermentation and decarboxylation? —— Yes —— **sideritic mudstones**

No

Is burial rate sufficiently slow for extensive generation and migration of liquid hydrocarbons? —— Yes —— **oil prospect**

No

gas

and

metamorphism

Russell et al. (1981) discussed the time – temperature contrast between volcanic and sedimentary rock-hosted exhalative sulfide deposits.

Barton (1981) modeled qualitatively the relative times needed for equilibration related to ore-mineral genesis (Fig. 258).

Dibble/Tiller (1981) examined the non-equilibrium water – rock interactions, which are time-dependent.

Sadler (1981) discussed the sediment accumulation rates and the completeness of stratigraphic sections, and Dott (1983) investigated the episodic sedimentation by inquiring "how normal the average is", "how rare it is" and "what is its importance"? Numerous syngenetic, diagenetic and later burial-metamorphic processes depend on the rates of sedimentation. For example, a steady-state diagenesis model must be established over time and depth scales (see Krishnaswami et al., 1984). The rate of sedimentation/accumulation can also control subsidence (and/or vice versa) and it, in turn, the dewatering and compaction rates, which likewise influence diagenesis.

Gundlach/Marchig (1982) considered two possible origins of the ocean-floor metalliferous sediments: (a) submarine exhalative – hydrothermal deposits composed of sulfides which are partly oxidized (e.g., brine deposits of the Red Sea); and (b) diagenetic products composed of metal oxides. The latter are divisible into autochthonous and terrigenous types. No distinction has been made between these
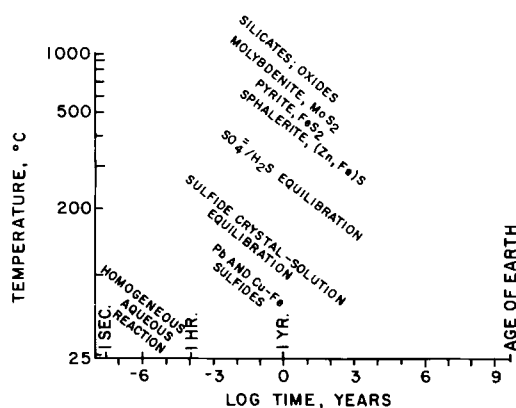

Fig. 258. Qualitative relative times for equilibration for some processes of geologic interest. The temperature is on the reciprocal absolute scale. The positions for the crystalline phases are chosen to represent the time – temperature region required for "complete" reaction of fine-grained, dry materials in a sintering experiment; to a large extent this involves solid-state diffusion on a scale of a few tens of μm. The slopes and approach to linearity of the time – temperature curves are unknown, but it is obvious that at earth surface conditions some reactions are effectively frozen, even in terms of geologic time, whereas others react so fast that natural "quenching" of the high-temperature state is improbable. (After Barton, 1981.)

by many researchers, although to do so might be helpful in the understanding of ore genesis and in exploration. The element-enrichments in the autochthonous and terrigenous phases are given in Figs. 259 and 260, respectively. The influence of time, i.e., time of exposure (?), is reflected in the sedimentation rates.

Burnett et al. (1982) measured the growth rates of phosphate nodules and compared growth rates with sedimentation rates, growth direction, fluid flux, P-source from sediments, etc.; and Reyes et al. (1982) dealt with the rapid growth of a deep-sea Mn-nodule.

Ibach (1982) and Lein (1983) attempted to correlate the sedimentation rate with the carbon content in Recent and ancient marine sediments.

Behrensmeyer (1983) discussed the "resolving time in paleobiology", including methods on calibrating sedimentation rates comprising also geochemical and geophysical techniques.

Anderson et al. (1983) considered the removal of Th- and Pa-isotopes at ocean margins, including their fluxes and residence times as measured in sedimentary traps.
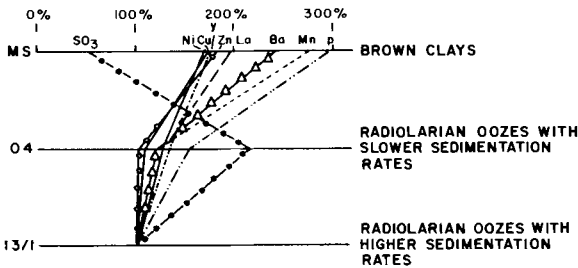

Fig. 259. Changes in the contents of elements which are enriched in the autochthonous phase of the sediment in different sediment types. The contents in the radiolarian oozes from the cruise VA 13/1 are taken as 100%. (After Gundlach/Marchig, 1982, p. 206.)
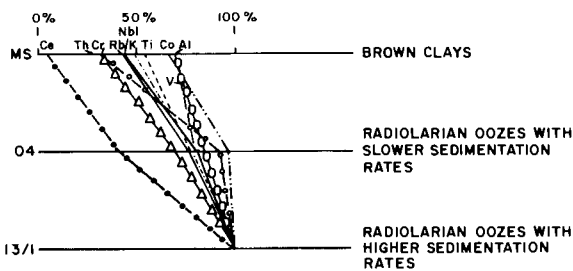

Fig. 260. Changes in the content of elements which are enriched in the terrigenous phase of the sediment in different sediment types. The contents in the radiolarian oozes from the cruise VA 13/1 are taken as 100%. (After Gundlach/Marchig, 1982, p. 207.)

Safronov (1983) determined the effect of time on the reservoir properties of sand-stones, including the ages of the rocks correlated with depth of burial. Such data, commonly utilized by petroleum petrophysicists, ought to be applied by the hydrologists who investigate the ore hostrocks of mineral concentrations that are known to have originated by subsurface fluid systems. How many ore petrophysicists are actively pursuing the problems of "Ore Reservoir Rocks"?

Morton (1985) proposed that "punctuated" (= periodic) diagenesis formed an illite − smectite assemblage due to sudden inflow of fluids, i.e., intense diagenetic periods were separated from less intense ones (or an absence of secondary altera-tions). Similar time-dependent variations in ore genesis and hostrock modifications (both on the surface and in the subsurface) must be considered.

Bayer (1985) in a book on pattern-recognition problems illustrated, among others, the self-evident relation between rates and time in geological and biogeological pro-cesses, as demonstrated by numerous natural consequences. Zhorov et al. (1984) showed that seasonal changes influence the distribution and space/time variation of the H_2S zone in the Black Sea. Volkov/Ivanov (1984) examined organic matter consumption during anaerobic diagenesis in ocean sediments; the consumption, quite obviously, is controlled by the rates of diagenesis and the latter, in turn, by variations in sedimentation rates and dilution effects of sedimentary influx changing through geologic time (Seslavinskiy, 1984).

− See also Evolution, Multi-factorial, and Uniformitarianism.

TRANSPORTATION

Freise (1931) mediated over Au-transport by organic underground solution (see Gold).

Berner (1969): By using three diagenetic models, he studied the migration of iron and sulfur within anaerobic sediments resulting in the formation of pyrite concre-tions, layers, and pyritized fossils (see Mobility).

Strakhov (1967, 1969, 1971) in a three-volume review advanced many concepts in transportation mechanisms related to ore genesis.

Huang/Keller (1972) discussed the geochemical mechanics for dissolution, transport and deposition of Al during weathering/supergenesis (see also Weathering), whereas Carroll (1958) described the role of clays in transporting iron. Khardar et al. (1968) dealt with stream supply of dissolved metals to the oceans; Gibbs (1973) with the mechanisms of trace-element transport in rivers in general; and Förstner/Pat-chineelam (1976) with the mobilization of heavy metals in river sediments (see River environments). Lee (1975) treated the role of hydrous metal oxides in transportation of heavy metals in aquatic environments.

Shanks/Bischoff (1977) modeled the ore transport and deposition of the Red Sea geothermal system.

Hilton et al. (1985) modeled mathematically the pathways of metal transportation in hydrological systems (Fig. 261) as to the cycles' implications in trace-metal enrichment, for instance.

– See also Mobility, Multi-factorial, Reworking, River environments, and Solubility.

TRAPS (DIAGENETIC TRAPS)

Perel'man (1967) offered a useful review of the various "barrier effects" and traps of metal ions which may result in economic concentrations.

Wilson (1977) discussed diagenetic traps controlling oil accumulation. If it is factual that there are similarities between the basin-generated fluids that form oil and those that create ore, then the diagenetic traps of the former ought to have equivalent traps for the latter.

Bernard/Samama (1976) outlined "trap structures" (i.e., marine and continental traps) in context of epigenetic stratabound and stratiform ore genesis.

Cobler/Dymond (1980) reported on a sediment trap experiment near a Recent Pacific spreading center during which numerous chemical elements were "trapped".
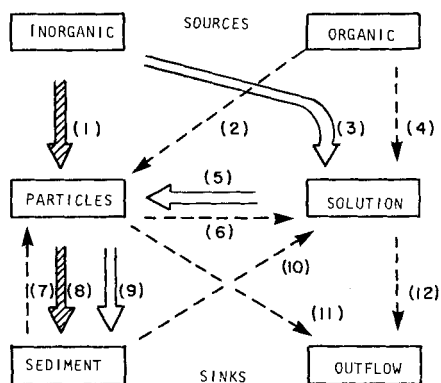

Fig. 261. Pathways for the transport of metals in hydrological systems. The bold arrows indicate pathways for the recruitment to the sediment of type-A metals (open arrows) and type-B metals (cross-hatched arrows). Other interactions are designated by dashed arrows. The processes are as follows: *1* = mineral erosion; *2* = supply of detrital material; *3* = leaching; *4* = decomposition (e.g., to humics); *5* = adsorption/coprecipitation; *6* = desorption/dissolution; *7* = resuspension; *8* and *9* = sinking; *10* = redox/desorption release; *11* and *12* = hydraulic losses. (After Hilton et al., 1985.)

Izdar et al. (1984) provided preliminary data of a similar experiment in the Black Sea deep-water region. Man-made traps have been used to study certain diagenetic processes, such as sedimentation rates controlling metal adsorption, dissolution, etc. A depression filled with an anoxic black sediment offers a natural trap.

Goudie/Pye (1983) described many geomorphological traps on all scales of importance in controlling chemical precipitation, for example. Lakes, depressions in volcanic terrains, karsts, among others, serve as sedimentological traps.

— See also Barriers, Oil — ore relationships, Multi-factorial, and Structures.

UNCONFORMITY — CONTROL

Zuffardi (1976) and Quinlan (1972) summarized the origin of various types of ores in paleokarst systems.

Note: (a) Many controversies still exist as to the syngenetic, diagenetic, and epigenetic influences operative in karst systems and, thus, along unconformities (see separate discussions on karst in this chapter). (b) Distinctions must be made between local diastems and regional unconformities in the study of microscopic textures and fabrics, on one hand, and large-scale structures and stratigraphic features, on the other. The time-intervals (hiatuses) represented by the diastems and unconformities are important in ore genesis, especially also the two hiatuses between the origin of the hostrock and the unconformity, and between the unconformity and the deposition of the ore.

Hoeve/Sibbald (1978) and Jones (1980) described the origin of the "unconformity-type" uranium and nickel deposits by the "diagenetic – hydrothermal" mechanism (Fig. 262): (a) Percolating oxidizing diagenetic solutions penetrating into the sand-

1 COLLINS BAY
2 "ROOT ZONE"(KEY LAKE)
3 DEEP "BLIND" DEPOSITS (JABILUKA)
4 RABBIT LAKE
5 MINERALIZED ALONG FAULTS (MIDWEST LAKE?)
6 "PERCHED" DEPOSITS IN ATHABASCA
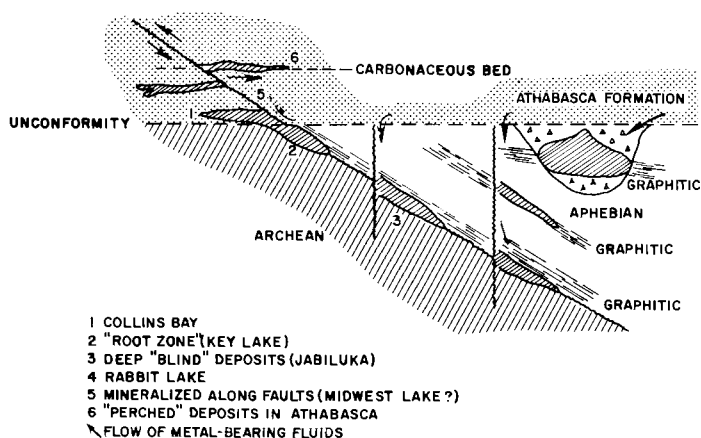↖FLOW OF METAL-BEARING FLUIDS

Fig. 262. Sketch showing possible types of mineralization by the "diagenetic – hydrothermal" mechanism. (After Jones, 1980.)

stone caused intrastratal weathering and oxidation of the rock. The percolation of the diagenetic solutions may have been triggered by magmatism and tectonism. (b) Fracture zones in the basement provided access of the diagenetic solutions to the graphite-bearing rocks. (c) Reduction of oxidizing diagenetic solutions by reaction with graphite took place, generating a mobile gaseous reductant. (d) Then, upward migration of the reductant-bearing solutions through the fracture system into the overlying sandstones occurred. (e) Finally, mineralization took place due to the mixing of reducing and oxidizing solutions.

Button/Tyler (1981) described the economic significance of Precambrian paleo-weathering and erosion (unconformity) surfaces on volcanic rocks, arenaneous sediments, shales, carbonates, and banded iron formations in Southern Africa. For example, unconformities have played an important role in the origin of uranium, copper, gold, platinoid, fluorite, lead – zinc, aluminum, manganese, iron ore, heavy minerals, and other types of deposits. Inasmuch as climate, weathering, paleosols, erosion, paleotopography, unconformities, etc., may have either an indirect or direct effect on diagenesis, a comparative summary is required.

Al-Gailani (1981) studied authigenic mineralization along unconformities and the implication for reservoir (or hostrock?) characteristics. Mixing of fluids seems to have occurred at the structural discontinuity.

Laznicka (1985b): A highly recommended contribution discussing the simple to complex relationships between unconformities and mineralizations.

Schlee (1985) reviewed inter-regional unconformities as related to hydrocarbon accumulation. Anyone interested in the control of stratigraphic discontinuities controlling hydrologic systems and the localization of ore deposits ought to read L.L. Sloss' "comparative anatomy of cratonic unconformities" in Schlee's memoir.

– See also Karst.

UNIFORMITARIANISM

Meylan et al. (1981), among many others, described the metalliferous deep-sea sediments forming at present.
   Note: There are numerous recent environments in oceans, lakes and rivers and on land that are conducive to the origin of diagenetically controlled deposits, both metalliferous and non-metallic. Here one can study qualitatively and quantitatively the dynamics of contemporary or actualistic diagenesis. In contrast, however, most of the information available on diagenesis, and consequently the concepts, hypotheses and theories developed thereof, are based on the observations of the geologically older rock sequences, i.e., from static fossilized systems. Most investigators have concentrated their examinations on the effects and not on the causes. From the effects they have attempted to unravel the causes. Thus, the princi-

ple of uniformitarianism has hardly begun to be used in diagenetic studies. Certainly, comparative/contrastive-type diagenetic investigations are in their infancy.

Shea (1982) and Scharnberger et al. (1983) outlined and discussed twelve fallacies of uniformitarianism, which also have to be applied to diagenesis in general and to ore genesis in particular. An excellent start to modify sensibly this famous Law!

Doe (1983) treated the "converse law" of *the past being the key to the future.* He dealt also with diagenesis of the past and present, using the data to predict future metal pollution (see also Pollution).

Hallam (1983) outlined the great geological controversies, including those related to neptunism – volcanism – catastrophism – uniformitarianism, the age of the Earth, continental drift, etc. The origin of ores must also be deliberated in the realm of such controversies. Berggren/Van Couvering (1984) dealt with catastrophes during the Earth history and considered this to be a new style of uniformitarianism.

– See also Evolution, and Time.

UPWELLING

Drever (1974) modeled geochemically the genesis of a BIF deposit, suggesting that upwelling was important in supplying the iron from the deeper part of the ocean (see also Maynard, 1983). This upwelling mechanism has been applied for many years to explain the origin of phosphorites (e.g., Baturin, 1982, and many others) (see Phosphates – phosphorites).

Parrish (1982) studied upwelling and the origin of Paleozoic source beds, i.e., black shale facies; Parrish/Curtis (1982) dealt with atmospheric circulation, upwelling and organic-rich rocks (reducing/anoxic/black mud facies) in the geologic past. (See also Reducing.)

Froelich et al. (1982) discussed the marine P- and C-cycles (see model in Fig. 263). Numerous diagenetic mechanisms are involved, including those controlled by upwelling (see also Cycles). Such quantitative flux models are the ultimate aim in diagenetic investigations in order to unravel all complexities of multi-component systems.

Maris/Bender (1982) treated the upwelling of hydrothermal solutions through flank sediments as shown by pore-water profiles. (See also Hydrothermal.)

Williams/Reimers (1983) discussed the role of bacterial muds in O-deficient marine basins and coastal upwelling regimes.

Thiede/Suess (1983) gave a good account of the sedimentary record of ancient

coastal upwelling, including a time scale, the distance – length scale of geological phenomena, flux rates of organic matter, and diagenesis.

Loughnan (1984) studied the phosphate authigenesis and in his model (his fig. 7) included upwelling.

— See also Phosphates – phosphorites.

URANIUM

R.W. Boyle (1982) reviewed several types of uranium deposits that are believed to have originated through diagenesis, and Rackley (1976) and Harshman/Adams (1981), among many others, dealt with the geology and recognition criteria of the roll-type uranium in continental sandstones (see also Reynolds/Goldhaber, 1983, for discussions on the biogenic and non-biogenic processes involved).

Tilsley (1980) offered genetic considerations of uranium deposits and in 1981 presented a model of the carbonaceous pelite-hosted types. Meneghel (1981a) discussed a genetic model of sediment-hosted U-concentrations, whereas Danchev/Shumlyanskiy (1981) examined the exogenic uranium mineralization of the
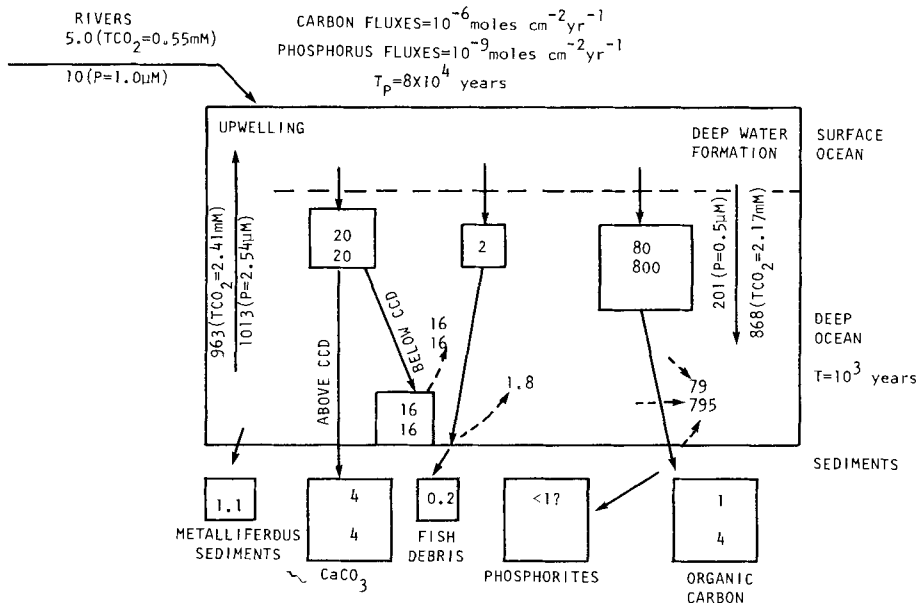

Fig. 263. Two-box model of the oceanic phosphorus and carbon cycles. Fluxes are in units of moles per cm^2 of ocean surface per year. Appropriate phosphate and T-CO_2 concentrations of rivers and upwelling and deep-water sources are given in parentheses. (After Froelich et al., 1982; see for original data sources.)

molassoid association in intermontane basins. The molasse-type uranium deposit formed is only one of many potential sedimentary systems, each with its own specific diagenetic processes.

Andreyev/Chumachenko (1964), Rouzand et al. (1980), Steacy/Boyle (1982), Bonnamy et al. (1982), and Goleva/Uspenskii (1983) studied the interactions (e.g., reduction) of U with organic matter in sediments, their form of occurrence, the types of organic facies, among others, including those related to Precambrian deposits. Maksimova/Shmariovich (1983) described the Re in infiltration-type U-coal deposits. Jianfeng (1984) discussed the implications of organic matter in the origin of U-mineralization: U is associated preferentially/selectively with specific types of carbon compounds. Pen'kov (1985) outlined the sequence of U-bitumen mineral genesis (see his comparative tables). (See also Organic matter.)

Stuart-Williams/Taylor (1983) offered a coalescence model based on a two-fluid mixing concept useful in uranium exploration (see Mixing).

Mueller/Halbach (1983) and Allen/Thomas (1984) studied, respectively, an early diagenetic uranium deposit in Miocene lake sediments and the uranium potential of diagenetically altered Permian sandstones. Goleva et al. (1981) described the relations between silicate and oxide forms of U-mineralizations in stratiform ores.

Zielinski (1982a) studied the mobility of U and other elements during alteration of rhyolite ash to montmorillonite, and Turner (1985) described the leaching of intrabasinal volcanic detritus consequenting U-mobilization during early diagenesis under an arid climate at $50°C$ and at less than 1400 m burial depth (see his models). (See also Sources, and Remobilization.)

Babinets et al. (1982), Anderson (1982), and Yamada/Tsunogai (1983/84) discussed the geochemistry of U in the Black Sea, including the influence of pH (see also pH and Eh); the concentration, vertical flux and remineralization of U in seawater; and postdepositional enrichment of U in sediments of the Bering Sea, respectively.

Beeson (1980a) dealt with the recognition of hydrothermal processes in the trace-element geochemistry of $U - Th$-enriched tuffs, and Rekharskaya (1981) discussed the $U - Ti - P$ hydrothermal mineralization in sedimentary rocks. Note that many uranium concentrations, believed to have been hydrothermal in origin, have been interpreted by other genetic concepts, including diagenesis.

Volzhin/Korolev (1982) described the characteristics of epigenetic U-mineralization in jasper − quartzites; and Stanworth/Badham (1984) examined the Proterozoic secondary sedimentary uranium deposits associated with red-beds and evaporites.

Grandstaff (1980) studied the implications of O_2 in the Precambrian atmosphere to the origin of conglomerate-hosted uranium deposits (see Climate and Evolution). Robinson/Spooner (1984a) and Smits (1984) discussed their post-depositional modification, including those by intrastratal solutions.

Lobato et al. (1983) opined on the uranium-enrichment in Archean crustal basements associated with faulting, i.e., meteoric water and formation brine movement were controlled by the faults. Hydrology also influenced secondary (diagenetic) alterations.

Beeson (1980a,b), Ellis (1980), Meneghel (1981a), Yilmaz (1981), R.W. Boyle (1982), and Ewers et al. (1983), among many others, have investigated particular sediment-hosted uranium deposits, dealing with diagenetic features.

Rosenberg/Hooper (1982) described the fission-track dating of sandstone-type uranium precipitates. How did diagenesis influence the reliability of the obtained dates?

VOLCANIC – EXHALATIVE PROCESSES (HYDROTHERMAL – DIAGENESIS)

Carozzi's (1960) book of "Microscopic sedimentary petrography" dealt with syngenetic – diagenetic iron-bearing and phosphatic rocks. However, it is listed here because in the chapters on rudaceous, pyroclastic, and argillaceous rocks, Carozzi described numerous primary and secondary volcanic textures and microstructures useful for the exploration geologist, for example. Many of these features are of diagenetic (alteration) origin, so that some experience is needed to recognize them in handspecimen and under the binocular and petrographic microscope. Inasmuch as many stratabound/stratiform ore deposits are believed to have originated by volcanic-exhalative processes, one of the best (even if indirect) guides to volcanism is the presence of pyroclastic and volcanic flow rocks. These rocks, however, can alter very quickly, especially those rocks that have a high permeability. Consequently, it is always a good idea to make a few thin-sections and let them be carefully described by an *experienced* petrographer. Handspecimen examination is too frequently insufficient for provenance and source rock recognition.

