

Zoning and Genesis of the Darwin Pb-Zn-Ag Skarn Deposit, California: A Reinterpretation Based on New Data

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Abstract

The >1-million-metric-ton Darwin Pb-Zn-Ag-W skarn deposit has been previously described as a group of sulfide replacement bodies zoned away from the Darwin quartz monzonite pluton and formed from magmatic fluids at $\sim 325^{\circ}\text{C}$. Detailed surface mapping and available radiometric data, however, indicate that the Pb-Zn skarn sulfide bodies are appreciably (>20 Ma) younger than the Darwin pluton, and underground mapping and core logging indicate there are several skarn sulfide pipes with strong concentric zoning. One of the pipes is zoned around a deep granite porphyry plug. The pipes exhibit outward zoning in wt percent Pb/Zn and oz/ton Ag/wt percent Pb (both ratios <0.5 core, >1.0 margin). The pipes show mineralogical zoning, with a core defined by higher sphalerite-galena, higher chalcopyrite, darker sphalerite, more abundant pyrite inclusions in sphalerite, and evidence for multiple sulfide depositional events. In contrast, both graphite in marble and pyrrhotite in sulfide ores are zoned around the Darwin pluton, which suggests that pyrrhotite stability is influenced by pre-Pb-Zn skarn (Darwin pluton related?) bleaching of marble beds. Garnet zoning is highly complex, with four generations identified by petrographic and compositional relations; younger garnet types are more abundant in upper and lateral parts of the pipe. Retrograde alteration of garnet is concentrated in the upper and laterally distal parts of the skarn, but garnet in apparent equilibrium with sulfide is present throughout the vertical extent of skarn. Systematic mineral compositional patterns include outward increase in hedenbergite + johannsenite components in clinopyroxene (<2-20 outward), increase in Sb + Bi contents of galena, initial increase followed by decrease in Mn contents of sphalerite (range from <0.2-1% Mn), and an initial increase followed by outward variable increase and decrease in FeS contents of sphalerite (range of <3-20% FeS). Previously published sulfur isotope data are compatible with a decrease in sulfur isotope ratios outward around the pipe core. Published isotopic data combined with temperature estimates from phase homogenization and arsenopyrite-sphalerite geothermometry show a systematic decrease in temperature from the skarn sulfide pipe center (>425°C) to the margin (<300°C).

Comparison of stope maps to isotherm cross sections indicates that the bulk of mined sulfides were from areas surrounding the pipe core, in which temperatures declined from approximately 375° to 300°C (gradient of 1°C/m). Combined mineral composition and assemblage and sulfur isotope systematics indicate that as the ore fluids flowed outward they underwent progressive decrease in oxidation state (~ 1 log unit) and increase in pH (2-3 units); upward-moving fluids underwent initial decrease in oxidation state and increase in pH followed by a reversal to higher oxidation state and lower pH. The process of ore deposition was chemically complex and may have involved remobilization of earlier deposited sulfides. Realistic ore depositional models at Darwin require simultaneous changes in (at least) temperature, pH, and oxidation state.

Introduction

THE DARWIN district, in southeast California (Fig. 1), contains Pb-Zn-Ag as well as Cu- and W-rich veins and skarns (Hall and MacKevett, 1962; Newberry, 1987). Production from the district includes more than 1 million metric tons of Ag-Pb-Zn ore, much of

which was direct-shipping, high-grade material, and 0.1 million tons of W ore. Average grades of sulfide ore mined after 1945 were approximately 6 percent Pb, 6 percent Zn, 0.2 percent Cu, and 6 oz/ton Ag (Hall and MacKevett, 1962). The Darwin mine per se consists of a series of isolated Pb-Zn-Ag $\pm$ W ore-bodies (Defiance, Thompson, Essex, Independence;

Appendix (Cont.)