Honnorez et al. (1973) described the present-day formation of exhalative sulfide deposition at Vulcano, Italy. Submarine fumaroles mineralize trachytic tephra along the shore and the bottom of a bay. Pyrite and marcasite, plus minor sulfur, alunite and opal, cement the grains of the volcanic sand and tuff. Various diagenetic replacement processes were operative. There is an enrichment of Fe, Si, S, B and Ba. The amount of iron sulfides is directly related to the distance from a given emanation site and to its intensity. Within the zone of fumarolic activity, the uppermost 30 – 40 cm of sediment are enriched in exhalative sulfides, precipitated by downward penetrating solutions. The hydrogeology of the island controls the hydrothermal system. The geochemical anomalies of the water influenced by the fumarolic activity are readily diluted and the concentration of heavy metals (e.g., Ti, Cu, Zn, Pb, Ag) is kept below the geochemical threshold over which solutions start precipitating sulfides and other metallic compounds. Thus, the Vulcano system precipitates only iron minerals. Many textures were described by Honnorez et al., including physicochemically formed framboidal pyrite in a submarine volcanic field.

Note that insofar as both iron sulfide and oxides/hydroxides have been reported from the Vulcano deposits, the fate of the other metals (Cu, Pb, Zn, etc.), which were not precipitated, could be important. For example, are they precipitated elsewhere as adsorbed elements on clay minerals or on manganese oxides (see Valette, 1973, below)? Numerous diagenetic mechanisms are operative in this actualistic system, all of which remain to be examined.

Puchelt (1973) described iron-rich sediments which are forming at present in several bays within the Santarini Caldera by precipitation from warm submarine springs associated with late stages of volcanism. The precipitated material is inhomogeneous, gel-like, and silica-rich. At the top, ferric hydroxide prevails, succeeded downwards by a half-meter thick ferrous carbonate deposit, ferrous hydroxide and, finally, basic sulfate, or water-rich ferrous silicate gel. Sulfate-reducing bacteria are present only in the uppermost ferrous sulfide layers. Puchelt discussed many aspects related to source, syngenesis – diagenesis, solubility, mode of transportation and precipitation, distribution of Fe- and Mn-compounds and silica, and influence of pH.

Valette (1973) studied, as a continuation (?) of the work of Honnorez et al. (1973), the distribution of certain trace elements in the marine sediments circumjacent to the Vulcano Island. The approximate maximum values of the respective elements are (in ppm): Mn (1900), Cu (200), Ni (25), Cr (90), Ba (1000), and Zn (90). Valette examined the relationships between the granulometry of the lutite and sandy sediments and trace elements, and between the mineralogy and trace elements. Although a connection exists between these three variables, the influence of fumarolic phenomena plays the major role in the trace-element distribution and, therefore, masks the other variables. Three different categories of trace-element occurrences exist: deep-water, fumarolic, and mixed concentrates. Valette concluded that much more additional research is required.
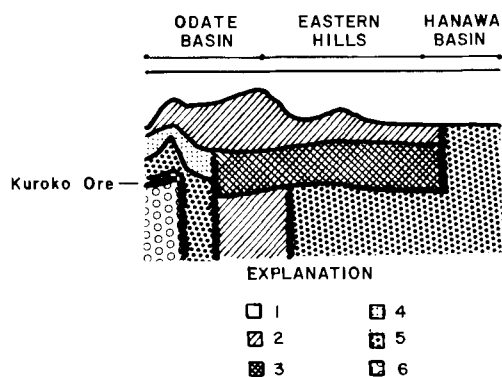

Fig. 264. Idealized regional alteration zones in the Kuroku district; the alteration zones II – IV, illustrated in fig. 69 in Franklin et al. (1981), are represented by circles. (After Franklin et al., 1981, p. 554; see for original data sources.) *1* = Quaternary; *2* = clinoptilolite – mordenite zone; *3* = analcime – calcite zone; *4* = montmorillonite and transitional zone; *5* = sericite – chlorite zone, including plagioclase; *6* = sericite – chlorite zone lacking plagioclase.
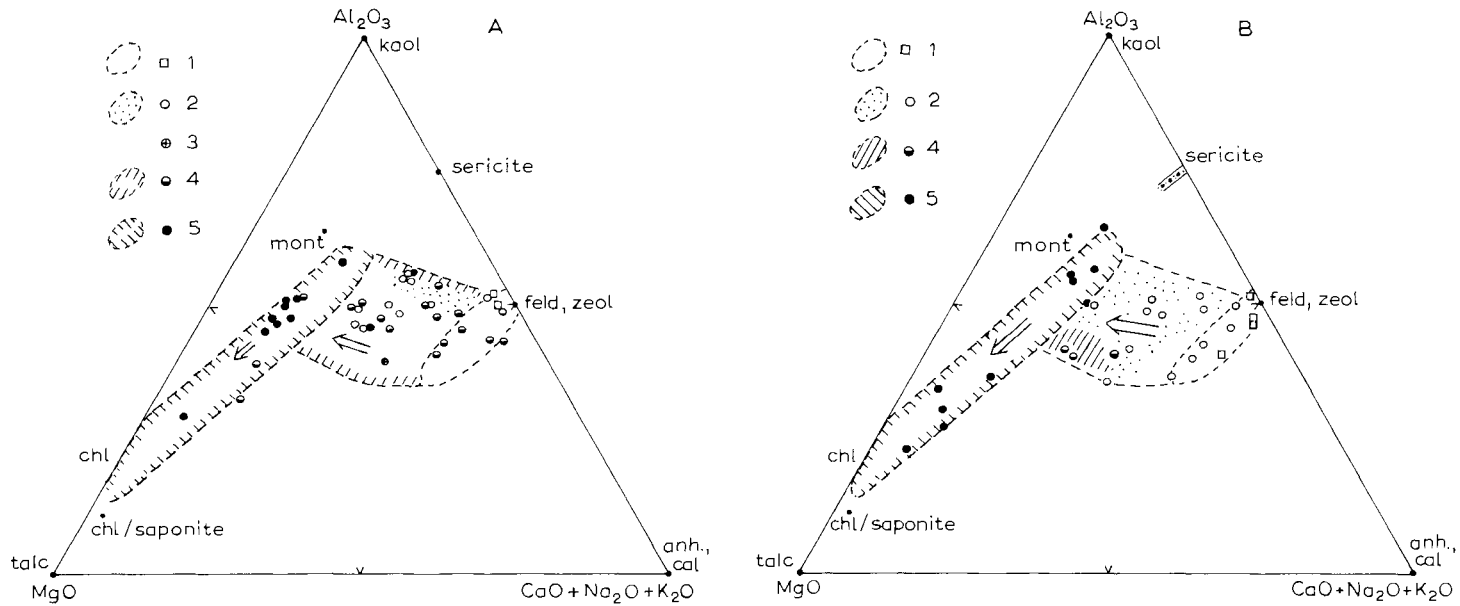
Fig. 265. Compositional trends in altered rocks near the Fukazawa (A) and Iwani (B) mines, Japan. Progressive alteration causes a shift in composition as shown: *1* = unaltered zone; *2* = zeolite – montmorillonite zone; *3* = analcime zone; *4* = chlorite – sericite – feldspar zone; *5* = chlorite – sericite zone. (After Franklin et al., 1981, p. 554; see for original data sources.)

Franklin et al. (1981) and Hutchinson et al. (1980) summarized the volcanic-associated massive sulfide deposits, including the alterations of hostrocks, e.g., see Figs. 264 and 265.

Note: (a) The surface and subsurface alterations caused by the hydrothermal – exhalative solutions have to be compared with the sedimentary diagenetic (= non-hydrothermal) alterations, and these in turn with burial metamorphic and regional metamorphic modifications. It is important to establish the mineralogical, geochemical and isotope, textural and paragenetic, structural and stratigraphic, and associative plus environmental criteria to recognize and distinguish between the several styles of alterations during exploration, for example.

(b) Similar zeolite, clay, chlorite, etc., facies, as shown in Figs. 264 and 265, can form under non-igneous hydrothermal conditions. For instance, pyroclastic-rich lake sediments have undergone intensive and extensive diagenetic mineralogical and textural alterations in a *sun-heated* surface milieu in many parts of the world at the present time and in the geologic past (e.g., Hay, 1966). What are the differences between these diagenetic alterations in contrast to those that are the consequence of igneous-hydrothermalism, e.g., the Kuroko-type alterations?

Goldie/Bottrill (1981) described modern hydrothermal systems and compared them with volcanic- and shale-hosted mineralizations. They discussed seawater – basalt interactions and alterations and the source of metals.

Meylan et al. (1981) summarized the metalliferous deep-sea sediments, including Recent volcanic – exhalative deposits, such as those of the East Pacific Rise, Mid-Atlantic Ridge, the Bauer Basin and Red Sea.

Wallace/Roper (1981) contrasted (p. 77) sedimentary – diagenetic and hydro-thermal – exhalative – diagenetic alterations of pyroclastic lake beds. Insofar as *"alteration mapping"* has been used in the study of mercury and uranium deposits in volcanics, the differences between ore-associated alteration and that unrelated to mineralization during such mapping may serve as an excellent exploration guide.

Russell et al. (1981) studied the origin of sediment-hosted, exhalative Zn – Pb deposits; G.R. Taylor (1983b) examined the Mn-oxide mineralogy in an exhalative environment; and Finlow-Bates/Stumpfl (1981) described the behaviour of so-called immobile elements in hydrothermally altered hostrocks with submarine – exhalative ores.

Nadeau/Reynolds (1981) and Fisher/Schmincke (1984) studied volcanic/pyroclastic rocks in general, offering much data to those interested in the diagenesis of hostrocks. Robertson (1984) examined the volcaniclastic deposits as indicators of paleoenvironments, as based for example on geochemical data and an Al – Fe – Mn triangle. Rona et al. (1984) studied the periodicity duration, varying intensity, low-temperature vs. high-temperature, etc., venting phenomena of a mid-oceanic hydrothermal field. Curly et al. (1984) described the plume particulates yielding trace metals in the vicinity of hydrothermal systems (e.g., Fe, Mn, P, As, etc.). Anhydrite was precipitated by fluid mixing.

Seyfried/Mottle (1982), among others, investigated hydrothermal alteration of volcanic rocks by seawater. They made an important distinction in their geochemical studies of diagenetic alterations, for example, separating the seawater-dominated from the rock-dominated alteration systems.

Henley/Ellis (1983) provided a recent geochemical review of the ancient and modern geothermal systems, with numerous comments on their ore-forming capabilities. Their figs. 1 and 2 demonstrate the exhalations debouching onto the seafloor, which resulted in the origin of mineralizations. The exhalations consist of aqueous solutions containing sulfate, bicarbonate and minor chloride.

G.R. Taylor (1983a) described a mechanism for framboid formation in a volcanic – exhalative sediment, exemplifying the overlapping of diagenesis with hydrothermal processes. See his model.

Baross et al. (1982a) studied the initial microbiological response to a volcanic-terrane associated lake. Are they different from the oceanic hydrothermal-vent associated organisms? How do these organisms affect diagenesis? (See also Bacteria and Biological factors.)

Henley et al. (1984) reviewed comprehensively the fluid-mineral equilibria in hydrothermal systems, e.g., higher- vs. lower-temperature/pressure systems and fluid mixing, among others. Contrast this to Lippmann's (1982) approach restricted to clays.

Plimer (1984a) investigated the role of F in submarine exhalative systems; does diagenesis make a contribution? Slack (1982) examined tourmaline in massive sulfide deposits, including several sedimentary – diagenetic, volcanic – exhalative, authigenic, and other processes.

Lydon (1984) reviewed volcanogenic sulfide ores; Ohmoto/Skinner (1983) provided a recent summary of the Kuroko-type and similar volcanogenic deposits (many of their facies lend themselves to diagenetic studies); and Rona et al. (1984) discussed comprehensively the hydrothermal processes at seafloor spreading centers.

– See also Hydrothermalism.

WATER (INCLUDING OCEAN SEAWATER)

Krauskopf (1956), Gibbs (1970), and Florence/Batley (1977) offered data on factors controlling the concentration of rare metals, for example, in seawater; on the mechanisms controlling worldwater chemistry; and on determining the chemical forms of trace metals (e.g., Cu, Pb, Cd, Zn) in natural waters, respectively. Weisel et al. (1984) treated the ocean-to-atmosphere transport of trace metals and made reference to metals in oceans.

Müller (1967) discussed the connection among water, bottom sediments and organisms in a lake.

Garrels/Christ (1965), Degens (1965), Mason (1965), Berner (1971, 1981), Krauskopf (1979) (see also Indexes in Wolf, 1976, 1981, 1985, 1986, vols, 4, 7, 10 and 14) discussed many general and specific problems related to geochemical processes in aqueous systems. The following topics were treated: (1) dielectric constants; (2) solubility in lavas and magmas; (3) solvent power; (4) thermal dissociation; (5) photochemical dissociation; (6) origin of the hydrosphere; (7) isotopic composition of natural waters; (8) classification of waters and hydrothermal fluids; (9) chemistry of interstitial water, subsurface water and petroleum; (10) ion filtration along charged-net clay membranes; (11) effect on crystallization; (12) activity in solutions; (13) fugacity values; and (14) various controls on water. A comprehensive summary of all factors that control diagenesis is obviously needed, as repeatedly pointed out in this chapter.

Swarbrick (1968) commented briefly on the role of connate water in diagenesis with reference to liquefaction by thixotropy, for example. He discussed, among others, sediment-injection structures, differentiation of intrusive sediments and differential remobilization of sediments in ore genesis.

Lerman (1971) reported on the time requirements to attain chemical steady-states in lakes and oceans (see the whole symposium for information).

Yariv/Cross (1979) and Goudie/Pye (1983), for example, considered the importance of water and solutions in controlling colloidal systems, including diagenesis. (See also Eitel, 1964, 1975, and similar books.)

Cronan (1980) discussed "underwater minerals", i.e. those formed in aqueous environments.

Shvartsev (1980) modelized the geochemical cycle of water in the Earth's crust (Fig. 266), comparing numerous parts that can be ascribed to syngenetic – diagenetic – catagenetic/burial metamorphic settings.

Schopf (1980) summarized extensively the status of paleoceanography; Veizer (1984) debated the evolving Earth as based on "water tales"; Gorgini et al. (1982) dealt with the isotopic evidence of paleowaters in a secondary basin.

Flörke et al. (1982) offered a good silica nomenclature, including diagenetic and other data, such as water in microcrystalline quartz (agates) of volcanic origin.

Kremling (1983) studied the trace-metal fronts in European shelf waters. (Compare with Pollution.)

Salomons/Förstner (1984) reviewed comprehensively the metals in the hydrocycle;

Broecker/Peng (1983) described the tracers in the sea (i.e., the geochemistry of oceans); and Wong et al. (1983) summarized the huge amount of data on trace metals in seawater as did Brewer (1975) who had concentrated on the minor elements in seawater.

— See also Eh, Fluids, Ph, Solutions, Solubility, and Time — rate — residence time.

WEATHERING — SUPERGENESIS

Yariv/Cross (1979) offered a basic introduction to colloid systems referring also to weathering processes and its products (see also Eitel, 1975, on clays, including bauxites, iron ores, and others).

Boulègne (1981) studied, among others, the concentration of dissolved element species vs. depth in a weathered sandstone layer that contains uranium (see model in his fig. 8 for neoformed minerals). How does this system compare to a diagenetically (pedogenetically or pedodiagenetically?) mobilized system?

Andreeva et al. (1982) opined on the mineralogic criteria of different weathering crusts and hydrothermal argillites.

Evans (1982) treated the paleosols; Walker/Dennis (1983) discussed exogenic processes and the origin of sialic crusts, including the supergenesis, soil-forming, and pre-Cambrian sedimentation processes resulting in the differentiation of quartz, iron oxides and carbonates; and Retallack (1983) dealt with a paleopedological con-
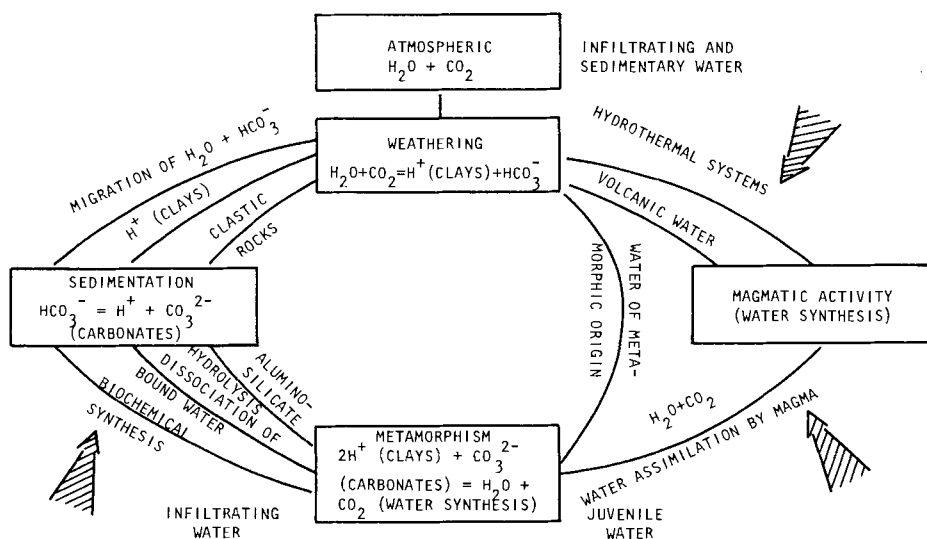

Fig. 266. Geochemical cycle of water in the Earth's crust. (After Shvartsev, 1980.)

cept to interpret terrestrial sedimentary rocks and discussed some diagenetic aspects and fossil soils. Gay/Grandstaff (1980) studied the chemistry and mineralogy of a Precambrian paleosol; and Goldberg (1982) described a Jurassic laterite-derivative facies. These paleosols must be distinguished from numerous similar-appearing facies, such as red-beds and some types of hydrothermal alterations (Andreeva et al., 1982).

Augusthithis' (1982) well-illustrated atlas on sphaeroidal textures/structures discussed also diagenetic and weathering-produced features of iron, bauxite, manganese and phosphate ores.

Zhukov et al. (1984) described the physicochemical and dynamic processes in bauxite formation during laterization and offered an example of supergenic zonation.

Von Damm/Edmond (1984) investigated the "reverse" weathering in closed-basin lakes of a rift zone, and compared the process to oceanic processes.

– See also Climate, Karst, Sources (e.g. Samama, 1973; Laznicka, 1985c), and Unconformities.

ZONING

Borchert (1965) reconstructed in his excellent chapter the genesis of fossil iron ores,
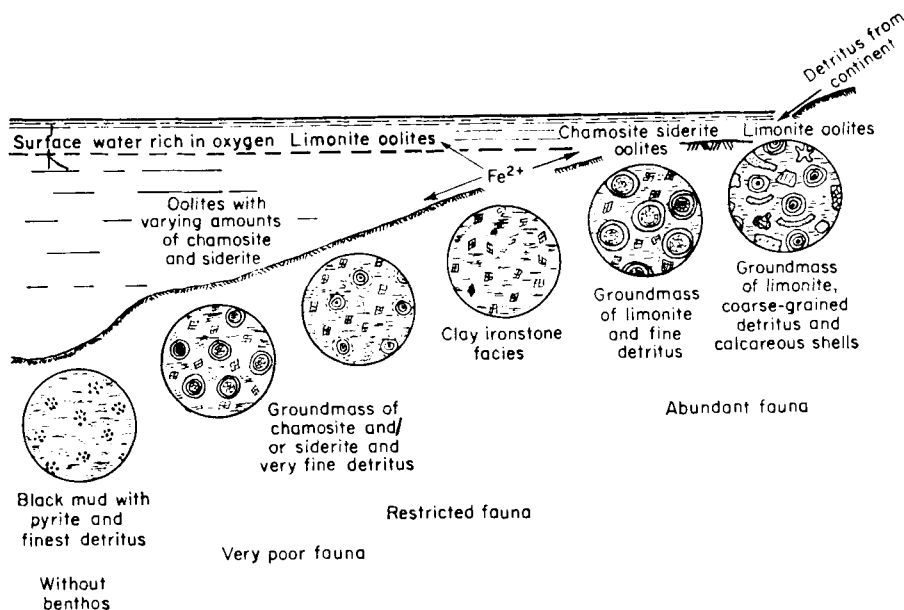

Fig. 267. General types of iron ore facies with thin section diagrams. (After Borchert, 1965.)

including, for example, the chemical and physical environments of the marine oolitic limonite – glauconite – chamosite – pyrite facies association (Figs. 267 and 268). Three chemical zones were involved (Figs. 268 and 269). Each offered characteristic syngenetic – diagenetic conditions as reflected by pH – Eh, O_2 and H_2S, organic matter, and other variables not mentioned in the diagrams, such as temperature, overturn or upwelling of the water, and $CaCO_3$ and elemental contents. Note that the three-fold chemical zoning has also been applied to the interpretation of other syngenetic – diagenetic facies and ore deposits, such as the Kupferschiefer-type ores.

Larsen/Chilingar (1967a, 1979) reproduced Strakhov et al.'s (1954) "zonation of new mineral formations in recent and fossil seas". These deposits comprise both syngenetic and diagenetic types, including ore mineralizations (Fe, Mn, Al, and Cu).

Berner (1970) (see also Leeder, 1981) modeled the various environments where diagenetic iron minerals may originate, which results in zoning. Hematite forms in the weathering zone of semi-arid climates (Fig. 270 and Table 78) and exhibits terrestrial zonation patterns distinctly different from those of marine deposits.

Barnes (1975) offered an excellent comparative/contrastive-type publication of volcanic – exhalative – hydrothermal (syngenetic and epigenetic) and sedimentary – syngenetic (diagenetic by implication and extrapolation) zoning. (See Tables 79 and 80, and Figs. 271, 272 and 273.) All the reviewed metal zonations fall into two basic types: (a) Hydrothermal – those commonly classified as vein, porphyry-Cu, contact metasomatic, and Mississippi Valley-type deposits belong to the epigenetic hydrothermal zoning. The syngenetic hydrothermal deposits are conformable, for-
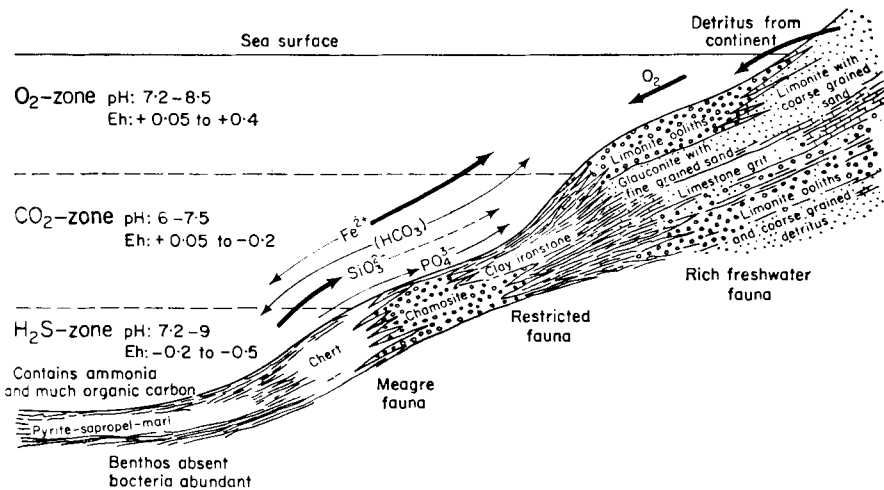

Fig. 268. Facies types in marine environment with corresponding Eh and pH values. (After Borchert, 1965.)
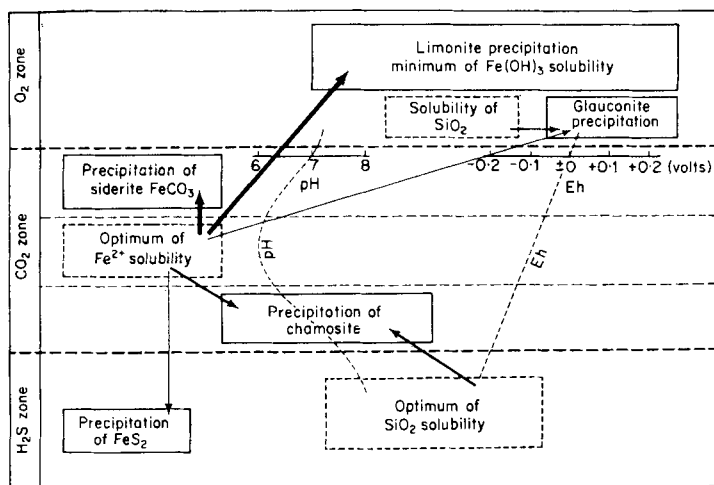
Fig. 269. The CO_2-zone in relation to iron ore formation; arrows show direction of migration of species. (After Borchert, 1965.)
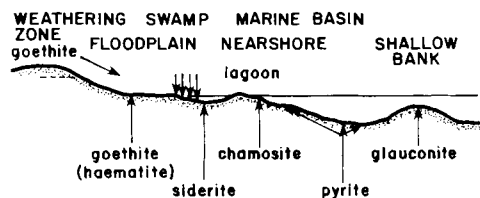

Fig. 270. Schematic section indicating the various environments where diagenetic iron minerals may form. Note hematite forms in the weathering zone of semi-arid climates. (After Leeder, 1981.)
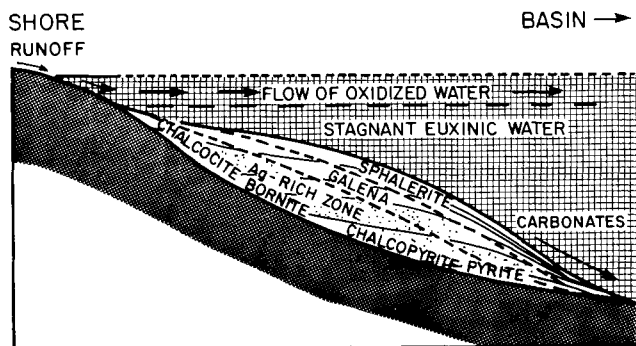

Fig. 271. Schematic portrayal of syngenetic sedimentary zoning. (Vertical scale is grossly exaggerated.) The distribution is shown by dashed contours only for the dominant sulphide within the shaly zones; solid lines represent bedding planes. The shore may be a bioherm. (After Barnes, 1975, p. 299.)

ming massive ores, such as the one at Rammelsberg. (b) Sedimentary — the Kupferschiefer-type, which exhibits the sedimentary syngenetic type of zoning. These two zoning sequences, from proximal to distal parts, are $Fe - Ni - Sn - Cu - Zn - Pb - Ag - Au - Sb - Hg$ in hydrothermal deposits, and $Cu - Ag - Pb - Zn$ in sedimentary deposits. The zoning sequence represents the natural order of increasing solubilities of the metallic sulfides, and others. Various considerations indicate that the hydrothermal zoning is the result of precipitation of sulfide complexes, and that chloride complexes may be the metal-carrying agents in sedimentary deposits.

Note: (a) The "syngenetic sedimentary" and "syngenetic – hydrothermal" processes discussed by Barnes (1975), no doubt, also comprise the "diagenetic – sedimentary" and "diagenetic – exhalative (hydrothermal)" mechanisms. He used the term "syngenetic" in a broader sense that automatically includes at least the very early diagenetic systems; however, *not* the late diagenetic and catagenetic systems. His review was only a preliminary attempt in comparative evaluation of zoning, leaving the finer details of the "evolution of zoning", for example (extending from syngenesis through early and late diagenesis) to be examined in the future. (b) Other aspects of zoning are to be comparatively evaluated, as for instance the differences and similarities of ore and gangue minerals from one type of deposit to the next.

TABLE 78

Diagenetic zones for marine mud successions. $\Delta T°C$ — increase in temperature with depth below sediment/water interface due to a gradient of $27.5°C$ km^{-1} (after Curtis, 1977, in Leeder, 1981)

Depth (km)	ΔT (°C)	Porosity (%)	Diagenetic zones (minerals formed)
			1. Oxidation
0.0005			
			2. Sulphate reduction
			Pyrite, calcite, dolomite (low-Fe carbonates ^{12}C enriched)
			kaolinite? phosphates?
0.01	0.2	80	
			3. Fermentation
			High-Fe carbonates, calcite, dolomite, ankerite, siderite,
			^{13}C enriched
1.00	28	31	
			4. Decarboxylation
			Siderite
2.50	69	21	
			5. Hydrocarbon formation
			(a) Wet – oil
			(b) Dry – methane
			Montmorillonite → illite
			(a) disordered, (b) ordered
7.00	192	9	
			6. Metamorphism
			(a) 200°C: chlorite
			(b) 300°C: mica, feldspar, epidote?

Fleischer et al. (1976) and Jung/Knitzschke (1976) examined two excellent examples of "sedimentary" zoning, as illustrated by the Zambian copper-belt and the Kupferschiefer districts.

Note: Although many aspects were explained by "syngenetic" processes, there is little doubt that early diagenetic mechanisms were operative as well. Some so-called epigenetic features may have been the result of diagenetic remobilization.
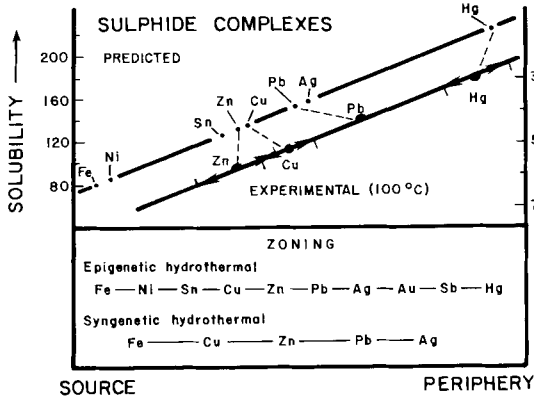

Fig. 272. The relative solubility functions of the metallic sulphides in sulphide complexes compared with zoning of epigenetic and syngenetic hydrothermal deposits. Values on the left are the predicted relative energies of complex formation (see table 6 in original publication) and those on the right are based on experimental solubility data (see table 5). See original publication for calculations. (After Barnes, 1975, p. 305.)
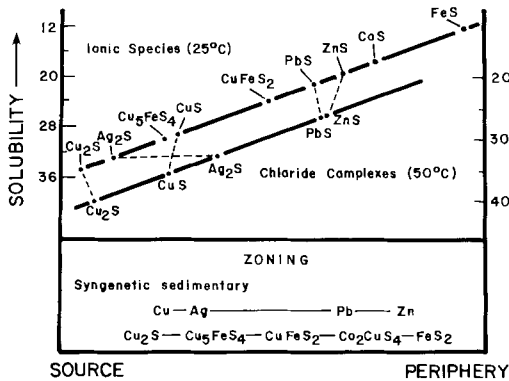

Fig. 273. Ionic and chloride complex solubility variables (see tables 7 and 8 in original publication) of the metallic sulphides compared to zoning of syngenetic sedimentary deposits (see table 4). The ordinate scale on the left for ionic species is numerically the same as the scale for chloride complexes on the right, but the values represent different functions that are not directly comparable. (After Barnes, 1975, p. 306.)

Curtis (1977) discussed the vertical diagenetic zoning for a marine succession as based on an increase in temperature with subsurface depth using a geothermal gradient of 27.5°C km^{-1} (see his table 28.1).

Wedepohl et al. (1978) determined that the source of Pb in the Kupferschiefer ores is the sedimentary material present in the region, including Precambrian clastic material. Based on several criteria, including zoning according to the solubility of sulfides and the thin regional distribution, it is believed that the ore precipitated syngenetically, followed by early diagenetic recrystallization (to explain the coarse crystal size). Comparisons were made with the Black Sea and Baltic Sea environments.

TABLE 79

Zoning in syngenetic hydrothermal deposits (relatively close zones are bracketed and a plus indicates elements that occupy the same zone; Barnes, 1975, p. 299)

Deposit	Sequence (earlier to later beds)
Typical hydrothermal type	
Rammelsberg	$As - Fe - Cu - Zn - Pb - Ba$
Kuroko	$Fe - Cu - Zn + Pb + Ag - Ba$
Cyprus	$Cu - Zn - Pb - Ag$
Canadian mines[1]	$Fe - Cu - Zn + Pb$
Others	
Bathurst	$Cu - (Ag - Zn - Pb)$
Sullivan[2]	$Fe - Sn + As - Ag + Pb - Zn$

[1] Includes several in the Flin-Flon and Noranda areas plus many others.
[2] Lateral zoning

TABLE 80

Zoning in syngenetic sedimentary deposits (relatively close zones are bracketed, and a plus sign indicates that both elements may occupy the same zone; Barnes, 1975, p. 300)

Deposit	← Shore .... Basin →
Kupferschiefer	$Cu + Ag - Pb - Zn$
Zambian Copperbelt	$Cu_2S - Cu_5FeS_4 - CuFeS_2 - Co_2CuS_4 - FeS_2$
Witvlei	$Cu + Ag - Pb - Zn$
Belt Series	$Cu + Ag - Pb$
Mt. Isa	$Cu - (Ag - Pb) - Zn$

Note: Interesting arguments were advanced by Wedepohl et al. to assist in distinguishing between syngenetic and diagenetic ore-mineral precipitation. Stanton (1966) also offered criteria to recognize "replacement" and "syngenetic/ diagenetic" precipitation.

Brown (1980) contrasted the origin of syngenetic (= primary, depositional − sedimentational) versus diagenetic (= secondary, epigenetic, subsurface-, burial-, compaction- and lithification-related) zoning of Pb − Zn and Cu among several copper deposits (e.g., White Pine, Kupferschiefer, Central African Cu-belt; see Fig. 274). Normal onlap-offlap (transgressive) sedimentation with sulfide precipitation may produce deposits superficially resembling zoning formed by subsurface circulation of brines during compaction.

Goleva (1980) established aqueous and "salt-sorption" aureoles in the vicinity of ore bodies during the study of hydrogeochemical exploration methods (see Table 81).
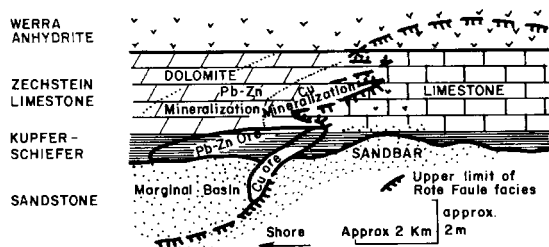

Fig. 274. Transgressive zoning of sulfides in the basal Zechstein strata of the Kupferschiefer. (After Brown, 1980; see for original data source.)

TABLE 81

Zoning of aqueous and saline aureoles (after Goleva, 1980)

Type of aureoles and medium of origin	Sequence of zoning (orebodies → aureoles)
Aqueous aureoles: in groundwaters in the zone of hypergenesis	$W - Be - Co - Bi - Au - Cd - As_1 - Sn - Hg - Ni - Cu - As_2 - Mo - Ag - Zn$ (at pH $5 - 7.5$ and Eh > 0.28 B)
in deep-lying thermal waters in the zone of catagenesis	$Be - Co - Bi - Cu_1 - Au - Ni - Sn - Mo_1 - Cu_2 Ag - Mo_2 - W - Zn - Pb - Cd - Mn - Sb$, As, B, Hg (at pH $5.5 - 6.5$ and Eh > 0.0 B)
Lithochemical salt-sorption-type aureoles in sedimentary rocks	$W - Be - Au - Bi - Co - Cd - Sn - Ni - Cu - Pb - As - Mo - Ag - Zn - Ba - Mn$

Such data ought to be used in comparative work in ore genesis, including the examination of the effects of remobilization of elements by various solutions. In some cases, precipitation of metals follows the sequence of decreasing solubility, in contrast to dissolution, leaching, and remobilization, which depict an increase in solubilization. However, many exceptions exist.

Large (1981): Among numerous aspects, he contrasted the metal zoning of eight stratiform sediment-hosted submarine exhalative Pb – Zn deposits (see also Multi-factorial; Large, 1981). In the future, these deposits should be compared with those hosted in volcanic rocks.

Lehne/Amstutz (1981 – 82) described Cu – Pb – Zn – Ag zoning of syngenetic hydrothermal – exhalative deposits in rhyolitic-to-rhyodacitic rocks. Syngenetic – diagenetic textures and structures are widespread, including geopetal features, boudinage, penecontemporaneous deformation due to the weight of overlying deposits, synsedimentary slumping of the ore, ore/non-ore laminations, flaser- and cross-bedding, crystal-growth orientation, framboidal pyrite, and colloform textures in open spaces or in soft sediments. An epigenetic-replacement origin was refuted. The zoning of Cu→Cu, Pb, Zn, U→Pb, Zn, Ag (vertical and horizontal) and the source of the metals was controlled by the proximity to the volcanic complex.

Elderfield et al. (1981a,b) compared the micro- and mega-zones of REE-distribution in the Pacific Fe – Mn nodules.

Stanton (1982a) proposed a new concept in which "the fluctuating seafloor interplay between warm, acid, concentrated hydrothermal waters with cold, alkaline, dilute seawater during stratiform ore formation, together with diagenetic processes,
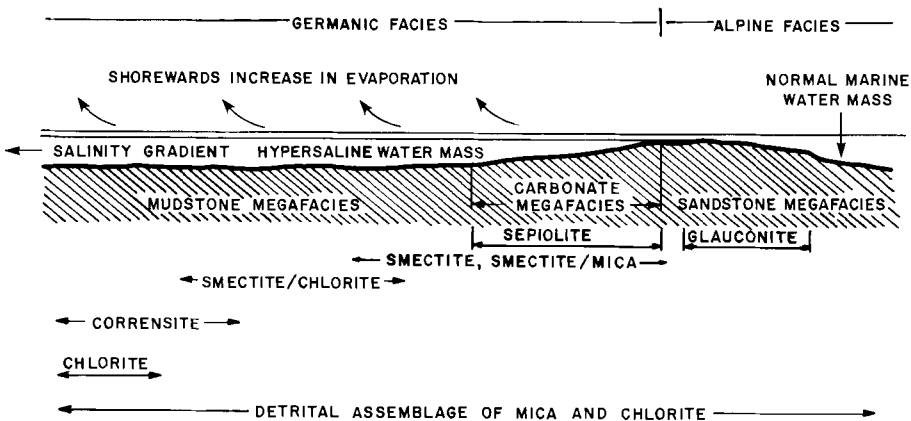

Fig. 275. Magnesium-rich clay-mineral patterns determined in the Triassic Keuper Marl, Tea Green Marl and Rhaetic sediments in England. (After Stanton, 1982a; see for original data source.)

leads to the formation of a wide range of clay, chlorite, mixed-layer clay and clay/chlorite, and zeolite precursor materials and hence, later, to the complex assemblages of metamorphic minerals closely associated with some stratiform ores". Such "mimicking of grade . . ., in at least some cases, reflects facies of clay
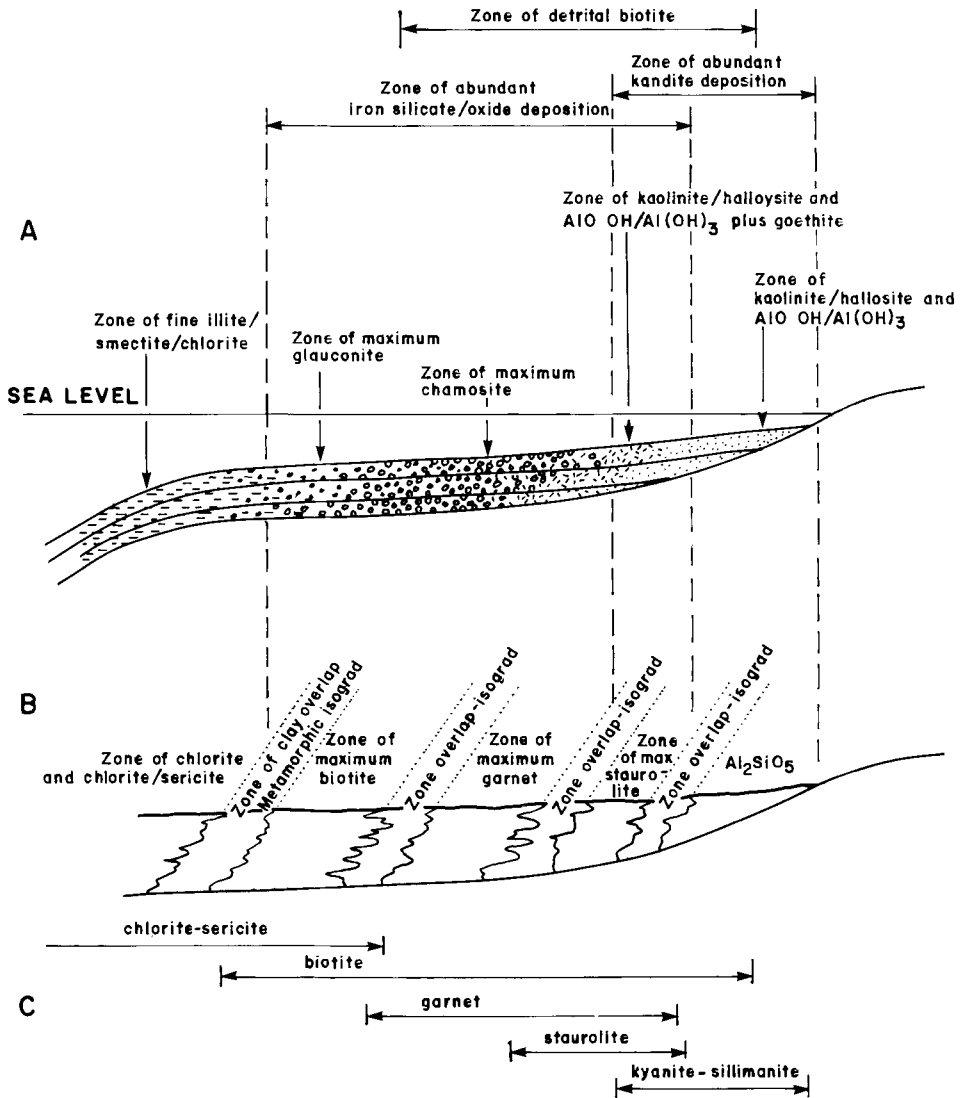

Fig. 276. (A) Diagrammatic, idealized representation of a pattern of notably aluminium- and iron-rich clays that might develop in the warm waters of a tropical shelf to which seaboard calc-alkaline volcanic and hydrothermal activity were contributing. (B) and (C) Similarly idealized representation of metamorphic mineral zones that might result from essentially isochemical metamorphism of the original pattern of detrital, sedimentary and diagenetic clays. (Note that the metamorphic zones cut across bedding, and would hence be transgressive to later fold structures.) (After Stanton, 1982a.)

and clay – chlorite mineral sedimentation on the relevant shelf, rather than variations in pressure-temperature conditions during subsequent metamorphism".

Figure 275 illustrates the relations among clay-mineral assemblages, sedimentary megafacies, and stratigraphy (plus their control on diagenesis). Two assemblages exist: (2) A detrital assemblage, with mica and minor chlorite being present throughout the sediments, and (b) a diagenetic ("neoformed") assemblage of Mg-rich clay minerals restricted to certain megafacies cycles, resulting from transgression and regression of lighter, normal marine water over heavier, highly saline Mg-rich water of a restricted hypersaline milieu. Figure 276 represents another example of "diagenetic" zoning, contrasted with metamorphic zoning. (For details, see Stanton's original paper.)

Susak/Crerar (1982) and Smith/Cronan (1983), respectively studied the factors controlling mineral zoning in hydrothermal ore deposits. They also studied the
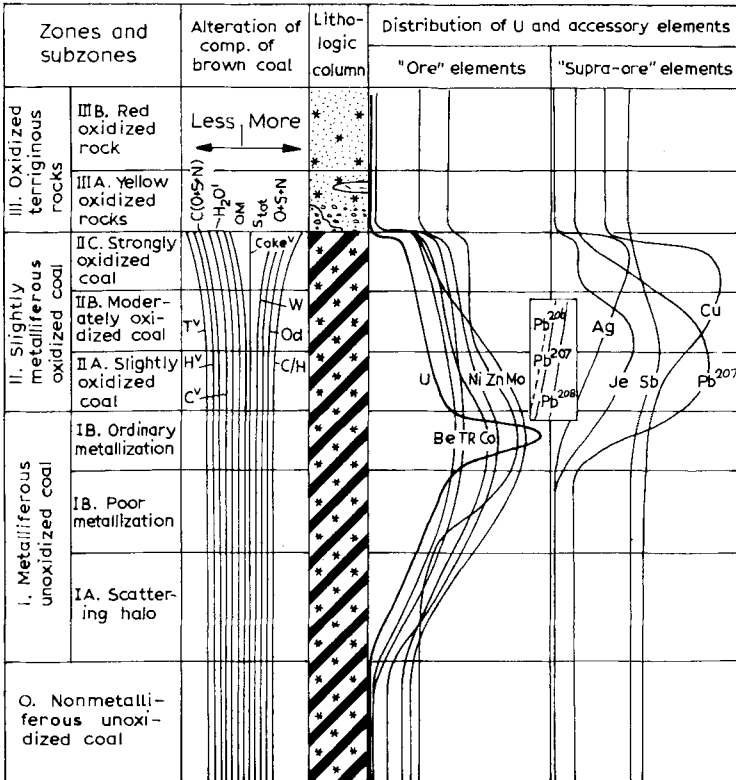

Fig. 277. The maximum amounts of Ni and Co are observed in the subzone II-1, which in this column is characterized by the highest sulfide content. The above differences in the distribution of elements are clearly attributable to the lithologically complex structure of the profile and the drastic variations in the coal composition. (After Uspenskii/Kislyakov, 1982.)

geochemistry of metalliferous sediments of a shallow submarine hydrothermal system characterized by compositional zoning which changes with distance from the vent: the minor elements depended on the rate of supply in hydrothermal fluids and on the removal by scavengers.

Uspenskii/Kislyakov (1982) outlined the ore-controlling oxidative zoning of an infiltration-type epigenetic U – coal association. For Ni and Co distribution, see Fig. 277. (See also Coal, especially Laznicka, 1985.)

Goodfellow et al. (1983) outlined the zoning of chalcophile elements in a Zn – Pb deposit and considered a diagenetic origin with numerous variables involved.

Strelyanov (1983) discussed the types of zonation in sediment-hosted uranium deposits, including the stages of formation, types of mineralization and their classification, and offered a model of the types. Gol'dshteyn et al. (1982) mentioned a new type of zoning in exogenous – epigenetic uranium accumulations.

Laznicka (1985b) discussed numerous problems of ore zonation of significance to both petrologist and explorationist.

Ripley et al. (1985) computer-modeled some quantitative aspects of mineral zoning of sediment-hosted copper ores.

– See also Facies (Monseur/Pel, 1973, for carbonate-hosted stratiform ore deposits), Multi-factorial, Multi-stage, Replacement (Finlow-Bates et al., 1977, for relationship between syngenetic and diagenetic processes controlling zoning), and Solubility (e.g., Finlow-Bates/Stumpfl, 1979, 1981).

Epilogue – Brief notes on criteria and models

"Order is heaven's first law."

Alexander Pope

". . . let us go down and there confound their language, that they may not understand one another's speech."

Genesis 11:7

"All data, hypotheses or theories, and methodologies – indeed all human activities, conceptual tools and products – are merely adumbrations."

K.H. Wolf, Sydney, N.S.W., December 10, 1985

"It is the theory which decides what we can observe."

Albert Einstein

"The close examination of scientific paradoxes, anomalies, and antinomies usually results in new insights."

K.H. Wolf, December 27, 1985

"Most interactions are circular: cause produces effect and effect turning into cause and feeding back to the original cause."