Area	Mining district	Location	Sample no.	Vein	Type of material	Pb content
Wall-rock samples						
	Limon	86°42' W/12°44' N	10		Strongly altered volcanic breccia, 10 cm from the Panteon vein	
	Limon	86°46' W/12°45' N	18		Strongly altered py-bearing wall rock, 5 cm from the Talavera vein	
Ore samples						
Quartz vein group						
Atlantic Coast	Bonanza	84°41' W/13°58' N	39	Vesubio	Gn, sph, cpy, and py in vein quartz	>1%
	Bonanza	84°38' W/14°00' N	40	Pioneer	Py and gn in banded, vuggy vein quartz	0.1%
	Bonanza	84°35' W/14°02' N	41	Venus	Gn, sph, cpy, and py in vein quartz	>1%
Highland	Matagalpa	85°49' W/12°55' N	26	La Reina	White vein quartz	141 ppm
	Matagalpa	85°49' W/12°52' N	48	Colorado	Gn and py in quartz veinlets	0.6%
	Matagalpa	85°49' W/12°52' N	78	Mina Verde	Gn in white vein quartz	
	Matagalpa	85°49' W/12°49' N	79	La Reina	Gn in white vein quartz	
	Matagalpa	85°50' W/12°56' N	80	Padre Eterna	Gn in white vein quartz	
	Matagalpa	85°50' W/12°56' N	81	La Leonesa	Gn in white vein quartz	
	La Libertad	85°12' W/12°14' N	28	Esmeralda	White, massive vein quartz	10 ppm
	La Libertad	85°11' W/12°14' N	30	Babilonia	White, massive vein quartz	176 ppm
	La Libertad	85°12' W/12°14' N	31	Tres Amigos	White, vuggy vein quartz	12 ppm
	La Libertad	85°12' W/12°14' N	32	Azul	Gn in white, massive vein quartz	0.26%
	La Libertad	85°05' W/12°15' N	34	Santo Domingo	Py and gn in vuggy vein quartz	0.81%
	Topacio	84°27' W/12°07' N	35	Topacio	White, massive vein quartz	60 ppm
Nicaraguan depression	La India	86°19' W/12°45' N	22	La India	White, massive, fine-grained vein quartz	38 ppm
	La India	86°19' W/12°45' N	24	La India	White, fine-grained, banded vein quartz	9 ppm
	La India	86°19' W/12°45' N	49	La India	White, banded vein quartz	
	La India	86°19' W/12°45' N	50	La India	White, quartz vein breccia	
	La India	86°19' W/12°45' N	51	La India	White, massive vein quartz	
	La India	86°19' W/12°45' N	52	La India	White, banded vein quartz	
	La India	86°19' W/12°45' N	54	La India	White, massive vein quartz	
	La India	86°18' W/12°46' N	25	Aguafria	White, fine-grained vein quartz	<5 ppm
	La India	86°20' W/12°48' N	21	El Chaparro	White reddish, vuggy vein quartz	50 ppm
	El Limon	86°44' W/12°46' N	6	Limon	Green quartz vein breccia	<5 ppm
	El Limon	86°44' W/12°46' N	7	Limon	Red quartz vein breccia	6 ppm
	El Limon	86°44' W/12°46' N	8	Limon	White, massive vein quartz	<5 ppm
	El Limon	86°44' W/12°46' N	9	Limon	White, banded vein quartz	<5 ppm
	El Limon	86°44' W/12°46' N	65	Limon	White-red quartz vein breccia	
	El Limon	86°44' W/12°46' N	67	Limon	White, massive vein quartz	
	El Limon	86°44' W/12°46' N	69	Limon	Weakly banded, white vein quartz	
	El Limon	86°44' W/12°46' N	70	Limon	White, banded vein quartz	
	El Limon	86°46' W/12°45' N	15	Talavera II	White, fine-grained, vuggy vein quartz	5 ppm
	El Limon	86°46' W/12°45' N	16	Talavera II	Fine-grained, slightly banded vein quartz	6 ppm
	El Limon	86°46' W/12°45' N	17	Talavera II	White, massive fine-grained vein quartz	<5 ppm
	El Limon	86°46' W/12°45' N	47	Talavera II	Py in massive, fine-grained vein quartz	126 ppm
	El Limon	86°52' W/12°41' N	19	Las Marias	White-blue, fine-grained vein quartz	<5 ppm
	El Limon	86°47' W/12°55' N	3	Rincon de Garcia	Vein quartz with 102 ppm Au	33 ppm
	El Limon	86°47' W/12°55' N	4	Rincon de Garcia	Vein quartz with 5% MnO and 110 ppm Au	<5 ppm
	El Limon	86°47' W/12°55' N	5	Rincon de Garcia	Vein quartz with 174 ppm Au	6 ppm
	Chorreadero	86°52' W/13°00' N	1	Las Palomas	White, massive vein quartz	24 ppm
	Chorreadero	86°52' W/13°00' N	2	Las Palomas	White, massive vein quartz	70 ppm
	Chorreadero	86°52' W/13°00' N	73	Las Palomas	White, massive vein quartz	
	Chorreadero	86°52' W/13°00' N	74	Las Palomas	White, massive vein quartz	
	Chorreadero	86°52' W/13°00' N	76	Las Palomas	White, massive vein quartz	
	Chorreadero	86°52' W/13°00' N	77	Las Palomas	Brown-weathered massive vein quartz	

The following criteria for alteration has been used: unaltered = no or only traces of secondary minerals; altered = secondary minerals present; strongly altered = all primary minerals decomposed and primary textures only poorly preserved

Data for this classification (based on chemical analysis, XRD, and thin sections) are from Nyström et al. (1988); Darce et al. (1989); and unpublished information