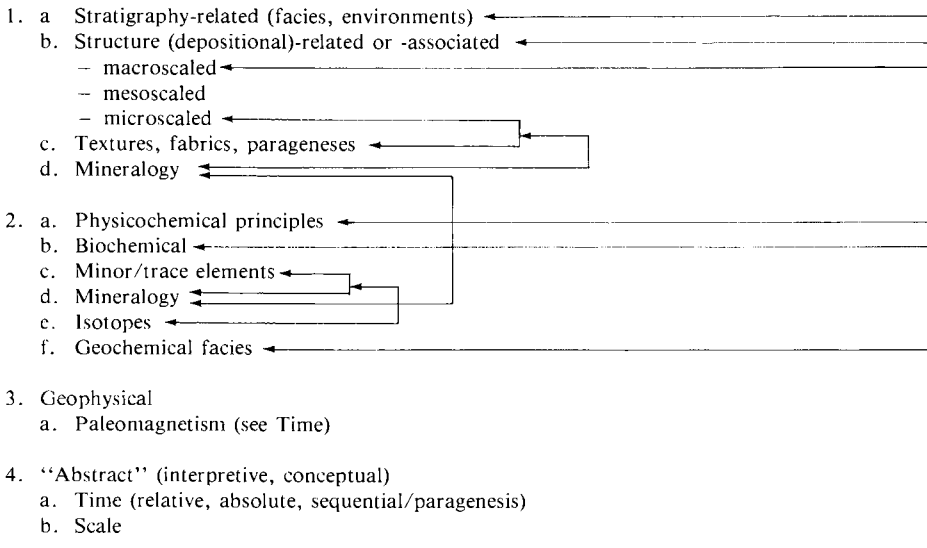*Paul Watzlawick,* in: How Real is Real? (1976, p. 97)

CRITERIA OR EVIDENCES OF DIAGENESIS

Perusing the literature on diagenesis in general, as well as specifically on ore genesis, there is no publication available as yet that summarizes (either haphazardly or systematically in a catalogue fashion, or in a comparative/contrastive style) the many criteria which "prove" that the material under investigation was of diagenetic origin. The word "prove" has been highlighted because so many so-called "proofs" depend not only on the definition of diagenesis, as repeatedly stated above, but each criterion or evidence has been interpreted in different ways, e.g., either of "diagenetic" or of "epigenetic" origin. The diageneticists offer too frequently criteria without considering alternatives, whereas the epigeneticists make their case by selectively presenting those "criteria" that support, but not contradict, their ideas. In addition, what may be true on a small scale, may not be applicable on a large scale.

It is fair to point out shortcomings and raise questions, as done above, without giving a remedy and a positive answer? The reply is "yes", because a comprehensive

TABLE 82

Grouping of diagenetic criteria (Wolf, 1982, unpublished)

1. a Stratigraphy-related (facies, environments)
   b. Structure (depositional)-related or -associated
       – macroscaled
       – mesoscaled
       – microscaled
   c. Textures, fabrics, parageneses
   d. Mineralogy

2. a. Physicochemical principles
   b. Biochemical
   c. Minor/trace elements
   d. Mineralogy
   e. Isotopes
   f. Geochemical facies

3. Geophysical
   a. Paleomagnetism (see Time)

4. "Abstract" (interpretive, conceptual)
   a. Time (relative, absolute, sequential/paragenesis)
   b. Scale

1 = Geological diagenetic criteria; 2 = geochemical diagenetic criteria; 3 = geophysical diagenetic criteria; 4 = "abstract" (in contrast to concrete) diagenetic criteria.

critical comparative review of all criteria in regard to syngenesis, diagenesis, epigenesis, catagenesis, etc., must be deferred to the future. At least a division of the types of criteria used in diagenetic studies, however, is provided here in Table 82. The list covers a wide spectrum of features of the three main earth-science disciplines, namely, geology, geochemistry, and geophysics. At the present time, many of the thought-stimulating questions posed in this chapter cannot be answered. They await extensive research!

CONCEPTUAL MODELS OF ORE GENESIS

"Nature is holistic; human endeavours are fragmentary; the sciences are segmented — thus, only a deliberate concerted conscious effort can overcome this imperfection."
K.H. Wolf, Sydney, N.S.W., February 8, 1983

"The conceptual modeling of geological phenomena involves the application of the reciprocal couples 'synthesis — analysis' and 'deduction — induction' in the study of the complex holistic relationships of nature."
K.H. Wolf, Sydney, N.S.W., February 20, 1983

"Analysis: The resolution of anything complex into its simple elements (opposite to synthesis); the exact determination of its components. In LOGIC, the tracing of things to their sources; the discovery of general principles underlying concrete phenomena."
The Shorter Oxford English Dictionary, Vol. I, 1975

"Synthesis: In LOGIC, the action of proceeding in thought from causes to effects or from laws or principles to their consequences; also the action of the understanding in combining and unifying the isolated data of sensation into a cognizable whole — the putting together of parts or elements so as to make up a complex whole."
The Shorter Oxford English Dictionary, Vol. II, 1975

As in society in general, so it ought to be in the sciences: "We should therefore claim, in the name of tolerance, the right not to tolerate the intolerant."
Karl Popper, The Open Society and its Enemies

Every geological — geochemical process and product can be modeled by utilizing a variety of available techniques. At present, most of the models (or analogues or paradigms) are still qualitative, at best semiquantitative, although a few plausible (non-controversial?) fully quantitative types have been proffered. Just to mention a few publications on modeling systems related to ore genesis, sedimentology, and diagenesis: Berner (1980b), Hallberg (1972), Rickard (1973), and Siever (1968). Wolf (1973a,b, 1976a,b, 1981, 1987) has prepared flow-chart-like, spider-web-like, reticulate- or net-type, linkage-cum-concatenation-type, and tabular and diagrammatic (= pictorial, cartoon-like) models.

The models range from general to specific types, and their coverage or scope varies accordingly. The *general* geological and geochemical processes and products modeled may be part of world-, continent-, and regional-scale dynamic (i.e., not a static) system. Several good examples of the large-scale analogues are provided by Gabelman (1977) on the origin of $U-Th$ ores; these models are utilized to summarize the known and to propose new ore types. Borchert has over many years supplied models on many chemical cycles (pers. commun., 1957 — 1979; see also Bor-
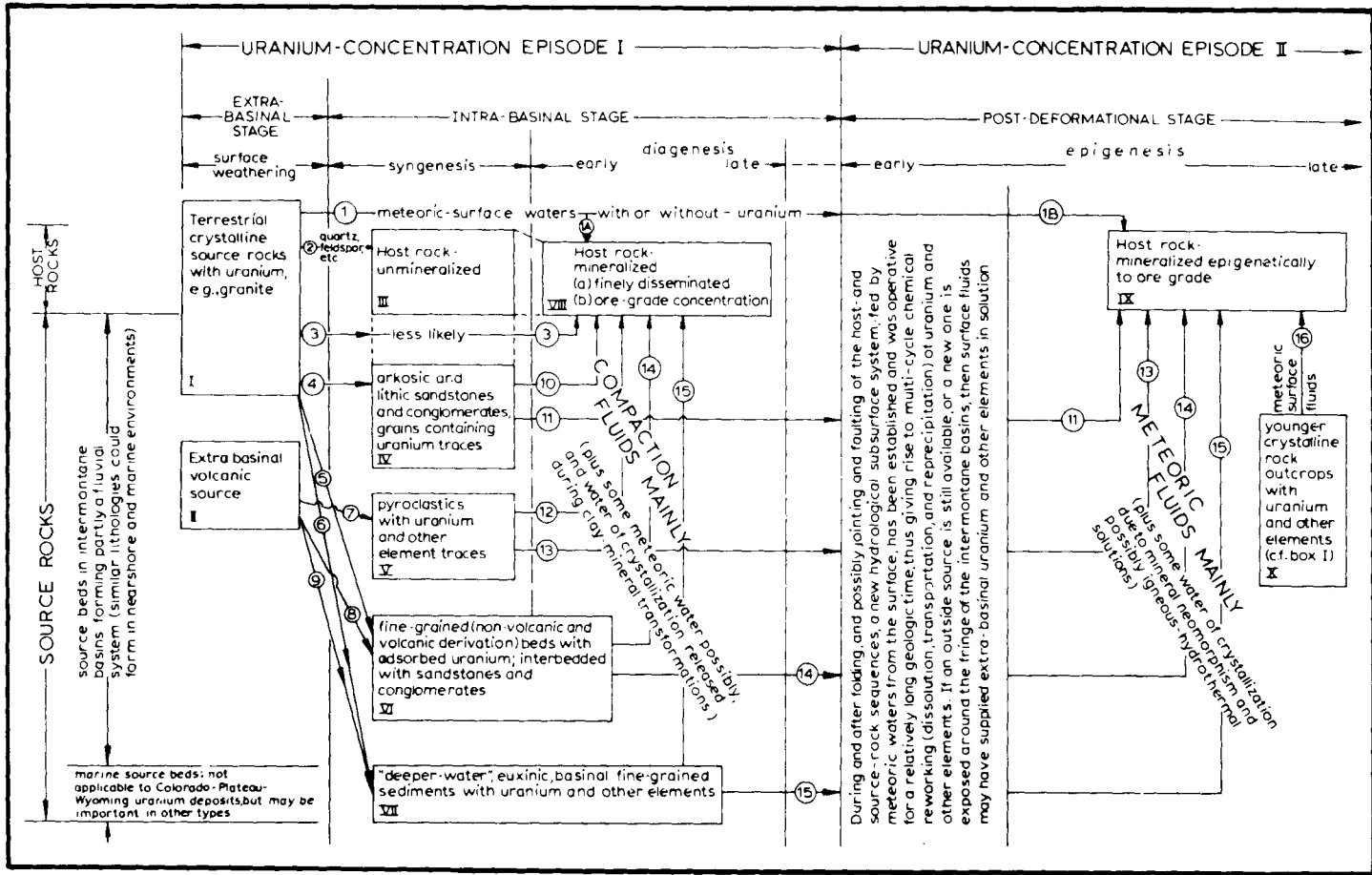
Fig. 278. Conceptual model of the origin of uranium deposits in sandstones. (After Wolf, 1976b, fig. 79; Wolf, 1976a, vol. 1, fig. 36.)
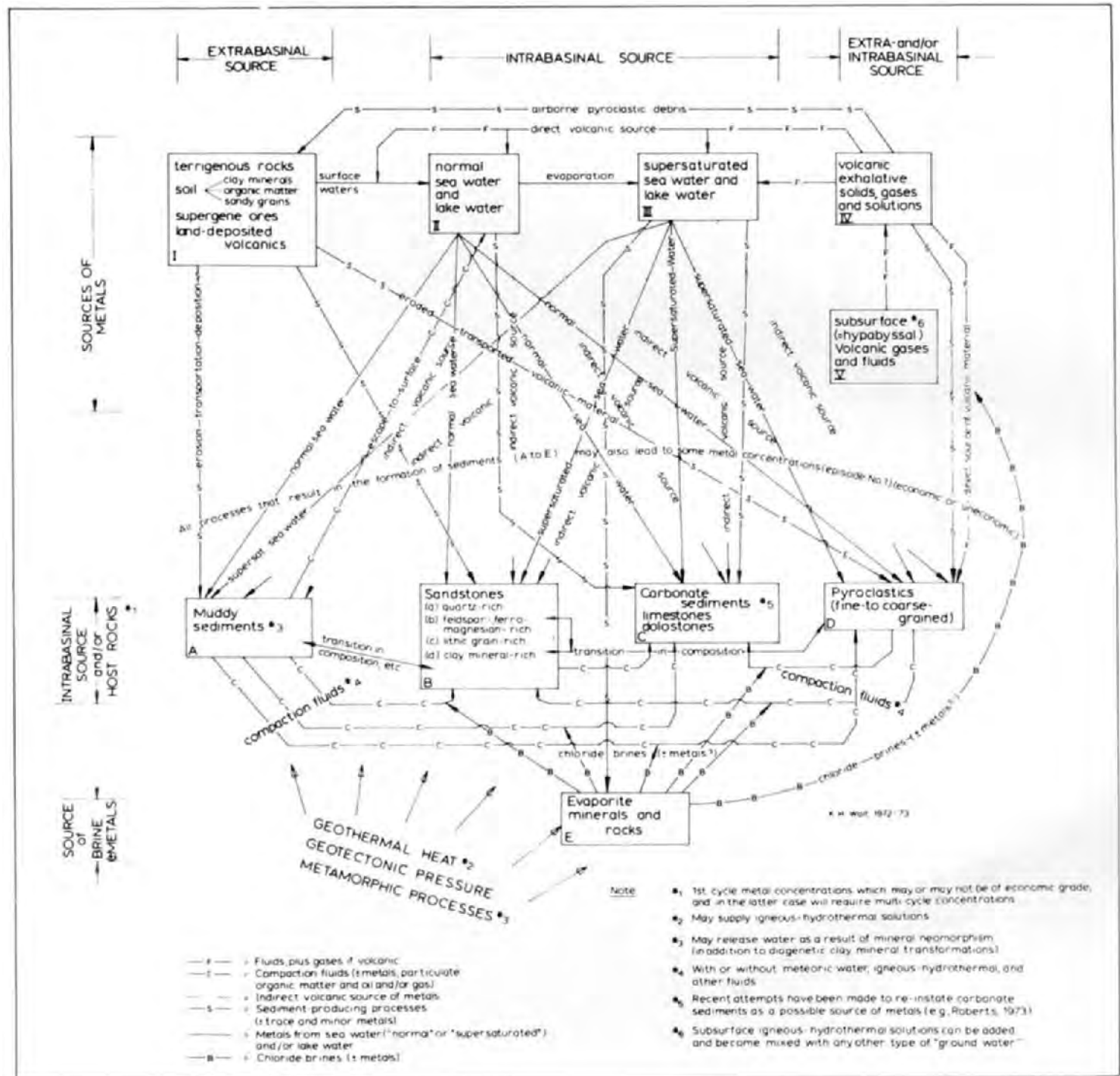
Fig. 279. Conceptual model that comprises all possible sources of metals, modes of tranportation, environments of precipitation, and types of hostrocks in the origin of stratabound ores in sedimentary and volcanic lithologies. (After Wolf, 1976b, fig. 92; Wolf, 1976a, vol. 1, fig. 38.)

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chert, 1978) of which several have been offered by Wolf (1976, 1981). As to *specific* models, using preferentially one small part of the complex natural system (albeit out-of-context), an example is provided by Wolf (1976a, vol. 1, fig. 1), who has shown the interrelationships of the variables controlling soil genesis and supergene ores, such as bauxites. The same model can also indicate the conditions of provenance or source area. When all parts of a system have been modeled, they can then be combined into a complex, nearly all-inclusive model (Figs. 278 and 279), as those provided, for example, in the just-cited publications (cf. figs. 10, 15 – 18, and 38, in Wolf, 1976a). These "complex" models, however, are only of "intermediate complexity", for they are still *relatively* simple and incomplete in contrast to what will be modeled in the future.

Where does *diagenesis* in general and that related to ore genesis in particular fit into the above? All the comments on models are equally applicable to sediment-hosted ores and to the diagenetic processes that influenced them, ranging from the world-wide to the local and microscopic scale, and from the general to the particular. Two general schemes (Figs. 278 and 279) are presented here that may not even mention the word "diagenesis", but every experienced geologist and geochemist can immediately see in which parts or during which stages diagenesis must have been operative. Within such generalized, "averaged-out" mega-models there are numerous parts that need to be modeled in the future; first in qualitative and then in quantitative terms.

In Table 5, many variables are listed that affect or, conversely, are affected by diagenesis. (It has been stated that causes result in effects which are the causes resulting in new effects within a chain of phenomena . . . It is a matter of "Semantic Punctuation"; see Watzlawick, 1976.) Can all these variables be modeled to depict their complex interconnections? In the future, no doubt, they will all be modeled. At the present time, however, one has to be content to go through several stages of selection for the sake of simplification: from among the three groups of parameters listed in Table 5 (i.e., from the chemical, physicochemical/physical/biological/miscellaneous, and geological variables) one will choose only the chemical factors, for example. Of these, not all will be utilized for a preliminary model, because of our present limitations in the study of super-complex natural systems. For instance, as Table 83 and Fig. 280 indicate, for illustrating purposes only the more obvious members were related.

Table 83 lists the chemical variables on both the vertical and horizontal axes. Thus, those parameters that influence each other in a particular system under investigation can be ticked off in the pertaining pigeonholes. Figure 280 is somewhat more comprehensive as it is of the spider-web, reticulate or net-like variety in which the variables (around the perimeter) that control each other can be connected by arrows, similar to the scheme shown by Wolf in an earlier publication (1976a, vol. 1, fig. 1).

Once all the geological and geochemical parameters are properly identified and listed and their complex interrelations have been modeled in the study of, or in the exploration for, a specific ore deposit, one ought to know what the methodology should be in the framework of financial, manpower, time, and other constraints.

464

TABLE 83

Chemical variables of a diagenetic system that influence each other − a (simplistic) example (Wolf, 1979, unpublished) (− = influence non-existent; + = influence/control present)

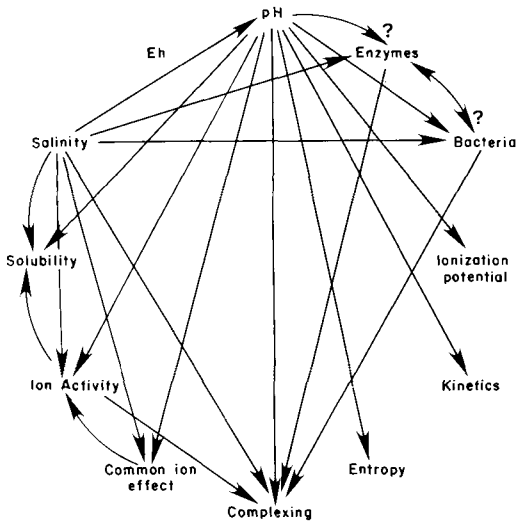|	pH	Eh	Salinity	Solubility	Ion activity	Common ion effect	Complexing	Entropy	Ionization potential	Bacteria	Enzymes
pH	−		+	+	+	+	+	+	+	+	
Eh		−		+	+	+		+		+	
Salinity	+		−	+	+	+	+		+	+	+
Solubility	+	+	+	−	+	+	+	+			
Ion activity	+	+	+	+	−	+	+	+	+	+	
Common ion effect	+	+	+	+	+	−	+	+	+	+	
Complexing	+		+	+	+	+	−	+	+	+	+
Entropy	+	+			+	+	+	−	+		
Ionization potential	+		+		+	+	+	+	−		
Bacteria	+	+	+		+	+	+			+	+
Enzymes							+			+	−

Fig. 280. Spider-web-type model depicting the complex interrelationships of the chemical variables in a diagenetic system (a simplistic example). The same variables as in Table 83 have been used, except that "kinetics" has been added. In order to keep the diagram simple, only a few "reaction arrows" are shown. (After Wolf, 1985, 1987.)

Inasmuch as each individual investigation or exploration program has to concentrate by necessity on preferentially selected aspects, and consequently cannot examine all geological features and employ all techniques, one at least should put those chosen into context with the whole for comparison's sake. By doing so, one can obtain a neat overview that permits the selection of the best-suited techniques. Poor planning will result in poor results!

ACKNOWLEDGEMENTS

John Wiley and Sons: Figs. 3, 204 and 205.
Mineralogical Society of Britain: Figs. 199, 200, 252 and 253.
Nature: Fig. 138.
Paleontological Society (Chicago): Fig. 37.
Pergamon Press: Figs. 20, 36, 38, 53, 63, 71, 76, 90, 91, 145, 152, 161, 167, 190, 191, 197, 208, 218, 219, 237, 254, 255 and 258.
Royal Society of Edinburgh: Figs. 271, 272 and 273; and Tables 79 and 80.
Royal Society of London: Tables 77 and 78.
Schweizerbart'sche Verlagsbuchhandlung (Stuttgart): Figs. 16, 45, 141, 209, 210, 211, 212, 227, 228 and 274.
Science: Fig. 129.
Society of Mining Geologists of Japan: Fig. 183.
Society of Economic Paleontologists and Mineralogists: Figs. 41, 46, 101, 118, 119, 120, 165, 203, 243, 244 and 245; and Tables 21, 48, 57 and 75.
Springer Verlag (Heidelberg): Figs. 13, 14, 15, 17, 35, 68, 78, 79, 123, 125, 136, 163, 175, 229, 230, 235, 236, 239, 247, 248, 259 and 260; and Tables 67 and 72.
University of Rhode Island: Fig. 256.
University of Stockholm: Figs. 27 and 69.
University of Western Australia: Table 37.
University of California: Fig. 39.
University of Chicago Press: Figs. 81 and 213.
University Park Press: Figs. 28 – 34.
Verlag Glückauf (Essen): Table 24.
Freeman and Co., Publishers: Figs. 162 and 188.

GLOSSARY

Definitions-cum-explanations of terms (Wolf, 1979, modified and supplemented from the literature)

Anadiagenesis: A term used by Fairbridge (1967) (Fig. 11) for the compaction and maturation phase of diagenesis, in which clastic sediment grains or chemical sediments become lithified during deep burial (extending to 10,000 m). It is characterized by expulsion and upward migration of connate waters and other non-magmatic fluids, such as petroleum, and often by reducing conditions; it may pass into metamorphism (cf: epi- and syndiagenesis.) Synonym: middle or intermediate diagenesis. Ana = Greek prefix for up (in place or time) back, again, anew.

Apo-epigenesis: Post-diagenetic changes that affect sediments while they are remote from the original environment of deposition, as when they are under a relatively thick overburden (Wolf, in Chilingar et al., 1967, p. 311) (cf: juxta-epigenesis). Apo = Greek prefix for off, from, away; detached.

Catagenesis: As used by sedimentologists, the changes occurring in an already formed sedimentary rock buried by a distinct (though sometimes thin) covering layer, characterized by pressure – temperature conditions that are much different from those of deposition (Fersman, 1922); specifically the breakdown of rocks. The term is more-or-less equivalent to "epigenesis" as applied by Soviet geologists. Synonym: Katagenesis. Cata- (kata-), cat-, cath- are Greek prefixes for down, away. Note: Some authors in English-language countries have used "epigenesis" as a near-synonym for "catagenesis"; when used, both should be clearly defined. See numerous tables here where catagenesis is the stage between diagenesis and metamorphism; epigenesis, in the traditional sense, has no such "time" or "stage" connotation (see Table 45).

Diagenesis: It includes all physicochemical, biochemical and physical/mechanical processes modifying epiclastic, pyroclastic and chemical sedimentary deposits after their initial accumulation, up to the stage of lithification, at low temperatures and pressures characteristic of surface and near-surface en-

vironments. Some researchers/explorationists apply the term diagenesis also to the secondary surface and near-surface alteration of volcanic flow-rocks, e.g., ignimbrites, rhyolites, andesites, and basalts; including submarine halmyrolysis.

In some instances, diagenesis can be sub-divided into pre-, syn- and post-cementation diagenetic stages. Some geologists prefer other divisions, such as "early" and "late" diagenesis, or even "proto-", "meso-" and "apo-" diagenesis; see Tables 41 – 45. In any case, diagenesis takes an intermediate position between syngenesis and "epigenesis" or "catagenesis" (see respective definitions). Under unusual conditions, diagenesis can grade into metamorphism, as in the Red Sea today. However, some of the hydrothermal – exhalative solutions cause "metasomatic" alterations that are still in the realm of diagenesis (with somewhat elevated temperatures). Therefore, diagenesis and surface and near-surface low-temperature metasomatism are overlapping or transitional in nature.

There is no universally accepted definition of the term diagenesis, and no delimitation (such as the boundary with metamorphism) is established, although attempts have been made by using the degree of maturation of organic matter, clays, zeolites, etc. See text for further elaborations, especially on the various uses of "diagenesis" causing confusion (also Bates/Jackson, 1980, p. 171). Dia = Greek prefix for through, during, across. Derived from the prefix di-, meaning two.

Note: (1) Diagenesis is always preceded by syngenesis and, vice versa, syngenesis is always succeeded by diagenesis; one is directly dependent on the other. They automatically co-exist. (2) Diagenesis is mostly a genetic, petrologic term and, thus, is based on interpretations; although in the context of petrographic (e.g., paragenetic) studies it may appear as a "pseudo-" descriptive (i.e., genetically flavoured) term. (3) Diagenesis can be subdivided into geochemically "open" and "partly closed" systems during "early" and "late" phases, respectively (see Amstutz/Fontboté, 1982, in regards to ore genesis). (4) Diagenesis has been used for processes, products, sources, and as a term denoting a phase, stage, episode or relative time (see Table 2). Consequently, the term must be unequivocally defined. The definition may vary to suit the purposes and conditions of the study, whether reconnaissance or detailed, whether local or regional, and whether for geological or geochemical purposes. (5) Note that veins are commonly referred to as "epigenetic", and inasmuch as "epigenesis" can take place at any time as soon as a sedimentary/volcanic deposit accumulated, "epigenetic veins" can be of early or late diagenetic origin (as well as of much later catagenetic, etc. origin; see Table 43). Some refer to the early-formed veins as "diagenetic – epigenetic veins" or "sedimentary – diagenetic veins", in contrast to other types, such as "catagenetic – epigenetic – lateral secretion" veins, for example.