Abbreviations: Cpy = chalcopyrite, Gn = galena, py = pyrite, sph = sphalerite

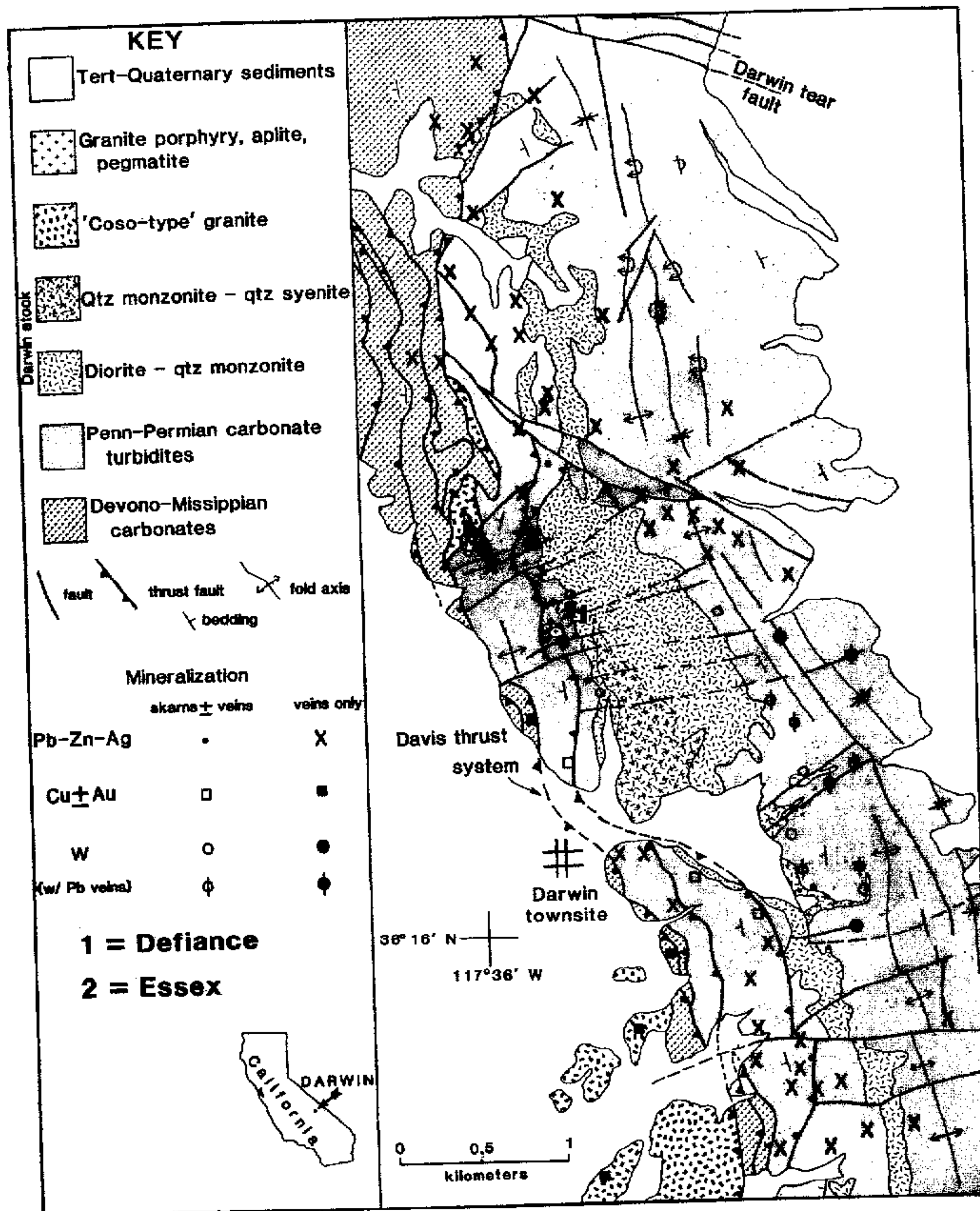


FIG. 1. Generalized geologic map of the Darwin district, showing distribution of various ore types. The Darwin mine consists of several orebodies located along the west margin of the Darwin stock; two of the major orebodies are the Essex (1) and Defiance (2). Modified from Newberry (1987) and Stone et al. (1989).

Fig. 2) which were linked by a common haulage level in 1945.

Although a relatively small deposit, Darwin is notable for a pioneering S isotope study (Rye et al., 1974) in which the authors integrated light stable isotope analyses with the known geology; and for comparative attempts at determining mineral formation temperatures by techniques such as minor element distribution (Hall et al., 1971), sulfide phase homogenization (Czamanske and Hall, 1975), and fluid inclusion systematics (Rye et al., 1974). Based on their study, Rye et al. (1974) concluded that the Pb-Zn-Ag sulfide stage of mineralization occurred at temperatures of $325^{\circ} \pm 55^{\circ}\text{C}$ and involved magmatic hydrothermal fluids flowing out of the magma which produced the adjacent Darwin stock. These authors noted horizontal zoning of S isotope values away from the Darwin stock and concluded that ore deposition took

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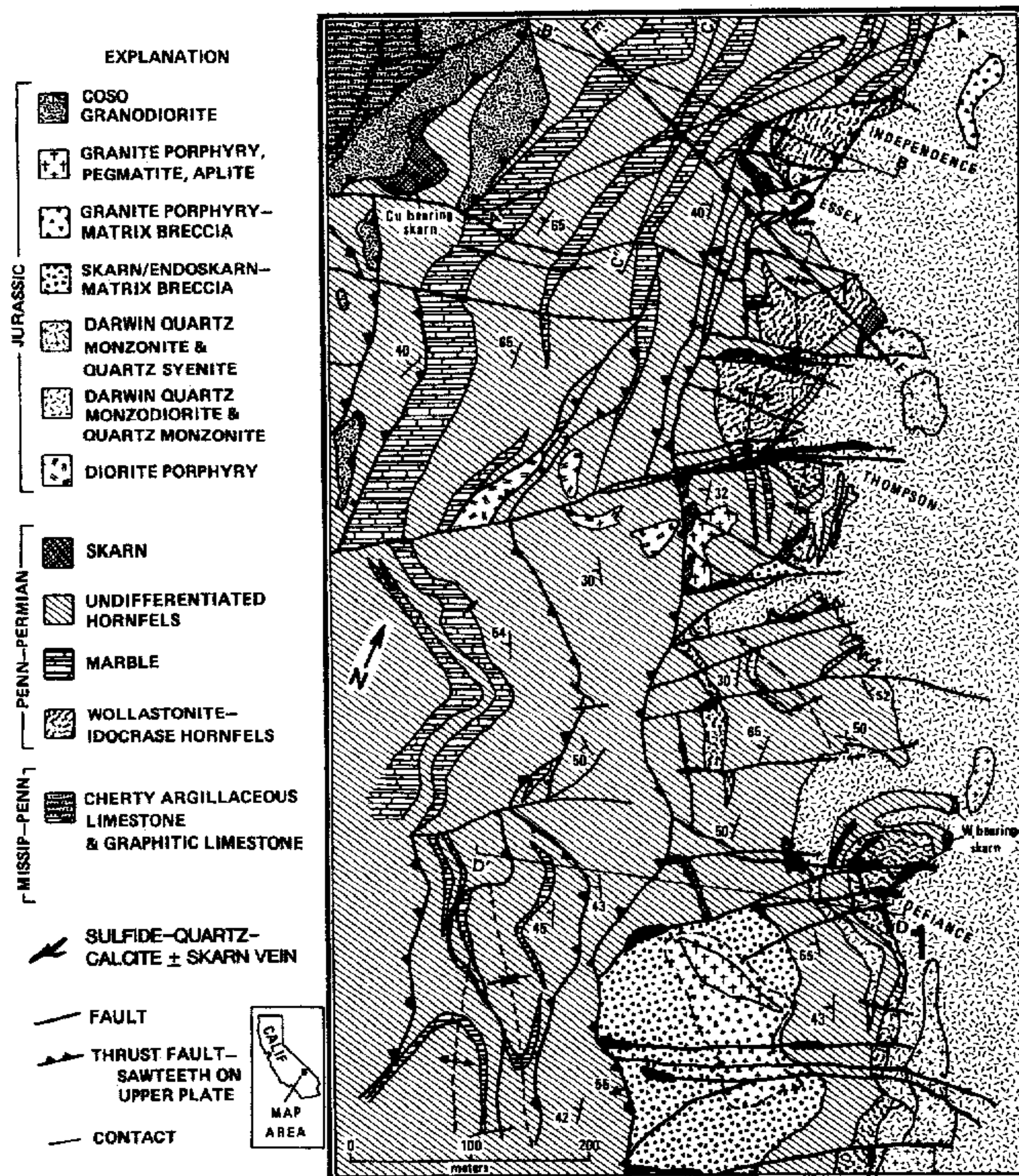


FIG. 2. Detailed geologic map of the Darwin mine area, based on unpublished mapping by R. Newberry and T. Sisson (1980-1982). Note the Pb-Zn-Ag skarn veins that cut and displace the Darwin pluton.

place primarily due to pH increase at constant f_{O_2} and temperature, caused by fluid reaction with carbonate and calc-silicate rocks.

Although widely quoted in the isotopic literature, there are several features of the Darwin study as presented by Rye et al. (1974) which invite scrutiny: (1) the Darwin quartz monzodiorite, with probable solidus temperatures $> 800^\circ\text{C}$ (Piwinski, 1973; Newberry, 1987), is located < 50 m from the sulfide deposits, but if this stock was the source of hydrothermal fluids, then temperatures of sulfide ore formation could be expected to range up to several hundred degrees higher than $325^\circ \pm 55^\circ\text{C}$ and skarn-related ores should be present; (2) the Darwin stock is un-

mineralized and virtually unaltered (Hall and MacKevett, 1962; Newberry, 1987), which may be incompatible with its being the source of hydrothermal fluids; and (3) the association of ore-grade W with ore-grade Pb-Zn-Ag is uncommon in limestone replacement and/or skarn deposits (e.g., Einaudi et al., 1981), raising the possibility of multiple, unrelated hydrothermal events. There also are problems with the relative timing of plutonism and Pb-Zn-Ag ore deposition; the 174-Ma (U-Pb; Chen, 1977) Darwin stock is cut by the Davis thrust (Eastman, 1980; Newberry, 1987), with movement dated at 154 to 148 Ma (Dunne et al., 1978), but Pb-Zn-Ag ores cut the thrust and hence postdate thrusting (Hall and

MacKevett, 1962; Eastman, 1980) and must be at least 20 m.y. younger than the Darwin stock.