Diplogenetic: A mineral deposit that is in part syngenetic and in part epigenetic in origin is called diplogenetic (Lovering, 1963, pp. 315 – 316). Diplo = Greek prefix for two, just as duo = Latin prefix for two; however, the latter has not been used in this petrologic context. – "Diplogenetic", if properly defined (redefined?), could also be used for *any* combination of two processes or products thereof for example, as shown in Tables 33 and 38. It is applied to two stages, two sources, two processes or mechanisms, two types of fluids, etc., which in combination gave rise for a deposit (see text). Thus, syngenesis + diagenesis, diagenesis + catagenesis, sedimentary diagenesis + exhalative (hydrothermal) diagenesis are possible combinations in addition to the syngenetic – epigenetic dual process (see triplogenesis). Note that there are mono-diplogenetic and multi-diplogenetic ore-forming systems; e.g., the elements of an ore deposit may have come from *two* sources, but the fluid from *three*. The possible combinations are nearly limitless; at least from a hypothetical, arm-chair geology viewpoint!

Endogenetic: Derived from within; in sedimentology derived from within the sedimentary formation or pile. Endo = Greek prefix for within. This term is also used for endogenic ore deposits that originate within the rocks that contain them (in contrast to the exogenic/exogenetic types); see Tables 12, 30 – 33. Synonym: endogenic.

Epidiagenesis: A term used by Fairbridge (1967) for the final emergent phase of diagenesis, in which sediments are lithified during and after uplift or emergence but before erosion. It is characterized by modification of connate solutions (by deeply penetrating and downward-migrating groundwaters) and by reintroduction on of oxidizing conditions; near the Earth's surface, it passes into a zone where weathering processes become dominant. Synonymous to some definitions of "late diagenesis". See also: syn- and anadiagenesis. Epi = Greek prefix for upon, at, or close upon; in addition (see Fig. 11).

Note: "Epidiagenesis" as defined above is somewhat confusing and, therefore, is not recommended. It is not the same as "diagenetic epigenesis" (= diaepigenesis) of some researchers, e.g., "epigenetic veins" formed during diagenesis.

Eogenetic: A term proposed by Choquette/Pray (1970, pp. 219–220) for the period of time between final deposition of a sediment and burial of that sediment below the depth to which surface or near-surface processes are effective. The upper limit of the eogenetic zone is the land surface; the lower boundary, less clearly defined due to the gradual diminishing of surface-related processes, is the "mesogenetic" zone. Cf: telogenetic and mesogenetic. Eo = Greek prefix for dawn, earliest. Synonym: eogenic (see Fig. 12).

Epigenesis: (1) In sedimentology, the term refers to the changes, transformations, or processes occurring at low temperatures and pressures, that affect sedimentary rocks subsequent to their compaction, exclusive of surficial alteration (weathering) and metamorphism; it is in-between syngenesis – diagenesis and metamorphism. Cf.: epidiagenesis. Synonyms: catagenesis, and metagenesis according to some geologists. Epi = Greek prefix for upon, at, or close upon; in addition. See figures and tables herein. (2) In sedimentology, epigenetic refers to a sedimentary mineral, texture or structure formed after the deposition of the sediment (cf. 3 below). (3) In ore petrology, epigenetic refers to a mineral deposit of origin later than that of the enclosing rocks. Cf.: syngenetic ore.
    Note: (a) Some geologists have used "catagenesis" as a near-synonym for "epigenesis". (b) The variable definitions of epigenesis have caused some contradictions.

Exogenic: In general, said of processes originating at or near the surface of the earth, such as weathering and denudation, and to rocks, ore deposits, and landforms that owe their origin to such processes (Bates/Jackson, 1980, p. 216). In the present context of ore genesis, exogenic refers to components derived from outside sources, i.e., either from above (supergene) or from below (hypogene) sources. Cf.: endogenic. Synonym: exogenetic. Exo = Greek prefix for without (= outside, exterior) (see Tables 12, 30–34).

Hypergenesis: A term introduced by Fersman (1922), and persisting to the present in Soviet geology, for surficial alteration (weathering) of sedimentary rocks. Synonyms: retrograde or retrogressive diagenesis; retrodiagenesis; supergenesis (some types of the latter). Hyper = Greek prefix for over, beyond; above measure; very, greatly (see Table 45).

Hypogene: (1) In general, said of a geologic process, and of its resultant features, occurring within and below the Earth's crust. Cf.: epigene. Synonym: hypogenic. (2) In ore petrology, said of a mineral deposit formed by ascending solutions; also said of those solutions and of that environment. Cf.: supergene, mesogene. Hypo = Greek prefix for under, beneath, below; nearly, to some extent.

Juxta-epigenesis: Proposed by Wolf (in Chilingar et al., 1967, p. 316) for post-diagenetic changes that affect sediments and/or volcanic deposits while they are near the original environment of deposition, either under a relatively thin overburden or exposed above sealevel. Cf.: apo-epigenesis. Juxta = Greek prefix for near, by the side of.

Lithogene: In general, said of a mineral deposit formed by the process of mobilization of elements from a solid rock and their transportation and redeposition elsewhere. On a local scale, the process may be called a product of "lateral secretion", a term or process especially employed in ore petrology; on a larger scale, the deposit is a product of regional (catagenetic – metamorphic, for example) processes. Cf.: stratafugic.

Mesogenetic: A term proposed by Choquette/Pray (1970, p. 220) for the period between the time when newly buried deposits are affected mainly by processes related to the depositional interface (eogenetic stage) and the time when long-buried deposits are affected by processes related to the erosional interface (telogenetic stage). Cf.: telogenetic, eogenetic. Meso = Greek prefix meaning middle (often used in connection with proto- and meta-) (see Fig. 12).

Metagenesis: (1) As used in sedimentology by Soviet geologists, a term applying to "epigenesis" (changes occurring in a more-or-less compacted sedimentary rock) or to late epigenesis (see Table 45). (2) In one of the schemes by Vassoevich (1962 and thereafter; see also Tissot/Welte, 1978) "metagenesis" is the stage between catagenesis and metamorphism (see Table 45 and Figs. 13, 14, 15). (In the Soviet Union, most geologists use Vassoevich's classification.)

Pedogenesis: The genesis of soils.

Predepositional: Refers to the stage when sedimentary material first is formed, e.g., in the source area prior to erosion and removal, ending with the final deposition of that material or of sedimentary particles. The predepositional features in clastic (terrigenous) lithic fragments provide evidence of that source area environment, as for example in limestone extraclasts that exhibit predepositional diagenetic criteria (Wolf, 1965b) (see table 45).

Prediagenesis: A term proposed by Wolf (in Chilingar et al., 1967, p. 322) for that part of syngenesis responsible for "those materials that were introduced subsequently to syngenesis or syndeposition but "before the principal processes of diagenesis began"; e.g., internal sedimentation of clastic material may be termed "prediagenetic" in one scheme, whereas in another paragenetic system may be called "very early diagenetic".

Primary: (1) In general, of the first order in time or temporal sequence; earliest, primitive, original. (2) In petrology or sedimentology, it refers to something that is in existence in a rock since the time of its formation. This definition is too all-inclusive and vague for detailed geological work, so that its use is discouraged. "Primary" can be used, however, in an unambiguous way only as a general colloquial term in connection with genetic deliberations when the context leaves absolutely no doubt. It must be defined properly. (3) In ore petrology, said of a mineral deposit unaffected by subsequent (secondary) alterations. Cf.: secondary.

Proto-: The Greek prefix for "first, first in time, earliest". Hence, when used to divide, for example, catagenesis into several sub-stages (i.e., proto-, meso-, apo-catagenesis), proto- denotes the first sub-stage thereof. Diagenesis could be similarly divided; see Table 45.

Secondary: (1) In general, it means derived from, based on, or dependent on something else which is primary; not original, derivative. (2) In petrology, something (like texture, mineral, nodule, bed, ore, etc.) formed later than the rock enclosing it, sometimes at the expense of an earlier-formed primary entity. This term is too ambiguous in precise studies − see Primary above.

Stratafugic: A term used by Jackson/Beales (1967) of material derived (endogenically) from associated sediments and/or volcanics, i.e., from within the sedimentary basin. Compactional fluids (hot or cold) are stratafugic in origin, in contrast to the igneous hydrothermal solutions. Some stratafugic solutions and materials are of lateral-secretion origin, but other mechanisms can give rise to stratafugic components; thus the two expressions are not synonyms. In contrast to the exogenic − supergene and exogenic − hypogene sources, the stratafugic material is of an endogenic origin.

Supergenesis: (1) In general, said of processes operative near the Earth's surface, commonly forming enrichments (with depletion of soluble material), involving oxidation that produces (descending) acidic solutions which leach metals, etc., carry them downward, and reprecipitate them, thus enriching sulfide minerals already present, for example. Consequently, the term applies to supergene environments, solutions, minerals, processes. Cf.: hypogenesis. Synonyms: hypergenesis; some secondary processes. Super = Greek prefix for over, above, on, upon, on the top; beyond.

Syndepositional: A term used by Chilingar et al. (1967, p. 322) for that part of syngenesis comprising "processes responsible for the formation of the sedimentary framework". Cf.: prediagenesis. Syn = Greek prefix for together, similarly, alike.

Syndiagenesis: A term used by Bissell (1959) (see also Fig. 11) for the sedimentational, prediastrophic

phase of diagenesis, including alteration occurring during transportation (halmyrolysis) and during deposition of sediments, and continuing through the early stages of compaction and cementation but ending before that of deep burial (less than about 100 m). It is characterized by the presence of large amounts of interstitial or connate water that is expelled only very slowly and by extreme variations in pH and Eh. Synonym: early diagenesis. See also epidiagenesis, anadiagenesis. Cf.: syngenesis.

Syngenesis: In sedimentology it has several meanings: (1) Used by Wolf (in Chilingar et al., 1967, p. 322) for the processes by, or the stage in, which sedimentary rock components are formed and/or accumulated simultaneously and penecontemporaneously in the depositional environment – it excludes the source area milieus, but includes syndeposition and prediagenesis. (2) Syngenesis is a term introduced by Fersman (1922) for the formation, or the stage of accumulation, of unconsolidated sediments in place, including the changes affecting detrital particles still in movement in the waters of the depositional basin. The term is in dispute by Soviet geologists (see Dunoyer de Segonzac, 1968, p. 170): some would apply it to initial diagenesis (designated exchange phenomena between fresh sediment and the sedimentary environment), whereas others would extend it to all the transformations undergone by a sediment before its compaction. This would be a synonym of early diagenesis. (3) Syngenetic is applied in sedimentology to sedimentary structures, for example, that are of primary origin, such as ripple marks, formed contemporaneously with the accumulation of the sediments. (4) In ore genesis, syngenetic refers to a mineral deposit said to be formed contemporaneously with, and by essentially the same processes as the enclosing rocks. Cf.: epigenetic ore; diplogenetic ore, triogenetic ore; and syndiagenesis. (See the text for discussions.) Syn = Greek prefix for together, similarly, alike.

Note: (a) See note (1) in the definition of diagenesis. (b) Syngenesis is succeeded by and is gradational or transitional into numerous possible types of diagenesis. (c) Syngenesis must include the processes and products related to the pyroclastic and volcanic – (hydrothermal –) exhalative deposits, which also fall into the realm of sedimentology. (d) Syngenesis has also been employed for plutonic-rock-associated (i.e., magmatically generated) ore deposits, which formed more-or-less simultaneously with their igneous hostrock.

Synsedimentary: Accompanying deposition; specifically said of a sedimentary ore deposit in which the ore minerals formed contemporaneously with the enclosing rock. Cf.: syngenesis, syndiagenesis. Syn = Greek prefix for together, similarly, alike.

Telogenetic: A term proposed by Choquette/Pray (1970, pp. 220 – 221) for the period during which long-buried carbonate rocks are affected significantly by processes related to weathering and subaerial and subaqueous erosion. Cf.: eogenetic, mesogenetic. Synonym: telogenic. Telo = Greek prefix for end, far off (see Fig. 12).

Triogenetic: Proposed by Wolf (1981, unpublished) for a mineral deposit or any other rock that has originated by the involvement of three processes or consists of three components each of a different derivation. It is similar to "diplogenetic", except that three stages, three sources, three processes, three fluids, etc., were involved. Cf.: diplogenetic. Synonym: triogenic. Trio = Greek prefix for three.

Vein (ore deposits): As used in ore petrology, an epigenetic mineral filling of a fault or other fracture in a host, in tabular or sheet-like form, often with associated replacement of the hostrock; a mineral deposit of this form and origin.

Note: This term has no time connotation, and is independent of orientation and degree of lithification or consolidation of the hostrock (see Table 43).

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512

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540

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546

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Chapter 2

SANDSTONE DIAGENESIS IN RELATION TO PRESERVATION, DESTRUCTION AND CREATION OF POROSITY

KNUT BJØRLYKKE

INTRODUCTION

In the last few years, there was an upsurge of strong interest in clastic diagenesis both within the petroleum industry and the academic community. It has become increasingly clear that it is of great importance to understand the diagenetic processes that take place from the time of deposition to deep burial.

It is of great practical importance to be able to evaluate the quality of potential reservoir rocks during the exploration for hydrocarbons. Only upon understanding these processes, one is able to construct models that are capable of predicting the distribution of porosity and other reservoir parameters in a sedimentary basin.

It is also important to establish models that can be used to predict the three-dimensional distribution of reservoir properties between the wells in oil fields which are being developed for production. The diagenetic reactions determine not only the porosity and permeability but also pore-size distribution, pore geometry, specific surface area, ion-exchange capacity, etc.

Well-sorted sandstones have a primary porosity of 35 – 45% shortly after deposition. This primary porosity may be reduced in principally two different ways (Fig. 1): (1) by mechanical compaction, pressure solution and isochemical diagenesis, and (2) by net cementation from solutions brought from outside the sandstones and precipitated in the available porespace (allochemical diagenesis).

In case No. 1, the reduction of porosity of the sandstones is accompanied by corresponding loss in rock volume and stratigraphic thickness (Manus and Coogan, 1974). There is no need for a supply or removal of solids in solution.

Cementation from solutions brought from outside the sandstone requires a very high flux of porewater which is supersaturated with respect to a mineral phase. In this case (No. 2), the volume of the sandstone is not changed. Porewater flowing through a sandstone may also be undersaturated with respect to one of the major mineral phases and cause leaching which creates secondary porosity.

Diagenetic processes can, therefore, only be understood if one has some idea about porewater flow in sedimentary basins. One can distinguish between porewater which is originally meteoric water flowing into the sedimentary basin and fluids flowing upwards due to increasing compaction with burial. Meteoric porewater is initially undersaturated with respect to most of the common clastic silicate minerals and this porewater approaches equilibrium with the minerals in the sandstone by dissolution and precipitation. The extent of meteoric porewater wedges in sedimentary basins and their importance in clastic diagenetic reactions have only recently been realized by sedimentologists.

I

II
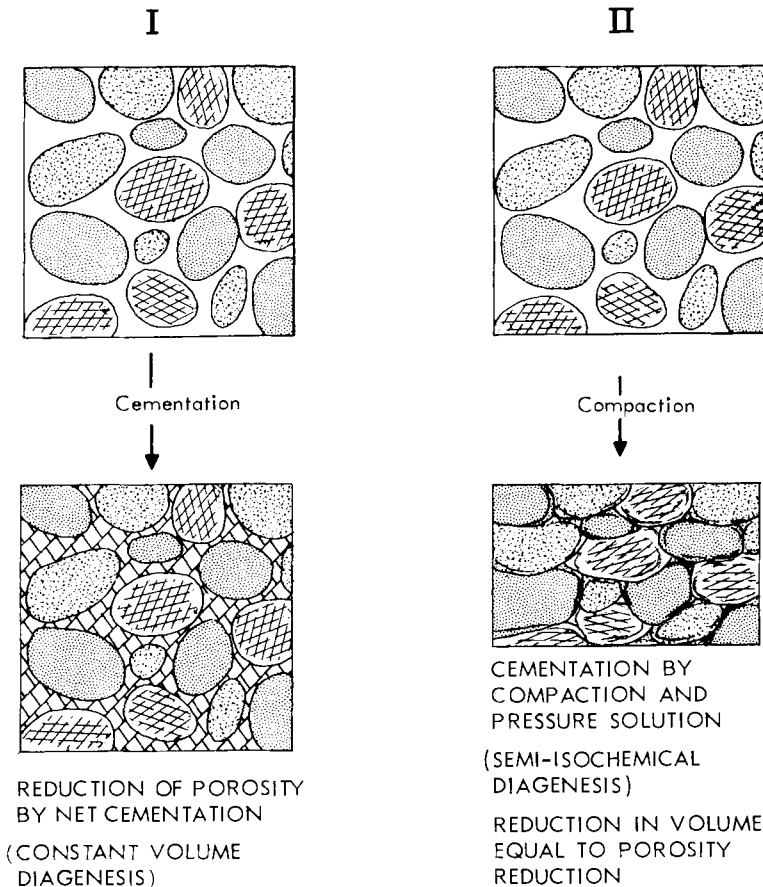
Fig. 1. Two principally different ways to destroy porosity in sandstones: (I) net supply of cement from circulating porewater (allochemical diagenesis); (II) mechanical compaction through deformation and pressure solution and reprecipitation (isochemical diagenesis). (From Bjørlykke, 1980.)

The composition of compactional porewater is controlled by diagenetic reactions which occurs with increasing burial. Reactions between organic matter within the shales (source rocks) and silicate minerals in sandstones may also be important (Surdam et al., 1984). The low solubility of Si and Al species in porewater puts important restrictions on models for diagenetic reactions. It has been shown that normal compactional porewater flow in sedimentary basins is insufficient to dissolve or cement larger volumes of sandstones (Bjørlykke, 1979, 1984). In order to have a larger transport of solids in sedimentary basins, one must either assume that large-scale convection currents are common (Wood and Hewett, 1982, 1984) or that the solubility of silica and aluminium is increased by complexing with organic acids (Surdam et al., 1984).

More high-quality porewater analyses are needed to establish what components are actually transported in porewater. Isotopic analyses of porewater and diagenetic minerals help us to reconstruct the reaction between porewater and sandstone.

MECHANICAL COMPACTION

The subject of mechanical compaction of sediments has been covered by extensive reviews published earlier in the Elsevier Sedimentology series (Rieke and Chilingarian, 1974; Chilingarian and Wolf, 1975/1976; Wolf and Chilingarian, 1976).

Clay-rich sandstones, particularly if they are matrix-supported, lose primary porosity rapidly upon loading and respond essentially as mudstone. Sandstones, which are inititally well sorted but have low mechanical grain strength, also deform under moderate overburden with primary grains sometimes being compressed (squashed) to effectively become part of the matrix. This is particularly the case for sandstones derived from volcanic and basic igneous rocks, and is typical of island arc-derived sandstones (Galloway, 1979). Sand grains of basalt and minerals like amphibole and pyroxene, are easily altered to chlorite and may be very difficult to distinguish from a chloritic clay matrix. Sandstones composed of more stable grains, like quartz and feldspar, however, may also be subject to considerable compaction. Wilson and Duncan (1978) estimated that reorientation of the grains and closer packing may account for up to 17% porosity reduction.

Further mechanical compaction may be due to fracturing of grains and ductile grain deformation (McBride, 1978). As pointed out by Taylor (1950), feldspar grains may fracture along their cleavage planes to form a closer packing. Also, quartz grains can be observed to have developed fractures which often are more concoidal due to the absence of good cleavage planes (Sippel, 1968). Although fracturing accompanied by compaction results in reduced total porosity, secondary porosity is created. Tectonic shear, however, may produce an increased porosity due to fracturing and well-cemented, tight sandstones may develop significant secondary porosity and become fractured reservoirs.

In a well-sorted sandstone, the effective stress (total overburden pressure minus the pore pressure) is transmitted to the grain contacts, which initially are very small areas. The stress per unit area, therefore, becomes very large, even for moderate burial depth, and causes grains to deform by ductile deformation, fracturing, or pressure solution. As a result of this deformation, the contact area becomes larger and the stress per unit area is reduced. Undulatory extinction of quartz and feldspar may be observed near the grain contacts. The stress at grain contacts deforms the crystal lattice and increases the solubility of minerals at the contact points where dissolution may occur. This will create a local supersaturation with respect to the other surfaces of the grains, which are subject to only hydrostatic pressures, and ions in solution may be transported by ionic diffusion and precipitate as overgrowth (Weyl, 1959; De Boer, 1977; De Boer et al., 1977; Dibble and Amos, 1981; Dibble and Tiller, 1981). It is important to note that both mechanical deformation and chemical pressure solution are dependent on the effective stress (p_e) and not on the thickness (weight) of the overburden or the geostatic stress p_t (i.e., $p_e = p_t - p_p$, where p_p is the pore pressure; Terzaghi and Peck, 1967; Plumley, 1980).

Thus, the pore pressure strongly influences the effective (grain-to-grain) stress and, in highly overpressured zones, the effective stress may approach zero (Fig. 2). In overpressured basins, the net (effective) stress may decrease with burial depth. In the North Sea, overpressures in the Jurassic sandstones of the Viking Graben may

correspond to drilling mud densities of $1.8 - 2.0$ g cm^{-3} or piezometric surfaces up to $2 - 3$ km above sea level (Chiarelli and Duffaud, 1980). As an example, a sandstone with 2.0 km piezometric surface at 2.5 km burial depth corresponds to a pore pressure of $(4.5 \times 10^3$ m) $\cdot$ $(0.1$ kg cm^{-2} m$^{-1}) = 450$ kg cm^{-2} $(4.41 \times$ MPa). The geostatic pressure assuming an average density of 2.2 g cm^{-3} is: $(2.5 \times 10^3$ m) $\cdot$ 0.22 kg cm^{-2} m$^{-1} = 550$ kg cm^{-2} $(5.44$ MPa). The effective stress would then be only 100 kg cm^{-2} $(= 550 - 450$ kg cm$^{-2})$. If the mud weight is equal to 1.8 g cm^{-3} at 2.5 km burial, the effective stress p_e is equal to 100 kg cm^{-2} $(2.5 \times 10^3$ m $\cdot$ 0.22 kg cm^{-2} m^{-1} $-$ 2.5×10^3 m $\cdot$ 0.18 kg cm^{-2} m$^{-1})$. The geostatic ratio, which is the ratio of the geostatic overburden to the pore pressure (p_t/p_p), is then equal to 1.2. In the Gulf Coast (USA), geostatic ratios of $1.3 - 1.17$ are common (Jones, 1969). With increasing content of dissolved salts, the hydrostatic pore pressure also increases due to the higher density of the porewater $(1.1 - 1.2$ g cm$^{-3})$.

High pore pressures build up during burial when sandstones are not able to be drained of the excess water during compaction, because they are surrounded by low-permeability barriers, such as clay or shale beds, and sealing faults. Rapid sedimentation rates may have the same effect. Also the transformation of smectite to mixed-layered minerals and to illite with increasing temperature, will release water which may increase the pore pressure when the permeability is low. The release of water contained in the minerals also reduces the salinity of the porewater by dilution. The thermal expansion of water will, in well sealed-off structures, contribute to building up the pore pressure. Salinity differences over clay-rich permeability barriers may also produce osmotic pressures which may be of importance (Jones, 1969; Graf, 1982).
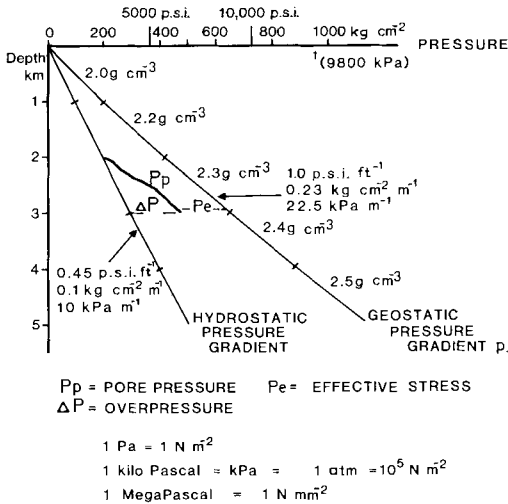
Fig. 2. Diagram illustrating subsurface pressures and stresses. The hydrostatic pressure is the weight of the water column and the geostatic pressure (p_t) equals the weight of the overlying sediments. The effective stress transmitted through the grain framework of grain-supported sandstones is equal to $p_c = p_t - p_p$, where p_p is the pore pressure, which may exceed hydrostatic pressure and is then referred to as overpressure.