Newberry (1987) resolved some of these apparent conflicts by showing that there are several different plutonic suites associated with different metasomatic skarn suites in the Darwin district. Newberry (1987) further showed that the contact-type W skarns are genetically related to the Darwin stock and that the Pb-Zn-Ag veins and skarns are related to younger quartz porphyry bodies. Supporting geologic data include the presence of Pb-Zn skarns along faults which cut across and displace the Darwin stock (Figs. 1 and 2) and granite porphyry and breccia bodies (Fig. 2) which intrude the Darwin stock and contain clasts of W-bearing but Pb-Zn-poor skarn. Newberry (1987) suggested that the Pb-Zn-Ag-W ore association may have resulted from superimposition of Pb-Zn skarns on older W skarns.

This paper investigates the apparent contradiction between isotopic studies of Rye et al. (1974), which concluded that ore was zoned around and caused by the Darwin stock, and petrologic-geologic studies presented by Newberry (1987), which indicated that Pb-Zn-Ag mineralization was unrelated to the Darwin stock. As there are no published maps for the deposit in which the skarns are distinguished or described and because pyroxene-rich skarns—so characteristic of Pb-Zn skarns (Einaudi et al., 1981)—have not been reported from the Darwin area, the investigation began with systematic surface and underground mapping and core logging. Because Rye et al. (1974) had stressed the horizontal zoning of ores and sulfur isotope ratios around the Darwin stock, a further investigation of zoning—based on ore and calc-silicate minerals, mineral compositions, and metal ratios—was undertaken. Given the new results from zoning studies, the thermal and sulfur isotope models of Rye et al. (1974) were reinterpreted. The zoning data reported herein are most consistent with a series of sub-vertical skarn pipes and related bedded skarns and veins, centered 100 to 300 m west of the Darwin stock. The sulfur isotope data are consistent with a model of vertical fluid flow through and away from these pipes.

General geology

Darwin area regional geology is summarized in Dunne et al. (1978) and Stone et al. (1989). Upper Paleozoic sedimentary rocks (Stone, 1984; Stevens, 1986) in the immediate Darwin mine area were deformed into broad folds in late Triassic time and subsequently intruded by mid-Jurassic alkalic plutons (including the 174-Ma Darwin stock; Chen, 1977) and, on the west side, by calc-alkalic granite plutons (including the 156-Ma Coso batholith; Chen, 1977). A 4- to 6-km depth of emplacement ($P_{\text{lithostatic}} = 1-2$ kbars) has been suggested for the calc-alkalic plutons

(Sylvester et al., 1978). Contact metamorphic recrystallization of impure carbonate rocks formed idocrase-wollastonite calc-silicate hornfels, garnet-rich skarnoid, and bleached marble around the Darwin stock (Fig. 2; Hall and MacKevett, 1962; Eastman, 1980; Newberry, 1987). Tungsten-bearing skarns are locally present along contacts of the more differentiated units of the Darwin stock with the surrounding carbonate-bearing rocks and are distributed symmetrically around the Darwin stock (e.g., Fig. 2; Newberry, 1987). Thrusting along the Davis fault system (Fig. 1) took place at 154 to 148 Ma (Dunne et al., 1978) and resulted in 1- to 3-km eastward displacement of the upper plate, juxtaposing the Coso batholith and its adjacent Cu skarns with the Darwin pluton and its adjacent W skarns (Newberry, 1987). Subsequent to thrusting, a series of granite porphyry dikes and breccia pipes (Fig. 2) intruded the metamorphic and igneous rocks along the northwest margin of the Darwin stock; aplite geobarometry indicates these rocks crystallized at a pressure of approximately 0.5 kbars (depth = 1.5 km, assuming $P = \text{lithostatic}$; Newberry, 1987). Pb-Zn-Ag skarns (restricted to the west side of the Darwin pluton) and Pb-Zn-Ag veins of the Darwin district formed along steeply dipping faults, which are commonly marginal to the granite breccia bodies and, less commonly, along granite porphyry dike contacts and along the Davis thrust (Fig. 2). Minor extensional reactivation of the Davis thrust accompanying Cenozoic basin range uplift (Dunne et al., 1978) caused slight deformation of ores in the vicinity of the thrust.

Investigative techniques

This study is based on underground (100-900 levels) and surface mapping of the Darwin mines at 1:2,400, detailed logging of approximately 1,000 m of diamond drill core, examination of approximately 300 polished and thin sections, approximately 450 microprobe analyses representing 80 thin sections and grain mounts, compilation of assay maps and drill assays, and sulfur isotope measurements for a galena-sphalerite pair and two galena samples. Mineral abundances were estimated using standard thin section point-counting techniques. Electron microprobe analyses were performed using a 9-spectrometer ARL microprobe at the University of California, Berkeley (silicates), as described in Newberry (1987), and a 3-spectrometer Chimeca microprobe at Washington State University (sulfides), as described in Meinert (1987). Mineral standards were employed and each analytical point represented the average of at least three analyses. Sulfide mineral separates were analyzed for sulfur isotope ratios by Krueger Enterprises, Cambridge, Massachusetts. Mine assay, production, and drill hole assay data were compiled onto level maps, averaged into 10-m (minimum) blocks, and a

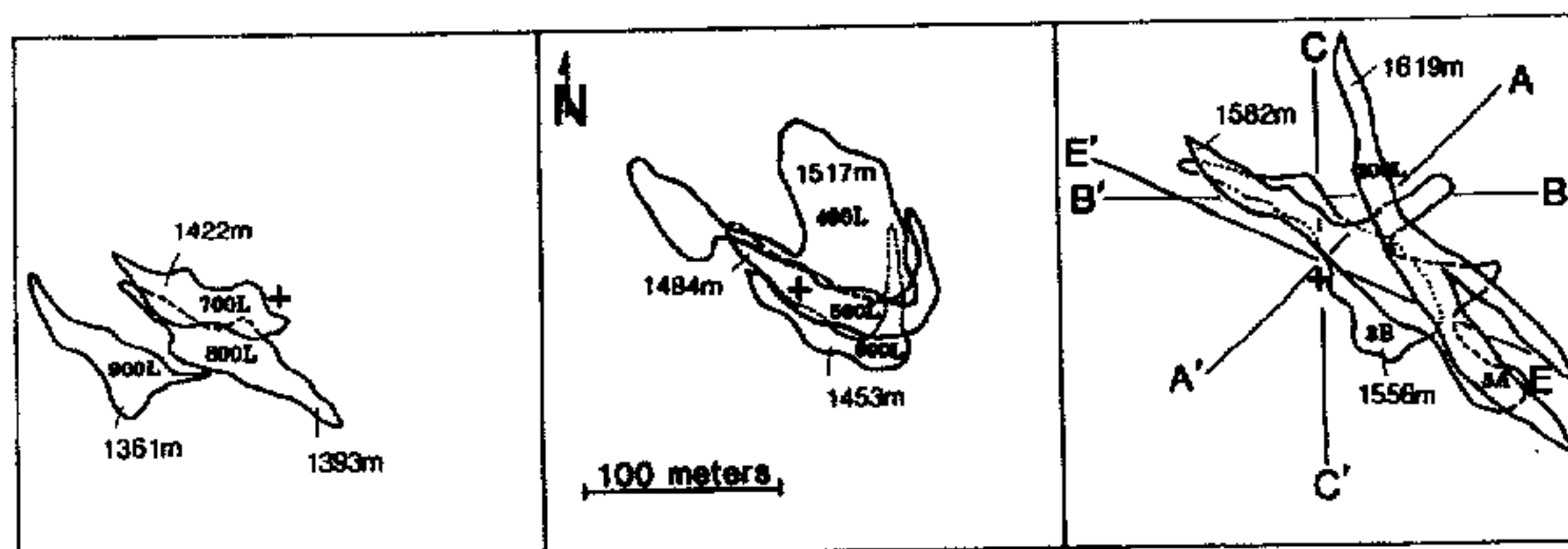


FIG. 3. Generalized outlines of skarn body in the Essex pipe area as a function of elevation. Variable skarn shapes are due to the intersections of the northwest-trending Essex zone with folded carbonate beds; larger skarn bodies are in the hinge region of the Darwin antiform. Most of the sulfide is in or immediately adjacent to the skarn. Based on underground mapping by R. Newberry and G. Wilson (unpub. map, 1982). Surface projections of cross-section lines are shown in Figure 2.

ratio was calculated. Ratios were then projected onto mine cross sections. Petrographic data and microprobe analyses (including those of Eastman, 1980), analyses of mineral separates, S isotope data, and sulfide deposition temperatures (including those determined by earlier workers) were plotted on mine cross sections. Because the data set for this paper integrates several different data sets acquired at different times by different workers and published on different mine cross sections, the data cannot be presented in an ideal fashion. Different projections for the petrographic, metal ratio, and microprobe data were employed to minimize projection distance, to best compare the results of this study with those of Rye et al. (1974), and to illustrate the three-dimensional character of the Essex orebody.

The Essex orebody (Fig. 2) of the Darwin deposit was selected for intensive study because all levels were accessible for underground mapping and because well-located sample collections from this orebody were available at Stanford University.