Formation of early cement may inhibit later cementation and also reduce pressure solution. A larger percentage of the primary porosity is preserved when chlorite cement forms in marine environment as coatings (pore linings) on quartz grains than when such cement does not develop (Tillman and Almon, 1979). Early silica or carbonate cements will distribute the grain-to-grain stress on a larger area of the grain framework and thereby reduce the later pressure solution (Nagtegaal, 1980). Early cementation, particularly of quartz cement, forms a strong grain framework of quartz which protects weaker grains from compaction.

POREWATER COMPOSITION AND POREWATER FLOW

Porewater which is stationary within a sandstone will approach equilibrium with the minerals present. At low temperature, however, this equilibration may be rather slow. If the pore water remains out-of-equilibrium with respect to the minerals present, so that continued precipitation or leaching is taking place, there must be a flow of porewater through the sandstone[1]. The subsurface circulation of porewater is, therefore, essential to understand sandstone diagenesis (Figs. 3 and 4).

Porewater in sedimentary basins have four principally different origins: (1) meteoric water flowing into the basin, driven by the head of an elevated ground water table; (2) porewater forced upwards by the compaction of the sediments; (3) water released by dehydration of minerals; and (4) water released during metamorphism beneath the sedimentary basin (Fig. 4). The flow of compactional water is limited by the amount of water contained in the underlying sedimentary sequence in the basin. The total average upwards flux will be in the order of $10^4 - 10^5$ cm^3 cm^{-2} of pore water for a bed of sandstone from the time of deposition to burial to about 3 km (Fig. 5). There is, however, no theoretical limit to the magnitude of meteoric porewater flux through sediments, although time and flow rates put some constraints on what may seem possible (Blatt, 1979).

Convection currents (Fig. 6) may be driven by the temperature gradient in sedimentary basins (Cassan et al., 1981; Wood and Hewett, 1982, 1984). However, they probably cannot flow across low-permeability barriers such as thin shales or clay laminae. Large-scale convection currents, therefore, require very massive sandstones without barriers to vertical porewater flow. The permeability must also be relatively high (Wood and Hewett, 1982, 1984). Where there are intervals of pressure gradients higher than hydrostatic, the porewater flow must be unidirectional because convection currents cannot flow back against the pressure gradient. Convection currents, are, therefore, probably of importance only within rather permeable sandstones and possibly on sets of intersecting fractures. Many types of sandstone facies, particularly turbidites and fluvial sandstones, have thin interlayered shale beds which are almost impermeable to vertical porewater flow. Shales will dewater by compaction and one must assume that porewater is flowing

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[1] Editorial comment: Possibly, diffusion alone could supply material to sustain the continued precipitation or leaching.

ZONE I. MARINE (CARBONATE) CEMENTATION
DEPENDS ON CIRCULATION OF
MARINE WATERS

MARINE EARLY
CEMENTATION

SEA LEVEL

MARINE

ZONE OF FRESH
METEORIC WATER

ZONE II. LOW pH
KAOLINITIZATION

K^+

ASCENDING
PORE WATER
EXPELLED BY
COMPACTION

FELDSPAR — KAOLINITE + K^+
DEPENDS ON FLUX OF WATER
WITH LOW IONIC STRENGTH
(LOW K^+/H^+)

ZONE III. MOSTLY HIGH PH
PRESSURE SOLUTION AND
PRECIPITATION OF AUTHI-
GENIC OVERGROWTH
DEPENDS ON GEOSTATIC
PRESSURE ≠ PORE PRESSURE

ESSENTIALLY ISOCHEMICAL SYSTEM

ZONE IV. ACID POREWATER PRODUCED
BY:
1) PRODUCTION OF CO_2 FROM KEROGEN
2) RELEASED PROTONS (H^+) BY MINERAL
   TRANSFORMATION: SMECTITE + K^+ ⟶ ILLITE + H^+:
   KAOLINITE + K^+ ⟶ ILLITE + H^+

Fig. 3. Simplified model for porewater circulation, dissolution, and precipitation of cement in a sedimentary basin.
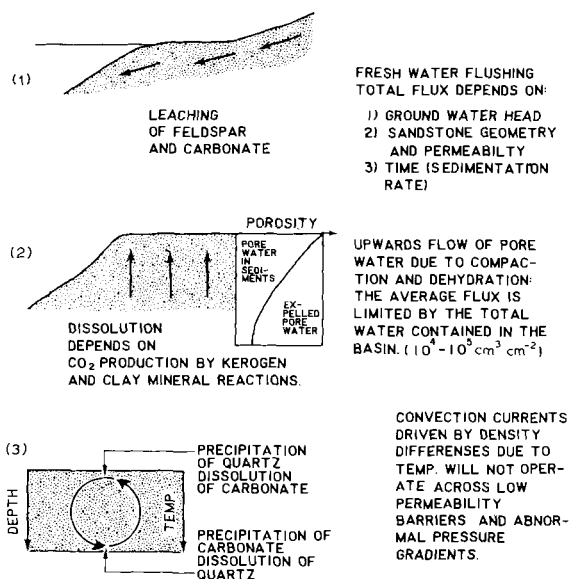
Fig. 4. Principal types of porewater flow in the subsurface controlling diagenetic processes: (1) meteoric (fresh) water flushing with a downward component; (2) compactional porewater flow with an upward component; and (3) convection currents driven by the temperature gradient.

POREWATER FLUX THROUGH
LAYER A BETWEEN I AND 3KM
BURIAL - 2.4 10^4 cm^3 cm^{-2}
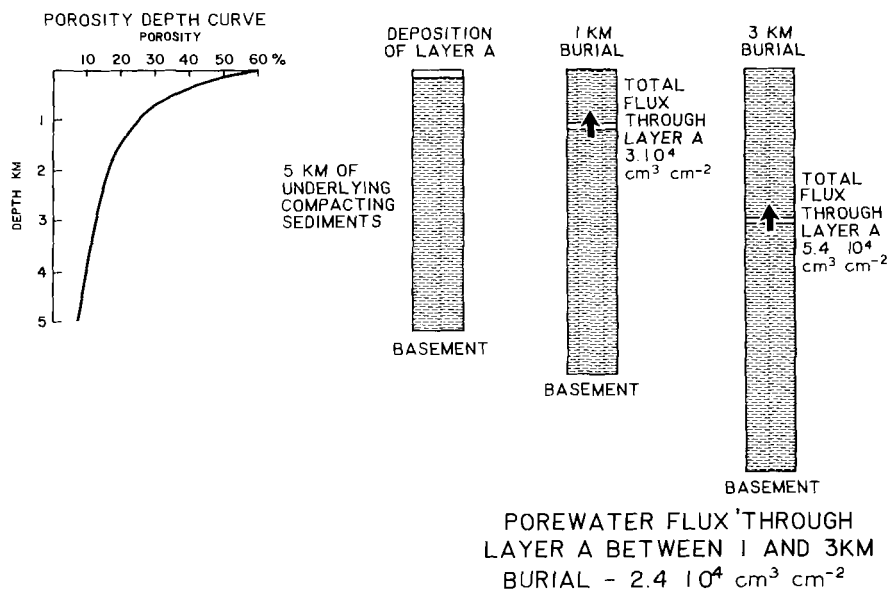
Fig. 5. Average upward porewater flux due to compaction as the layer A sinks through the porewater column. It is here assumed that the underlying sequence is 5 km and the porewater flow resulting from loss of porosity due to burial is integrated. The porosity – depth curve is an average curve for shales.

out of the shale into the more permeable sandstones and that porewater rarely flows from sandstones into shales. This will tend to limit the scale of the convection currents[1].

The use of convection currents as a mechanism for transfer of solids in solution in the subsurface is an attractive idea, because it allows porewater to be used over again in dissolving and precipitating minerals, and thereby overcomes the main problem one is facing in understanding large-scale dissolution of minerals as implied by formation of net secondary porosity. As pointed out by Cassan et al. (1981), however, the convection model predicts that carbonates will dissolve near the top of convection cells, because their solubility is inversely related to temperature, whereas silicate minerals will dissolve in the lower part of the cell. In an anticline structure, one would expect secondary porosity due to leaching of carbonates, whereas in the syncline one would expect leaching of silicates (Fig. 6).

Meteoric water flow

Whereas the circulation of shallow groundwater has been well known and studied by hydrogeologists (Davis and DeWiest,1966), only in recent years has the significance of the extent of deep meteoric water flow become apparent. Fresh water was found to discharge on the seafloor as far as 120 km offshore in Florida (Manheim, 1967). The deep-sea drilling projects have encountered extensive evidence of low-salinity water below the continental shelves (Gieskes, 1981). Also, in the Gulf Coast there is evidence for meteoric water penetration (Land and Prez-bindowski, 1981; Galloway et al. 1982; Galloway, 1984). A combination of onshore and offshore well data enabled Manheim and Paull (1981) to draw a
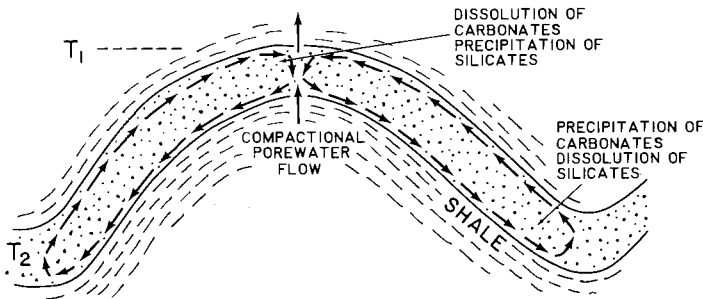
Fig. 6. Theoretical model for convection currents in an anticlinal structure (folded sandstone). Inasmuch as the solubility of carbonates decreases with increasing temperature, secondary porosity due to leaching of carbonates should be expected to occur near the top of the convection cells. Dissolution of feldspar, however, should be expected to occur near the bottom of the convection cells.

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[1] Editorial comment: Much more research is required on convection currents (when, where and how they are established) within individual sedimentary units as well as in thicker sequences. What initiates, controls, and sustains convection cells?

salinity – stratigraphy transect from onshore Georgia to the Blake Plateau. The salinity measurements are based on electric logs from oil wells, drill-stem tests, and porewater squeezed out of sediments. This profile (Fig. 7) shows that practically fresh porewater (salinity < 1‰) extends as far as the shelf break, 100 km offshore and down to several hundred meters. This implies that sediments deposited in shallow-marine environments may undergo diagenesis in meteoric *fresh* porewater from burial depths of a few tens of meters to several hundred meters. This is very important in formulating diagenetic models, because marine shelf sediments may undergo a long period of fresh-water diagenesis.

The total flux of meteoric water through sandstones depends on the head defined by the elevation of the groundwater table and the permeability and the large-scale "connectedness" of the sandstone bodies. Fluvial and proximal facies near the foot
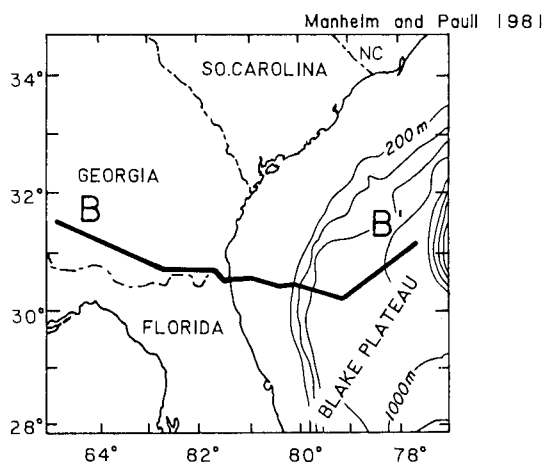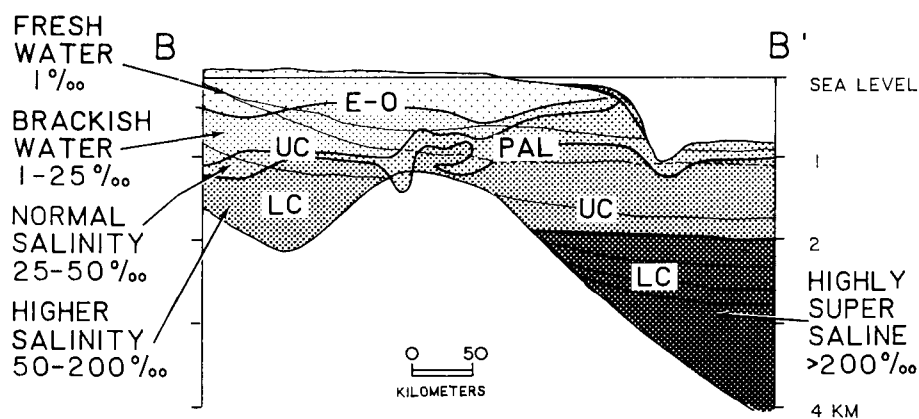
Fig. 7. Salinity of porewater in the subsurface in a transect through onshore Georgia to the Blake Plateau (eastern USA). Fresh water is extending out underneath the continental shelf. The deeper part of the section is dominated by dissolution of Mesozoic evaporites producing supersaline porewaters. (Redrawn from Manheim and Paull, 1981.)

of uplifted highs will normally receive the highest flux. Meteoric water will initially be undersaturated with respect to minerals like feldspar and carbonates. By reacting with such minerals during early meteoric water diagenesis, the porewater will approach equilibrium and gradually lose its capacity to dissolve minerals and create secondary porosity. The paleohydrological regimes in a sedimentary basin (Galloway, 1984) must, therefore, be reconstructed and the distribution of secondary porosity produced by meteoric water leaching can be predicted on that basis.

Hypersaline porewater

At about $1 - 1.5$ km burial depth in the Georgia – Blake Plateau section, hypersaline porewaters ($100 - 200‰$) are encountered (Manheim and Paull, 1981). This high-salinity porewater is derived from Mesozoic evaporites and is transported upwards by a combination of compactional porewater flow and molecular diffusion. The hypersaline water mixes with meteoric water, leaving a very narrow depth interval of intermediate salinities and, probably very little porewater having normal seawater composition. The sediments therefore pass rather quickly from a freshwater into a hypersaline diagenetic environment.

In the Gulf Coast (USA), the sedimentary sequence is also underlain and intruded by evaporites which influence the porewater composition in the overlying sediments (Land and Prezbindowski, 1981). Also, in the offshore area of West Africa and the Atlantic margin of South America, there are extensive evaporites in the basal (Jurassic – Cretaceous) part of the sequence (Brown and Fisher, 1977). Passive continental margin sequences may have very different diagenetic histories depending on whether they are underlain by evaporites or not, which in turn is related to the paleolatitude of the sediments during Mesozoic rifting.

CLOSED SYSTEM (ISOCHEMICAL) DIAGENESIS

X_1 DISSOLUTION OF UN-STABLE MINERALS

X_2 PRECIPITATION OF AU-THIGENIC CLAY MINERALS

X_3 PRESSURE SOLUTION

X_4 OVERGROWTH

$$X_1 \times X_3 = X_2 \times X_4$$
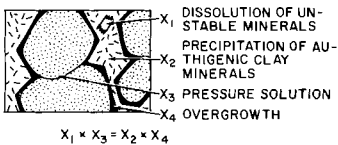
CONTROLLING FACTORS

1) INITIAL CLASTIC COMPOSITION
2) PORE PRESSURE

OPEN SYSTEM (ALLOCHEMICAL) DIAGENESIS

Y_2 PPM IN SOLUTION IN PORE WATER

PORE WATER FLUX Z cm^3 cm^2

Y_1 PPM IN SOLUTION IN PORE WATER

CEMENTATION CAPACITY $(Y_1 - Y_2) Z$
LEACHING CAPACITY $(Y_2 - Y_1) Z$
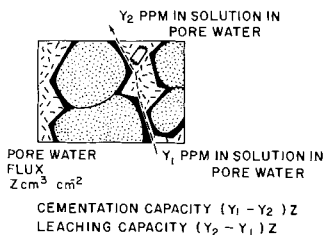
Fig. 8. Diagenetic reactions in relatively stationary porewater (closed systems) and in areas with relatively high porewater flux (open systems).

REDUCTION IN POROSITY DUE TO PRECIPITATION OF CEMENT

Precipitation of cement requires (1) a flow of porewater from an area of higher solubility with respect to the cementing mineral, or (2) transportation of ions by diffusion in stationary porewater due to concentration gradients (Fig. 8), or (3) dissolution of the locally stable minerals. Diffusion coefficients in porous sediments are typically of the order of 10^{-6} cm^2 s^{-1} (Berner, 1980) and may be as low as 7×10^{-8} cm^2 s^{-1} in well-cemented sandstones (Manheim, 1970). As shown by Berner (1980), diffusion is most important in short-distance transport ($<$ 100 m) in surface sediments, whereas flow overshadows diffusion for longer transport distances. With increasing depth of burial, flow rate due to compaction is reduced to very low values. As the average pore size decreases, the specific surface area increases and the percentage of water influenced by mineral surfaces (and, therefore, of lower mobility) increases. Diagenetic mineral growths increase specific surface area and thus may also contribute to the reduction of the diffusion rate. In general, the concentration gradient which is the driving force for diffusion must be assumed to be relatively small over longer distances. Porewater flow is, therefore, responsible for most of the mass transfer of ions in sedimentary basins over distances of more than a few hundred meters (see also Kastner and Siever, 1979, pp. 473 – 474). Diffusion, however, is important in the short-distance transport of ions from mineral surfaces to the surrounding grains, i.e., during pressure solution. It is also important around evaporites where we have high concentration gradients.

Should sandstones be regarded as chemically open systems during burial diagenesis? In other words, are the cements in sandstones derived from within or from outside these sandstones? Immediately after deposition, a sand may be subjected to through-flow or percolation of porewater at a relatively high rate and may therefore be subjected to early cementation or leaching, depending upon whether the porewater is supersaturated or undersaturated with respect to the most common silicate or carbonate minerals present (Fig. 8). In this way, sandstones deposited in shallow-marine environments may be cemented by early aragonite or high-Mg-calcite, and by calcite in the fresh-water vadose zone in arid regions (Fig. 9). The presence of volcanic glass or biogenic amorphous silica in sandstones will raise the silica concentration in the porewater and may cause precipitation of early opal CT or quartz cement. Sandstones serving as aquifers, i.e., for meteoric water, represent
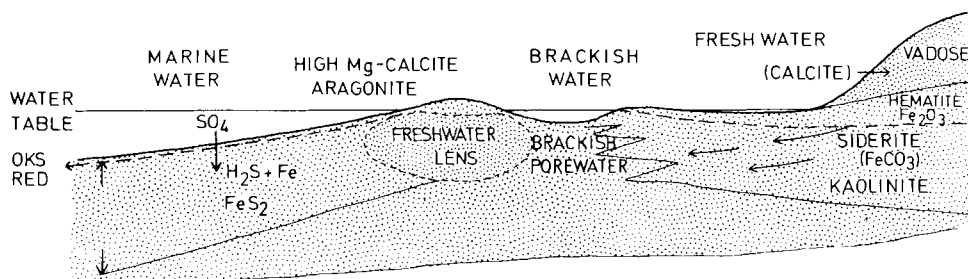
Fig. 9. Distribution of cements in different early diagenetic environments.

open systems where feldspar and carbonates may be subject to leaching. Although meteoric water may be undersaturated with respect to many of the minerals in the sandstone, it is, as pointed out by Blatt (1979), usually supersaturated with respect to quartz and precipitate early quartz cement. Generally, the silica content of meteoric water is only $10-20$ ppm (Payne, 1968), averaging 13 ppm (Blatt, 1979). Thus, only about 10 mg of SiO_2 can precipitate from every liter of porewater. Calculations by Blatt (1979) suggest that during typical meteoric groundwater flow rates of 20 m yr^{-1}, it may take about 10^8 years to precipitate only 2% silicate cement in a 6.4 km-long sandstone body, assuming a silica supersaturation of 26.5 ppm (total silica concentration of 37.5 ppm).

Kaolinitization of feldspar produces silica corresponding to 40% of the altered feldspar, and this silica may precipitate as quartz cement. Mica may also be altered to kaolinite, and biotite will release iron to precipitate siderite or ankerite (Fig. 10). Early quartz cementation of sandstones will also be favored by the presence of volcanic rocks, hydrothermal water, and large through-flows of meteoric water with high silica content. Meteoric water flow may extend several hundred meters, even $1-2$ km or more into the subsurface below sealevel, depending upon the groundwater head. Below this zone of meteoric flow, the flow of porewater principally oc-
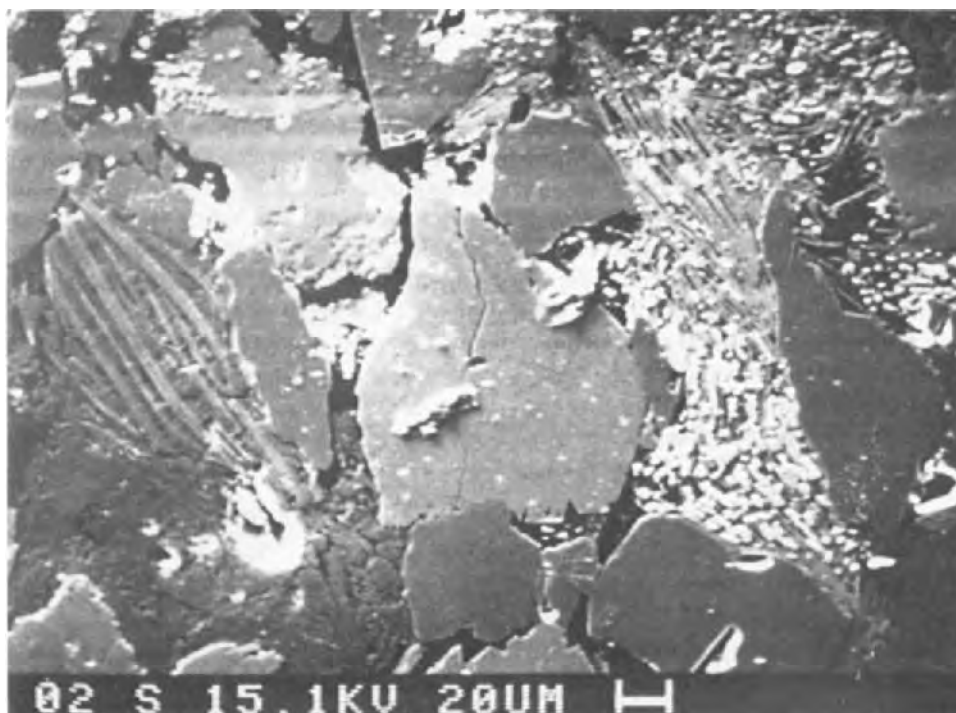
Fig. 10. Secondary electron picture from backscatter on microprobe. Note the distribution of kaolinite, siderite, and calcite between the sheets of mica. Brent Sandstone (Jurassic), Statfjord field, Norway.

curs in the upward direction, although the actual flow path may be controlled by near-horizontal porous beds and by non-sealing fault planes. The total average flux due to compaction is on the order of 3×10^4 cm^3 cm^{-2} through a sandstone during burial to 1 km (Fig. 5). This volume of porewater is only capable of precipitating less than 3 g ($\approx$ 1 cm^3) of silica cement assuming solubilities less than 100 ppm. In the case of a 100 m-thick sandstone (10^4 cm^3 of sandstone per cm^2), this 1 cm^3 of cement corresponds to about 0.01% porosity reduction. Even this figure is too high because only a fraction of the silica buildup in solution (100 ppm) will precipitate in this sandstone. In the case of porewater flow of 10^4 cm^3 cm^{-2} resulting from dewatering of a shale by 10%, and if 10 ppm (out of 100 ppm) precipitates out of solution, only 0.1 g of cement will precipitate in the sandstone. In order to reduce the porosity in the sandstone by 10% due to silica cementation, $10^3 \times 10^5 = 10^8$ cm^3 cm^{-2} throughflow is required (Bjørlykke, 1979). Mathematical calculations by Berner (1980, p. 124) have also shown that very large volumes of porewater are needed to cement sands from external sources. In the case of carbonate cementation, Berner showed that at least 300,000 pore volumes of water are needed to fill one volume of porespace completely. Other authors have arrived at similar figures (Bathurst, 1975). On the basis of these calculations, it is very difficult to envisage that thicker sandstones (> 10 m) can be cemented mainly from outside sources. Even if very large volumes of basinal mudstone (shale) are drained and fluids flow through volumetrically smaller sandstone, it is difficult to obtain sufficient cement. Assuming that mudstones are dewatered by 10% and that 20 ppm of the silica held in solution precipitates flowing through sandstones, then the volumetric ratio of mudstones to sandstones must be 10^5 in order for the porosity of the sandstone to be reduced by 10%. Even in very mud-rich basins, this figure is too high by a factor of $10^3 - 10^4$. This calculation suggests that shales and mudstones cannot be important sources for silica cement in thicker sandstones. Microscopic examination of thin-sections of well-cemented sandstones often suggest that a large percentage of the cement is derived from outside the sandstone. Particularly, cathodoluminescence microscopy often indicates that the amount of cement present cannot be explained as being derived from pressure solution alone.