Geology of the Darwin Pb-Zn-Ag skarns

Pb-Zn-Ag ores of the Darwin deposit occur predominantly as bedded replacements and veins (Hall and MacKevett, 1962; Eastman, 1980) in skarn, calc-silicate hornfels, and marble. There are, in addition, at least two major pipelike orebodies, the Defiance and Essex pipes. The Essex pipe is an irregular body elongated to the northwest-southeast and plunging at about 70° to the southwest. Its shape is controlled by intersections of the $N 65^\circ W$ Essex fissure zone with receptive carbonate units near the hinge zone of the doubly plunging, $N 30^\circ W$ -trending, Darwin antiform (Figs. 3 and 4). Major bedded skarn zones also are present adjacent to the main pipe in marble beds immediately underlying sills of the Darwin pluton. This is especially the case in the upper levels of the mine.

In the Essex pipe area narrow skarn and/or sulfide veins are present in calc-silicate hornfels; the bulk of

skarn appears to replace marble. Unreplaced marble is locally present between skarn and the Darwin stock (Fig. 5). Sulfides occur disseminated throughout the skarn, in minor veins in the skarn, as through-going veins, and as bedded replacement bodies beyond the skarn.

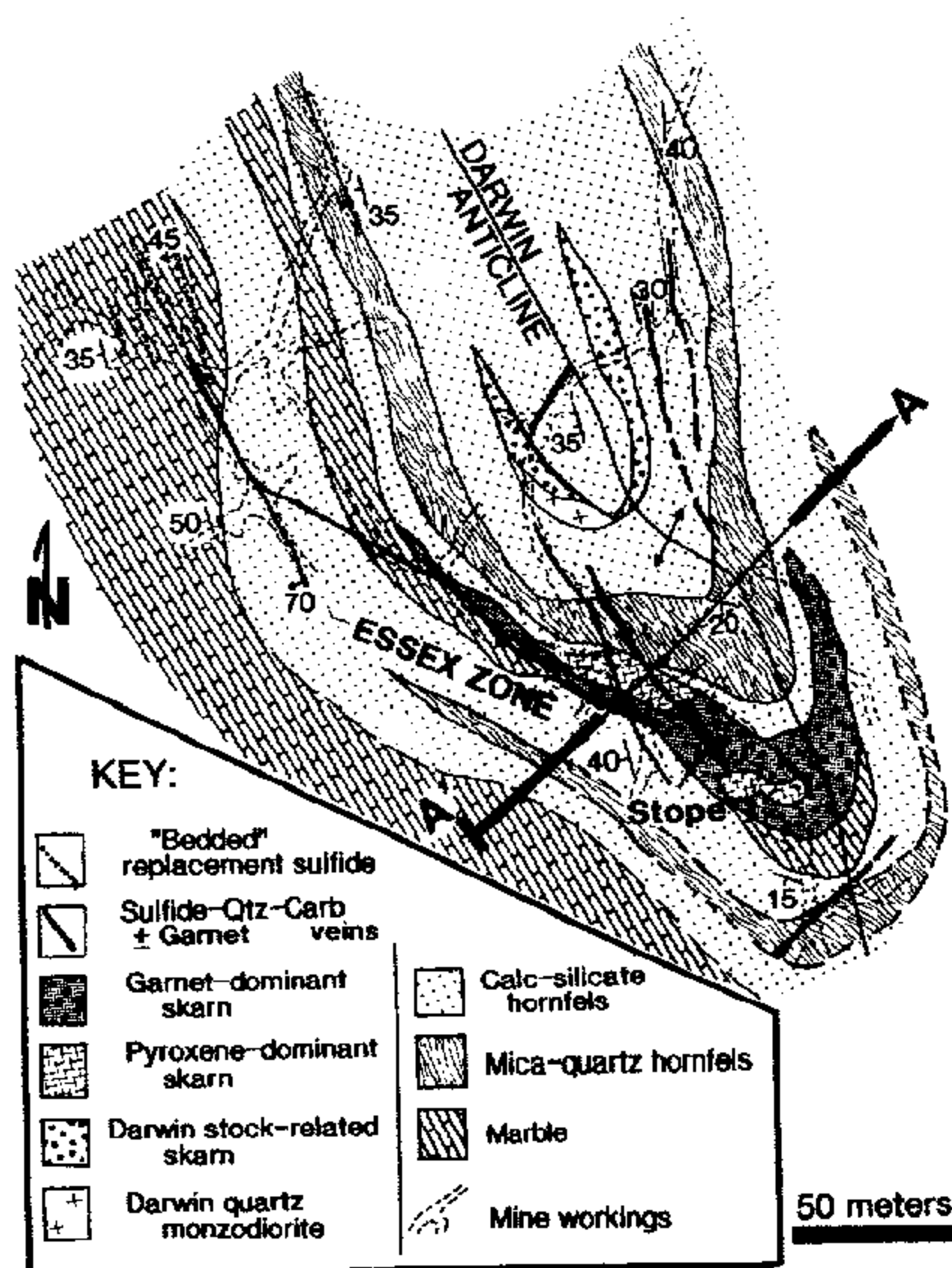


FIG. 4. Geologic map of the Essex pipe, 600 level, showing distribution of various skarn and ore types and relations to structure and lithology. Most of the skarn replaces marble; some pyroxene-rich skarn may replace calc-silicate hornfels. The bulk of the sulfides are restricted to the skarns. Mapping by R. Newberry and G. Wilson (unpub. map, 1982).