It is, however, easier to quantify the amount of cement precipitated than the amount that has been dissolved. Earlier overgrowth on second-generation quartz grains, however, may sometimes confuse the cathodoluminescence picture. Pressure solution is often concentrated in certain horizons where regular stylolites may develop. This makes quantitative estimation of the volume of pressure solution and cementation very difficult. Alternative internal sources of quartz cement are: (1) biogenic silica (diatoms, radiolaria, etc.); (2) silica released by kaolinitization of feldspar; and (3) dissolution of silt- and clay-size quartz which is more soluble than the quartz having coarser grains (Füchtbauer, 1978).

Quantitatively, quartz and carbonates are the most important types of cements in sandstones. The introduction of such cements from sources outside the sandstone not only requires large volumes of water, but also a physicochemical environment necessary for significant part of the solids held in solution to precipitate.

Feldspar may also occur as authigenic cement in sandstones, usually as authigenic rims on clastic feldspars (Fig. 11). The authigenic phases can easily be distinguished

optically from the clastic grain under the microscope and also chemically as low-temperature feldspars (Kastner and Siever, 1979). Potash feldspars have authigenic phases which are pure potash feldspars (adularia) with very low Na content (0.1% Na$_2$O; Bjørlykke et al., 1979). In sediments containing plagioclases, feldspar may break down to form pure albite; this is described as albitization by Boles (1982).

Feldspar is relatively stable in normal seawater and evaporitic water is often supersaturated with respect to feldspar; thus authigenic feldspar may form early cement. Feldspars may also be subjected to pressure solution in the same way as quartz and the overgrowth will then consist of a characteristic low-temperature phase, which usually can readily be distinguished under optical microscope and can be shown by microprobe studies to have a different chemical composition than the clastic grain.

Authigenic feldspar rarely constitutes more than 1 − 2% of the total rock volume. The overgrowth often develops as a rim of sawtooth-shaped crystals; however, smooth crystal faces may also be present on a larger overgrowth (Fig. 11). In the Gulf Coast, i.e., the Frio Formation, K-feldspar is selectively leached and albite is a more stable phase (Land, 1984). In the Jurassic reservoir sandstone of the North Sea, however, plagioclase and albite are usually selectively leached and K-feldspar appears to be more stable than Na-feldspar at shallow burial (Bjørlykke, 1984).
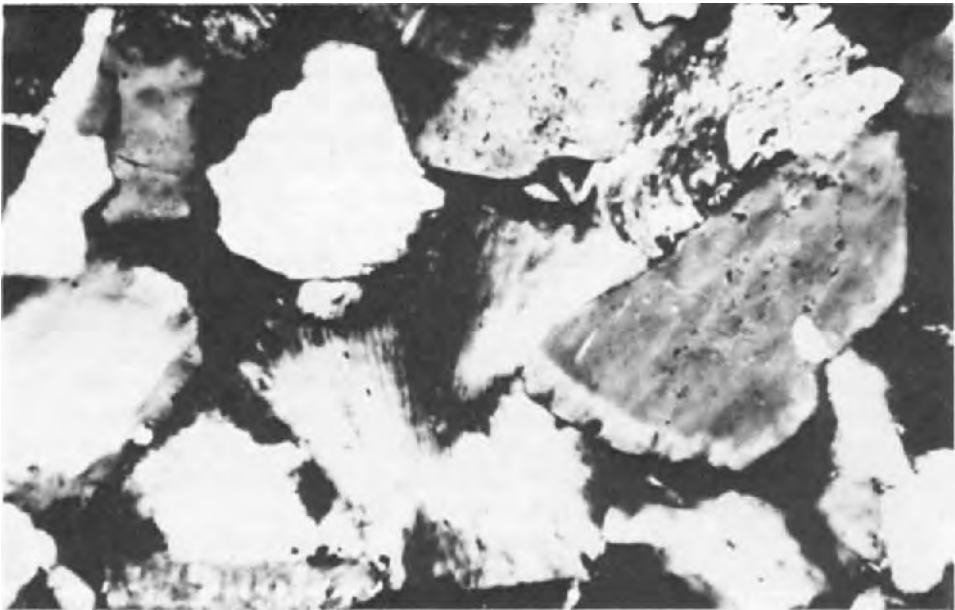
Fig. 11. Authigenic feldspar cement on clastic feldspar. Brent Sandstone, Statfjord field. The splaying mica is partly altered to kaolinite (in the centre of the picture); picture section = 1 mm.

FORMATION OF NEW POROSITY DURING DIAGENESIS (SECONDARY POROSITY)

In recent years, geologists engaged in subsurface sandstone petrology have become increasingly aware that a significant part of the porosity observed in thin-section is formed after deposition. This porosity, therefore, is of secondary nature (Parker, 1974; McBride, 1977; Schmidt and McDonald, 1979a, b; Loucks et al., 1977, 1980; Lindquist, 1977; Stanton, 1977; Pittman, 1979a, b; Hayes, 1979; Loucks et al., 1980). Most commonly, secondary porosity is observed as voids after leaching of clastic feldspar or carbonate cement, evidenced by dissolution surfaces and oversized pores (Schmidt and McDonald, 1979a).

There are several different causes for development of secondary porosity: (1) dissolution of grains, fossils, etc.; (2) dissolution of cement and matrix; (3) pore volume decrease due to dehydration of minerals (i.e., transformation of kaolinite or smectite to illite); and (4) formation of fractures.

Even when there is unequivocal evidence that secondary porosity has formed, it is often very difficult to quantify the percentage of secondary porosity in relation to the primary porosity. Estimation of the volume of grain dissolution requires reconstruction of the original outline of the grain, which is usually very difficult to do accurately. It is even more difficult to estimate partial leaching of cement. The presence of patches of carbonate cement in a sandstone and evidence of corrosion of silicate grains may indicate dissolution of a fully cemented sandstone. It is, however, difficult to estimate the amount of initial carbonate cement and how much was actually dissolved. Fully cemented sandstones are not very permeable to porewater which can dissolve carbonate cement and, usually, sandstones with high primary porosity exhibit most evidence of leaching. Even relatively small patches of carbonate cement may buffer the porewater with respect to carbonate, and may cause corrosion of silicate grains.

According to Schmidt and McDonald (1979a, b), the main mechanism causing leaching is the release of CO_2 produced as a result of maturation of kerogen. The amount of CO_2 produced from kerogen during maturation depends on the type of kerogen. Inasmuch as there is little oxygen available in the sediments during deep burial, the amount of CO_2 that a specific quantity of kerogen can yield is limited by the amount of oxygen contained in the organic molecules of the kerogen. Humic kerogen, which has a higher O/C ratio, therefore, will produce significantly more CO_2 than sapropelic kerogen (Hunt, 1979). Analyses published by Tissot and Welte (1978, p. 164) show that in the Paris Basin only 0.5% of the carbon atoms were released as CO_2 between 700 and 2500 m of burial. Humic kerogen, however, may produce as much as 20 cm^3 CO_2 g^{-1} kerogen or 44 mg CO_2 g^{-1} kerogen (Tissot and Welte, 1978, p. 219), whereas the transformation of lignite to anthracite at 250°C may produce as much as 75 cm^3 CO_2 g^{-1} or 140 mg CO_2 g^{-1} (Hunt, 1979). Thus, one can assume that the production of CO_2 varies between 0.5 and 15% of the kerogen by weight. Inasmuch as each mole of CO_2 can dissolve one mole of calcite, the leaching capacities of maturing kerogen can be calculated. For example, a 1 km-thick shale with an average kerogen content of 1% may produce enough CO_2 to dissolve carbonate cement in a 100 m-thick sandstone, which is sufficient to increase the porosity by 0.1 – 3%. It should also be taken into account that part

of the total CO_2 will be released very early and some later after oil migration. It is probable, however, that a very significant part of the CO_2 released by the kerogen will be neutralized in the source rock. Carbonate present in the shale (source rock) may be subject to dissolution as CO_2 is formed from finely dispersed kerogen. In the Gulf Coast (USA) the carbonates almost disappear between 3 and 4 km of burial (Hower et al., 1976). The presence of carbonate in a mature source rock (shale) may suggest that it was not an effective producer of CO_2 and, thus unable to leach carbonate cement in an overlying sandstone. Feldspar and certain clay minerals may also react with acidic porewater and neutralize some of the CO_2 released. Only a fraction of the CO_2 produced is, therefore, capable of leaching sandstones.

Vertical porewater flow was assumed in the above calculations. If large volumes of CO_2 from basinal shale with humic kerogen pass through overlying sandstones, a much larger leaching capacity may be obtained than by the average vertical porewater flow. The total amount of CO_2 generated in the shale, however, will be insufficient to cause large-scale leaching. Calculations based on data by Galloway (1982) from the Frio Formation in Texas suggest that the CO_2 generated from the mature shales can only account for 1% of the observed porosity (Table 1). Calculations by Lundegard et al. (1984) gave very similar results.

TABLE 1

Calculated examples of CO_2 generation from kerogen and its leaching capacity assuming upwards compactional porewater flow from the Frio Formation of the Texas Gulf Coast Basin (based on data from Galloway et al., 1982)

Sand volume:	1.15×10^{13} m^3
Mudstone volume:	4.2×10^{13} m^3
Thermally mature mudstone:	3.7×10^{13} m^3
Total organic carbon:	0.3% (humic kerogen)
Total kerogen:	1.1×10^{11} m^3 = 2.210^{14} kg
Total gas (methane):	2.5×10^{11} m^3
Sand porosity (18%):	2.1×10^{12} m^3

Approach 1
Assume that the CO_2 generated is 50% of the methane volume – 1.25×10^{11} m^3 CO_2 gas. This equals to 5.4×10^{12} moles (see Hunt, 1979, p. 16). If all the CO_2 reacts with carbonates (5.4×10^{14} g), 1.9×10^{14} cm^3 of porespace is created, which is less than 0.01% of the sand porosity (2.1×10^{12} m^3).

Approach 2
Assume a CO_2 yield of 50 l of CO_2 kg^{-1} (50 cm^3 g^{-1}) of gas-prone kerogen (humic kerogen) during heating to 150°C (Tissot and Welte, 1978, p. 219); 2.2×10^{14} kg of kerogen will produce 1.1×10^{16} l of CO_2 or 4.8×10^{14} moles l^{-1}. This amount of CO_2 may dissolve 4.8×10^{16} g of $CaCO_3$ or 1.8×10^{10} m^3. This is less than 1% of the observed porosity (2.1×10^{12} m^3).

During maturation, the shales may dewater by $5 - 10\%$ and expel $1.8 - 3.7 \times 10^{12}$ m^3 H_2O. This volume of water is sufficient to dissolve the total amount CO_2 produced from kerogen (2.6×10^3 m^3 CO_2), as each m^3 of water dissolves 30 m^3 of CO_2 at a pressure of 300 atm and a temperature of 100°C (Hunt, 1979).

Calcic plagioclase is rather unstable and may precipitate as albite or if the Na^+/H^+ ratio is low as kaolinite. This process, which has been referred to as albitization, has been reviewed by Boles (1982). Reactions in the Frio sandstones of the Gulf Coast in USA may be summarized as follows:

$$2(Na,Ca)Al(Si,Al)Si_2O_8 + Na^+ + H_4SiO_4 \rightarrow 2NaAlSi_3O_8 + Al^{3+}$$

$$\text{andesine} \qquad\qquad\qquad \text{albite}$$

$$+ Ca^{2+} + 4(OH^-) \tag{1}$$
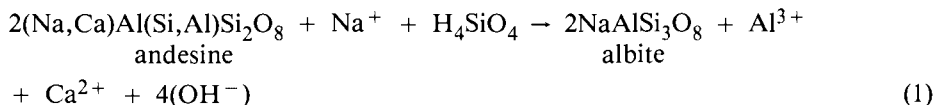
The excess of aluminium released will probably form some other aluminous minerals, e.g., kaolinite and illite, depending upon the K^+/H^+ ratio in the porewater. The Ca^{2+} cation may combine with CO_2 to form calcite: $Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+$. If the aluminium content in the sandstone remains constant during this reaction, one would expect no increase in porosity, because the volume of albite formed will be approximately the same as the volume of plagioclase dissolved, and the volume of kaolinite or illite forming from the released aluminium will exceed the volume of dissolved silica. In addition, carbonate cement may also form. Complete albitization by itself, therefore, is unlikely to produce net secondary porosity. Porespace resulting from leaching of plagioclase may be compensated for by precipitation of albite in primary porespace and also by aluminous minerals, such as kaolinite and illite, and by carbonates in other parts of the same sandstone. At low pH of the porewater (pH < 4), however, aluminium may be more soluble than at normal pH. The porewater, however, will be buffered by any carbonate present and also by feldspar and mica; therefore, it is difficult to assume such a low pH.

In neutral to moderately acid solution, aluminium has a very low solubility of 0.1 ppm (Garrels and MacKenzie, 1971). Surdam et al. (1984), however, suggested that Al is much more soluble and mobile because it may form complexes with carboxylic acids released from kerogen. High Al and Si concentrations, however, so far have not been reported in formation waters. The complexing of Al and Si with carboxylic acid, therefore, may not be stable with time. It seems that Al and Si are in equilibrium with the silicate phases like quartz.

It is difficult to estimate the quantitative importance of secondary porosity. When there is evidence of leaching of carbonate cement, one may conclude that new porosity has been created, but it is often not possible to determine how much cement has been leached. It is difficult to determine whether initially the sandstone was totally or only partially cemented with carbonate.

According to Loucks et al. (1977, 1984), the formation of iron carbonate and kaolinite in Gulf Coast sandstones occurs at a greater burial depth (3 – 5 km) and postdates the leaching. This implies very large mass transfer at great burial depth. They suggested that (1) a significant percentage of the sandstone (10 – 30%) must be removed in solution to create secondary porosity, and (2) new cement (carbonate and kaolinite) must be introduced. On assuming an upward flow of porewater, kaolinite could not have formed from the dissolution of feldspar creating secondary porosity. When feldspar is leached, both aluminium and silica must be efficiently removed from the sandstone; later they are reintroduced, presumably from greater depth, to precipitate kaolinite. Unless Al is considerably more mobile than earlier

assumed, as suggested by Surdam et al. (1984), this interpretation is very difficult to reconcile with theoretical considerations. At a depth of $3-5$ km, the upward flow of compactional porewater is very slow and is on the order of $10^3 - 10^4$ cm^3 cm^{-2} km^{-1} of burial depth, which is quite insufficient to transport in solution significant quantities of silicates and carbonates, having low solubility. The presence of over-pressure (Loucks et al., 1977) in these structures also suggests that the porewater flow out of these sandstones is rather slow.

The origin of late diagenetic kaolinite is poorly understood. In the zone of meteoric water flushing there is a constant supply of porewater with low Na$^+$/H$^+$ and K$^+$/H$^+$ ratios. Kaolinite then remains the stable phase when the H$_4$SiO$_4$-concentration is in near-equilibrium with quartz (Fig. 12). At deeper burial upward-moving compactional porewater is likely to be in equilibrium with feldspar and mica. If the porewater is capable of dissolving feldspar, the Na$^+$/H$^+$ and K$^+$/H$^+$ ratios will build up in the porewater until the solution is no longer in the kaolinite stability field. A sink for Na$^+$ or K$^+$ + is, therefore, required. Smectite transform-ing into illite will require K$^+$ and provide such a sink. This model then requires a coprecipitation of kaolinite and illite.

In the case of the Brent Sandstone in the North Sea, interpreted by Schmidt and McDonald (1979a) to have mostly secondary porosity, I consider that there is insuf-ficient evidence to suggest that this sandstone had pervasive early carbonate cement which was later dissolved (Bjørlykke and Brendsdal, 1985). It can be shown in the Brent Sandstone that kaolinite formation predates quartz overgrowth (Fig. 13). Leached feldspars commonly have a rim of authigenic feldspar, showing that leaching of feldspar and kaolinite formation must have occurred during an early stage, before precipitation of feldspar cement, probably related to meteoric-water flushing (Bjørlykke et al., 1979; and Fig. 14). Formation of diagenetic ankerite and siderite took place later (Blanche and Whitaker, 1979), indicating the presence of alkaline porewaters during late diagenesis. The presence of unaltered volcanic glass
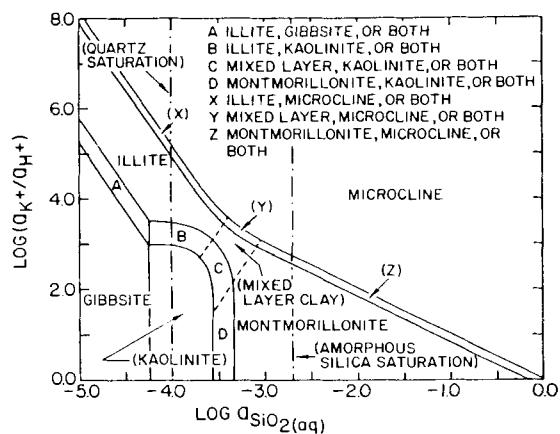
Fig. 12. Stability diagram for minerals in aqueous solution at a temperature of 25°C and pressure of 1 bar. (After Aagaard, 1979, and Aagaard and Helgesson, 1982.)

of Middle Jurassic age (Malm et al., 1979) also suggests that the sandstone was not subjected to strong leaching. The porosity of the Brent Sandstone can, for the most part, be explained as primary, preserved from destruction by the presence of high pore pressure and closed-system diagenesis (Bjørlykke et al., 1979). Secondary porosity can form whenever porewater, undersaturated with respect to sandstone grains or cement, is flowing through the sandstone. The most obvious example of this is the near-surface dissolution by meteoric water. In subsurface aquifers, leaching of carbonate-cemented sandstones creates secondary porosity. Leaching of

Fig. 13. Precipitation of quartz overgrowth enclosing early and possibly also partly contemporaneous kaolinite. Brent Formation, Statfjord field.
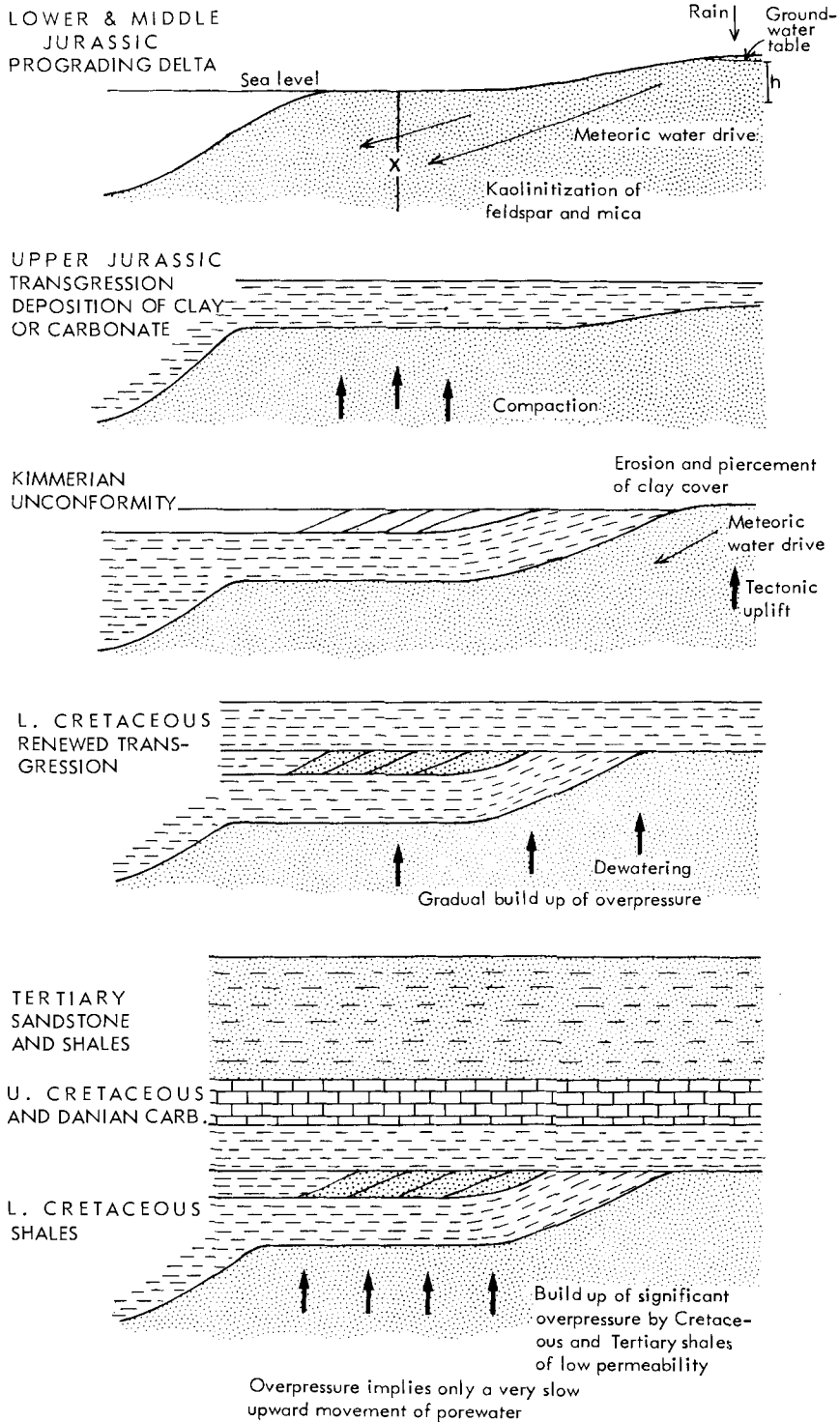
Fig. 14. Interpretation of the diagenetic history of the Jurassic sandstones of the Statfjord field. The upper Jurassic and lower Cretaceous shales draped over the underlying sandstones, and strongly reduced vertical communication causing overpressures in the rapidly subsiding Viking Graben. (From Bjørlykke, 1981.)

feldspar, however, may either create oversized pores or result in replacement by kaolinite. Because of the low solubility of aluminium, the reaction:

$$2 \text{ KAlSi}_3\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4 \text{ SiO}_2 + 2\text{K}^+ \qquad (2)$$
$$\text{feldspar} \qquad\qquad\qquad \text{kaolinite} \qquad \text{quartz}$$
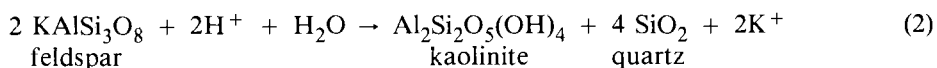
will not create any net increase in porosity for the sandstone as a whole (Bjørlykke, 1982). The most pronounced leaching occurs in areas with large porewater flux which serves as an efficient removal medium for K^+. If the reaction products are not removed from the sandstone, leached feldspar will form 60% kaolinite and 40% quartz. The leaching capacity of meteoric water will be highest in the most proximal facies. Rainwater will, in most cases, first percolate through sediments of fluvial and shallow-marine facies and then penetrate more distally marine facies. Tectonic uplift may subject sediments to a second phase of meteoric-water flushing.

Estimates of the porosity formed by secondary processes are unreliable. It is difficult to measure the enlargement of pores resulting from leaching and, in particular, determine the net gain in porosity when possible reprecipitated minerals are considered. To obtain a net increase in porosity by the late-stage leaching, very large volumes of water must flow through the sandstones. This requires concentrated flow from basinal muds. Theoretically, the highest potential for the formation of secondary porosity exists where there is a maximum water flow. This cannot be expected in overpressured areas or in the presence of oil and gas traps. Relationship between porosity and burial depth, therefore, should be evaluated taking into consideration the overpressured zones. The net (grain-to-grain) stress[1] is often reduced with increasing depth on passing into an overpressured zone. Abnormal porosity – depth relationships may, therefore, reflect differences in the degree of preservation of primary porosity due to variations in the effective stress, and should not be taken as evidence of secondary porosity. One should also remember that the present porewater pressures may not be representative of the whole burial history. Particularly in areas with active faulting, sediments may be compacted during periods of low pore pressure and then sealed off so that the pore pressure is increased.

ALTERNATIVE SOURCES OF ACID REACTIONS DURING DEEP BURIAL

Weathering and early diagenesis are processes which essentially release cations from silicate minerals into solution. In turn, the weathering products take up protons (H^+) in forming kaolinite, smectite, and mixed-layered minerals which are, therefore, charged with protons in a sense. At greater burial depth and higher temperature, these minerals become less stable and the reverse reactions may occur.

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[1] Editorial comment: The actual cause of compaction is increase in the effective (grain-to-grain) pressure, p_e, which is equal to the total overburden pressure, p_t, minus the pore pressure, p_p. Thus, reduction in the latter causes compaction.

Kaolinite becomes unstable between 120° and 150°C and may be transformed into illite if potassium is available (Hower et al., 1976):

$$3Al_2Si_2O_5(OH)_4 + 2K^+ \rightarrow 2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \qquad (3)$$
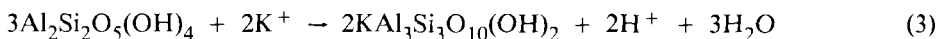
As suggested by Hower et al. (1976), feldspar is the most likely source for potassium. These authors were able to show that the feldspar and kaolinite contents decrease proportionally with depth as illite content increases. If feldspar is transformed to illite, potassium is released:

$$3KAlSi_3O_8 + 2H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+ \qquad (4)$$

On combining Eqns. 3 and 4:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{feldspar}}{KAlSi_3O_8} \rightarrow \underset{\text{illite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{quartz}}{2SiO_2} + H_2O \qquad (5)$$
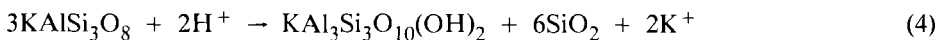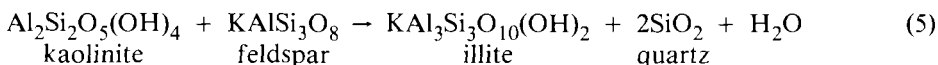
Also, smectite releases H^+ when transformed into illite and chlorite (Boles and Franks, 1979; Hower, 1981):

$$K^+ + \text{smectite} \rightarrow \text{illite} + \text{chlorite} + \text{quartz} + H^+ \qquad (6)$$
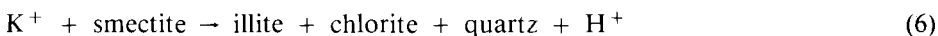
In the latter reaction, potassium may be derived from the transformation of feldspar to illite. In a sandstone, diagenetic kaolinite may also react with feldspar to form illite, thus forming a sandstone with a more clay-rich matrix (Bjørlykke, 1980). These processes release water into solution, generally forming denser minerals, and may facilitate denser packing if excess porewater is able to escape from the sandstone.

Hutcheon et al. (1980) have pointed out that clays may react with carbonate and release carbon dioxide. Reactions such as: (a) kaolinite + 5 dolomite + quartz + $2H_2O \rightarrow$ Mg-chlorite + 5 calcite + $5CO_2$, and (b) 15 dolomite + 2 muscovite + 3 quartz + $11H_2O \rightarrow$ 3 Mg-chlorite + 15 calcite + $2K^+$ + $2OH^+$ + 15 CO_2, may be important at higher temperatures (180° $-$ 250°C). They may be responsible for the inorganic formation of an important part of CO_2 at greater burial depth (5 $-$ 6 km) (Hutcheon et al., 1980).

DIAGENESIS AND PLATE-TECTONIC SETTING

Diagenetic processes in sandstones depend primarily on the mineralogical composition of the clastic grains, geothermal gradients, subsurface pressures, porewater composition, and circulation. Inasmuch as these parameters can to a large extent be related to the plate-tectonic position of the basin (Siever, 1979), sandstone diagenesis is also a function of the latter. Meteoric porewater flow is controlled by climate and drainage area (Fig. 15), because the flow depends on the total volume of meteoric water available.

Epicontinental sea environments are characterized by very low relief, both in the basin and in the surrounding source area because of the stable cratonic basement (Shaw, 1963). In such basins, sedimentation rates are low and sandstones tend to have high mineralogical maturity and be interbedded with shales and carbonates (Bjørlykke, 1974). In these generally very flat-lying sequences there is little potential for horizontal pressure gradients which can cause increased porewater flow. Meteoric water around the basin has low-pressure gradients, but local exposure (unconformity) may produce fresh-water penetration. Also, interbedded pockets of shales will tend to isolate sandstones and produce almost isochemical diagenesis.

Basins along Atlantic-type continental margins normally are dominated by a prograding sequence of sandstones and shales where the sand/shale ratio decreases distally. In fluvial, deltaic and in some cases, marine environments, sediments may be flushed by meteoric water from the groundwater on the continent, causing kaolinitization of feldspar and leaching of carbonate cement. During compactional diagenesis the sandstone often has good updip connection so that water released by compaction may escape, preventing buildup of overpressure. Growth faults, however, often provide an important seal causing high overpressures. Onlapping sequences frequently have an updip pinch out, producing a natural trap for oil (Brown and Fisher, 1977); they are also conducive to buildup of overpressures (Bjørlykke
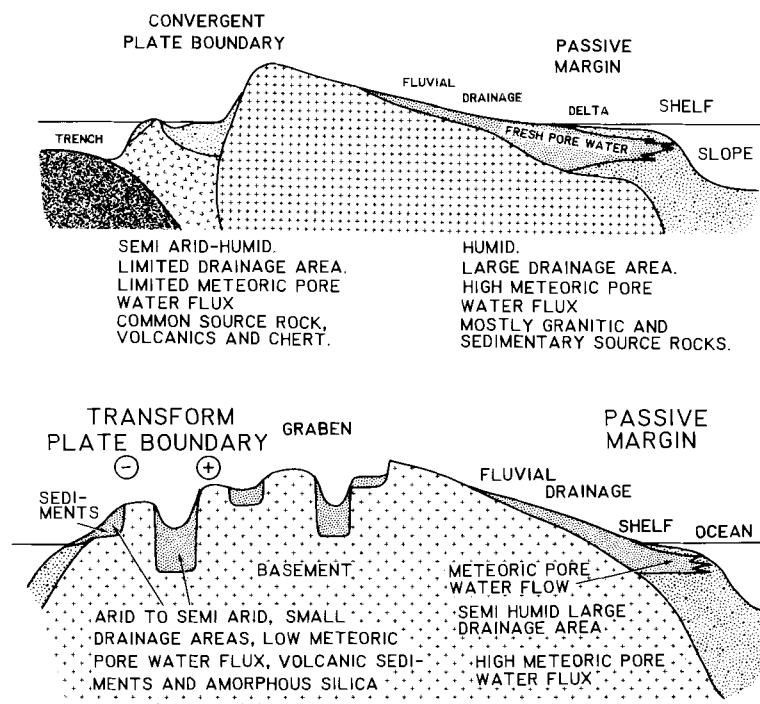
Fig. 15. Diagenetic environments as a function of tectonic position, drainage area, climate, and porewater flow. See discussion in the text.

578

et al., 1979; and Fig. 16). Underlying evaporites strongly influence diagenetic reactions. A large amount of the groundwater is drained towards the Atlantic margins producing a strong meteoric water flow underneath the continental shelves (Fig. 15).

Rifted basins subside due to thinning of the continental crust, whereas high thermal expansion causes an uplift of the shoulders of the rift and the horsts (Kinsman, 1975). Sediment infill, to a large extent, is dominated by erosional products of continental basement rocks deposited as fluvial deposits, fan deltas, and turbidites in the basin. Periods of less-intense rifting cause cooling, which will result in contraction of the continental crust and transgression. Such transgression may deposit a blanket of clay over underlying sands and also cover up horsts, thereby producing
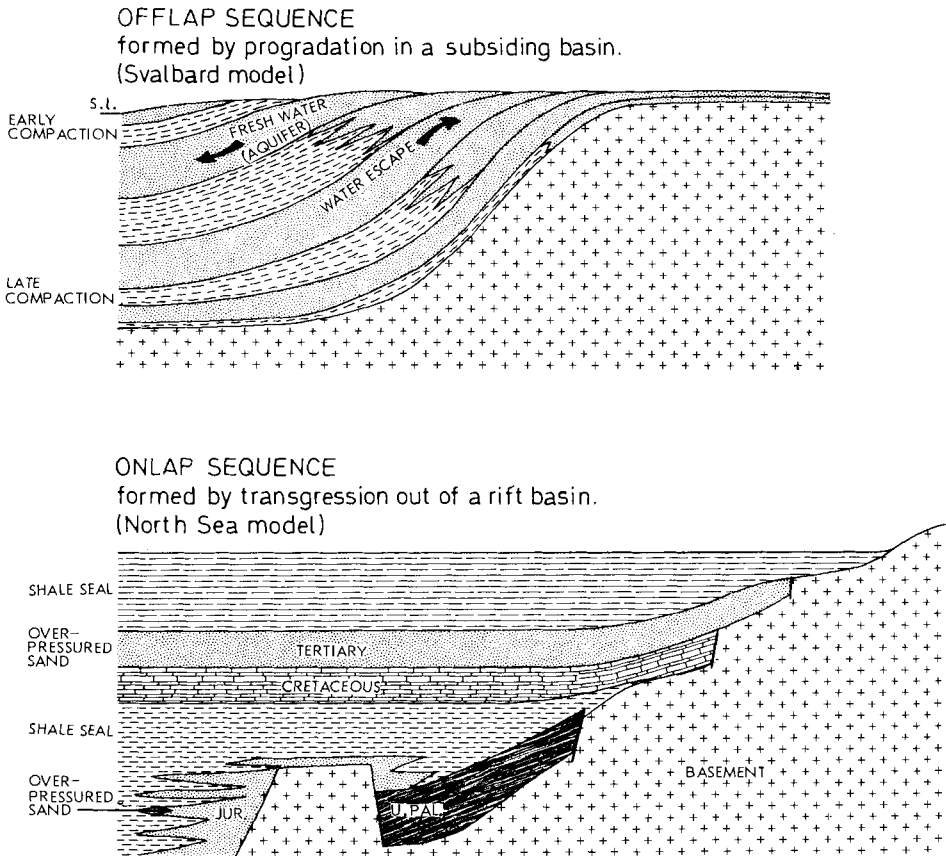
Fig. 16. Comparison between offlapping progradational and onlapping transgressive sedimentary sequences, illustrating their control on porewater flow, pore pressure, and diagenesis. In an offlapping progradational sequence sandstone tends to pinch out basinward and there is good communication of compactional water updip from the slope facies to the shelf or delta top facies, unless there are sealing faults. In an onlapping sequence, shales are often deposited during transgressive periods like a blanket over the underlying sand, strongly reducing vertical communication.

an effective seal for compactional water as is the case in the North Sea (Bjørlykke et al., 1979) (Fig. 15). The high pore pressures encountered in rift basins, like the North Sea (Chiarelli and Duffaud, 1980), reduce compaction. A high degree of preservation of primary porosity, therefore, is implicit in the rift basin model and is one of the most important assets of such basins. Rift basins normally have smaller drainage areas and in arid regions meteoric water fluxes are small (Fig. 15). In rifted granitic basement, rocks are often exposed on tectonically uplifted highs. This may provide a supply of unstable minerals like mica, including biotite, which is a very characteristic and important component in North Sea sandstones.

Basins formed along continental transforms, such as those in California, may form as a result of complex faulting (Crowell, 1974) and subside at a very rapid rate. Because of the absence of long-lived persistent drainage patterns, major deltas producing fluvial facies are less predominant than marine sediments. Sandstones deposited in deep marine environments probably are not flushed by meteoric water and have less authigenic kaolinite than fluvial deposits. Systematic studies of the diagenetic minerals in the Tertiary sandstones in the transverse range show that diagenetic kaolinite is relatively minor and that biogenetic and volcanic silica may favor the growth of zeolites and smectites, which reduce porosity and permeability (Helmold, 1979, 1980).

Basins associated with subduction zones and island arcs are characterized by a high content of unstable grains from volcanic rocks and igneous intrusives. Their low mechanical strength and low chemical stability lead to a more rapid destruction of porosity with burial depth. Thus, the low porosity forms an economic basement, which may occur at shallower depth (1 – 1.5 km) than oil maturation zone. For oil migration to occur before the porosity in the reservoir rocks is reduced too much, the geothermal gradient must be very high (Galloway, 1979). The chemical instability of basaltic and gabbroic debris will favor extensive growth of secondary minerals, such as chlorite, montmorillonite, and zeolite (Surdam and Boles, 1979), which reduce porosity and permeability.

CLASTIC DIAGENESIS AND THE PROPERTIES OF SANDSTONE RESERVOIR

As discussed above, clastic diagenesis is a field of research which is concerned, among others, with the processes that cause changes in the porosity in the sandstones after deposition. Porosity and permeability of rocks do not decrease with depth in a regular way in sedimentary basins. The depth at which a sandstone becomes too tight for oil production varies greatly. It is, therefore, an important part of the exploration strategy to be able to predict the distribution of porosity in sandstones within sedimentary basins. This can only be done successfully when one understands the processes that destroy and create porosity.

The effects of mechanical compaction and pore pressure have been discussed above. This discussion clarified why sandstones in oil fields with a significant overpressure have experienced less mechanical compaction and pressure solution than normally-pressured reservoirs at the same depth. It is important to note here that

the maximum stress that a sandstone has been subjected to is only the geostatic pressure (total overburden pressure) minus the pore pressure.

The mechanical compaction is also a function of the strength of the grain framework in the sandstones. As pointed out by Galloway (1979), high percentage of grains from basalt or other basic rocks, which are both mechanically and chemically unstable, results in a destruction of porosity at shallow depth (1 − 2 km) before associated source rocks have become mature.

Early cementation by quartz or by limited amounts of carbonates, initially destroys porosity, but will strengthen the grain framework and reduce the mechanical compaction with increasing overburden.

Pressure-solution of quartz grains is enhanced by the presence of clay or mica, and the dissolution of minerals, mostly quartz, may give rise to an important source of silica cement. Thin clay laminae often develop into microstylolites at a burial depth of 2.5 − 3.5 km.

At a burial depth of 4 − 5 km, fully developed stylolites are common in sandstone reservoirs. Clean sands deposited in a high-energy environment generally have a higher potential for preserving the primary porosity at critical depths (3 − 5 km) than more low-energy facies with frequent clayey laminae.

The timing of the diagenetic processes, which can either reduce or increase porosity, is very important when evaluating potential reservoir rocks. The porosity of the sandstone at the time of oil migration determines the volume available to be filled with oil. Once the pores have become filled with oil, the remaining porewater is no longer an effective carrier of ions in solution. Thus diagenetic processes that may reduce the porosity below the oil − water contact may not affect the sandstone in the oil-saturated interval. Compaction, pressure solution, and other isochemical processes may, however, proceed after a sandstone has become oil saturated. Reservoir properties (porosity and permeability) may, therefore, be better in the oil-saturated sandstone than those below the oil − water contact.

Diagenetic processes do not always change the total porosity, but they do change the pore size distribution and the pore geometry. The formation of secondary porosity by dissolution of feldspar and precipitation of kaolinite in nearby open porespace create (1) some large oversized pores (Schmidt and McDonald, 1979a, b) and (2) very small pores between the authigenic kaolinite or illite crystals. On assuming that aluminium is not very mobile and is being conserved in the sandstone, there is no net gain in the overall porosity. The pore-size distribution and the pore geometry are, however, drastically changed. The small pores between authigenic clay may be too small to be filled with oil; therefore, increasing the water saturation. Authigenic clays may also be carried by the oil or water during production and cause formation damage. The large oversized pores formed by feldspar dissolution may be connected by relatively small pore throats and this may cause low permeability and low oil recovery. This effect may be particularly important in a condensate field where three-phase flow may occur.

ANALYTICAL AND PETROGRAPHIC METHODS USED IN THE STUDY OF DIAGENESIS OF SANDSTONES

Standard optical microscopy is still the most important tool in the studies of sandstones. Impregnation of sandstones with a colored (usually green or blue) resin gives a good visual impression of the porosity, but the smallest pores may not be impregnated. For coarser sandstones point-counting may give a relatively accurate and reproducible representation of the porosity in addition to the mineral concentrations. By dissolving the silicate minerals in hydrofluoric acid (HF) a pore cast of the pore structure is obtained which can also be studied by the use of electron microscopy (SEM).

Cathodoluminescence has become a useful method for studying cement in sandstones. Carbonate cement usually produces good cathodoluminescence, which may make it easier to distinguish between several phases of carbonate precipitations. Quartz cement has a weaker luminescence; however, cathodoluminescence usually enables good distinction between the clastic quartz grains and the overgrowth. It is, however, important to distinguish quartz grains recycled from older sedimentary rocks with earlier quartz cement. Cathodoluminescence is also very useful for distinguishing between different types of feldspar (Nickel, 1978).

The SEM, which became a standard petrographic instrument in the nineteen-seventies, made it possible to study the authigenic clays in sandstones and the detailed crystal morphology of other authigenic phases (Welton, 1984). Energy-dispersive analytical systems attached to the electron microscope have become an important aid in mineral identification and analysis of mineral compositions. They are becoming increasingly sophisticated and accurate. Microprobe analysis will, however, usually give the best mineral analysis. The SEM is also capable of producing good cathodoluminescence pictures and electron backscatter pictures (Pye and Krinsley, 1984).

Image analysis system now offers new methods for quantifying textural relationships in the SEM pictures. Textural studies of sandstones usually aim at establishing a sequence of diagenetic events, such as the dissolution and precipitation of mineral phases. The so-called "cement stratigraphy" represents an interpretation of the relative age of different types of cement. Several diagenetic processes may, however, take place at the same time and petrographic criteria for age relationships may often be ambiguous. Isotopic analysis of the authigenic phases often offer an independent method for determining the age of different types of cement. In the case of carbonate cement in sandstones, oxygen ($^{18}O/^{16}O$) and carbon ($^{13}C/^{12}C$) isotopes have frequently been successfully used to distinguish between early and late cement. But because of the many factors influencing the isotopic composition of carbonate minerals, and the assumptions that have to be made about the initial porewater composition, the isotopic analyses are not always entirely conclusive. Isotopic data, however, are frequently (based on our present knowledge) capable of excluding certain, otherwise possible, interpretations (Irwin, 1980; Milliken et al., 1981; Irwin and Hurst, 1983).

Carbon derived from organic matter may be recognized isotopically as distinctly different (more negative) from carbon in marine carbonates. The oxygen isotopic

composition is a function of temperature, but also of the initial porewater composition. If independent evidence about the temperature is available, the paleosalinity of the porewater can be calculated. Modern analytical techniques of mass spectrometric analysis enable analysis of very small amounts of cement sampled from thin-sections. Isotopic analysis of silicate minerals requires more elaborate sample preparation, but isotopic analysis of quartz cement and kaolinite has produced promising results (Land, 1984).

Age dating by the $^{87}Rb/^{86}Sr$ ratio method may also be very useful for dating the formation of authigenic clays in sandstones.

CONCLUSIONS

Factors favoring the preservation or destruction of primary porosity and the formation of secondary porosity (Table 2 and Fig. 17) can be summarized as follows:

(1) Diagenetic processes in sandstones are mainly a function of the primary composition of the sandstone, porewater flow, effective or grain-to-grain stress, and temperature[1]. These parameters can, to a large extent, be related to the source rock, depositional facies and stratigraphy, and tectonism, which, in turn, are related to the plate-tectonic setting of the basin.

(2) A distinction should be made between diagenetic processes which may proceed in stationary (static) porewater (isochemical diagenesis) and processes that require supply and removal of ions in solution through porewater (dynamic) flow (allochemical diagenesis).

(3) Primary porosity is reduced isochemically by mechanical compaction and pressure solution due to the effective stress. The degree of mechanical compaction is not a function of overburden, but of the effective stress. Consequently, higher pore pressures (lower geostatic pressure/pore pressure ratio) are effective in preserving primary porosity. Pressure solution is enhanced by mica and clay laminae in the fine-grained sandstones.
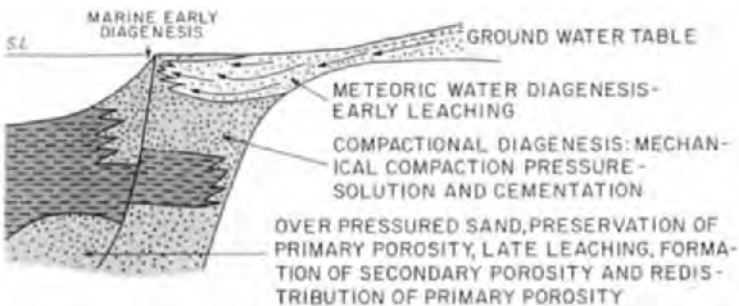
Fig. 17. A summary of diagenetic environments for sandstone. See discussion in text.

[1] Editorial comment: Bacteria also play an important role.

(4) Net cementation of sandstones (i.e., by carbonates or quartz) is a function of total passage of porewater and its degree of supersaturation with respect to the cementing minerals. Very large volumes of porewater flow ($10^4 - 10^5$ pore volumes) are required to precipitate one pore volume (1 cm^3) of cement. Porewater must be flowing from areas of higher solubility to areas of lower solubility due to variations in pH, porewater composition, and/or temperature.

(5) Secondary porosity may be caused by fracturing of the sandstone due to tectonic stresses or overpressure (hydrofracturing) and chemical dissolution. Leaching of minerals and cement may occur when the sandstone is flushed by meteoric water undersaturated with respect to carbonate cement or feldspar grains. At greater burial depth (2 − 4 km), leaching may be caused by carbonic acid formed from CO_2 released by maturing kerogen. Calculations, however, suggest that the CO_2 released may be insufficient to cause quantitatively important leaching. In addition, CO_2 may be neutralized by carbonate in the shales (source rocks). The formation of this type of secondary porosity will be favored by high contents of humic kerogen in the shale, a high shale/sandstone ratio, and good updip drainage from basinal shale. Feldspar may also dissolve when kaolinite is altered to form illite.

TABLE 2

Factors favoring the (1) preservation versus (2) destruction of primary porosity, and (3) formation of secondary porosity

(1) Factors favoring the preservation of porosity	(2) Factors contributing to reduction of porosity	(3) Factors favoring the formation of secondary porosity
High primary grain strength	High percentage of ductile grains, i.e., volcanic and basic igneous rocks	Early flushing of meteoric water causing leaching of feldspar and carbonates
Low content of highly soluble minerals or amorphous silica		
Precipitation of limited early cement, supporting the grain framework	High content of more soluble grains, i.e., volcanic glass, organic silica, and soluble minerals	A high content of humic kerogen in adjacent carbonate-free shale, producing large amounts of CO_2
Formation of early grain-coating cement (pore lining) of chlorite, hindering quartz overgrowth	Low (hydrostatic) pore pressure (good updip communication of porewater), increasing net stress, mechanical compaction, and pressure solution	Transformation of kaolinite, smectite, and mixed-layered minerals to illite, which may also cause the leaching of feldspar.
	Expansion of mica to kaolinite, or mixed-layered minerals	
Overpressure, reducing grain-to-grain stress		A high pore pressure may form secondary porosity by hydraulic fracturing
Early introduction of hydrocarbons, reducing precipitation from porewater		

(6) Porewater flow, which will strongly influence diagenetic reactions, is controlled by sandstone permeability and degree of connection between sand bodies of the sedimentary facies and the stratigraphic and tectonic framework in a sedimentary basin.

(7) Diagenetic processes control not only the porosity and permeability of potential reservoir sandstones, but also the pore-size distribution and the pore geometry. The formation of secondary porosity by leaching of feldspar and precipitation of diagenetic clay (kaolinite or illite) may not change the overall porosity, but will strongly influence the reservoir characteristics of the sandstone.

FUTURE RESEARCH

As emphasized above, a better understanding of diagenetic reactions in sedimentary basins requires more data on the composition of porewater and its capacity to transport materials in solution and the pattern of porewater flow in sedimentary basins. More isotopic analyses, both of the minerals and the porewater are needed to better comprehend diagenetic reactions. For example, the solubility of inorganic ions, in particular Al^{3+}, is critical to the understanding of diagenetic processes in clastic sediments.

There is still a very incomplete understanding of the mechanical properties of sandstones during compaction and tectonic deformation, and more experimental work similar to what has been done in the geotechnical field should be carried out.

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SUBJECT INDEX

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