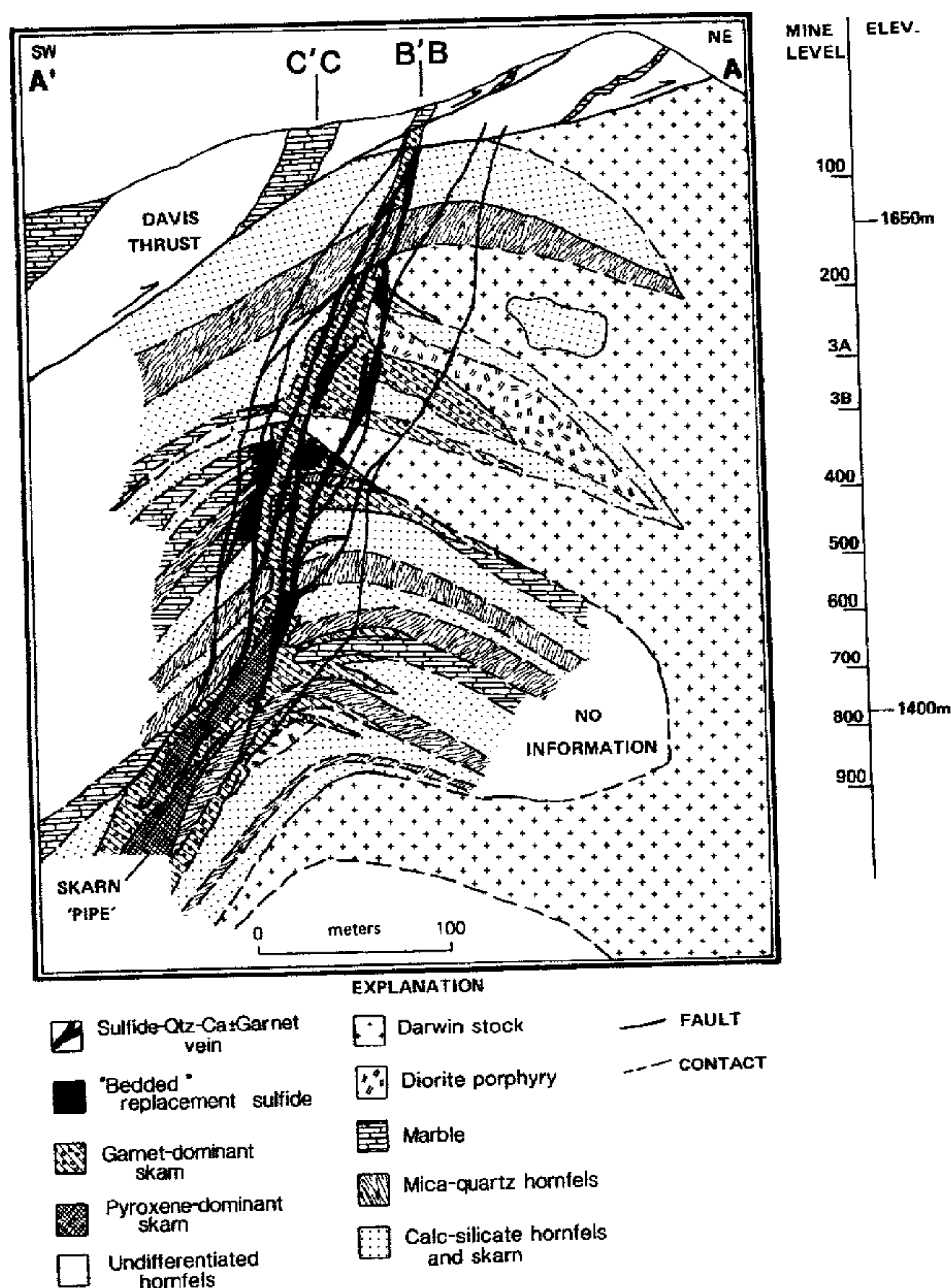


FIG. 5. Northeast-southwest cross section through the Essex pipe, at approximately right angles to the pipe elongation, showing pipe morphology and southwest rake to the pipe. Skarns dominantly replace marble, but narrow replacements of calc-silicate hornfels also are present. Massive sulfide replacements and veins are more abundant toward the surface; sulfide-bearing skarns are present throughout the vertical exposure. Based on underground mapping by R. Newberry and G. Wilson (unpub. map, 1982).

Lateral and vertical zoning in the Essex pipe is illustrated by a vertical (A'-A) cross section (Fig. 5) constructed at approximately right angles to the northwest-southeast elongation of the pipe (Fig. 3). The Essex pipe contains subequal amounts of pyroxene and garnet-rich skarn at depth; pyroxene skarn is both cut and vertically supplanted by garnet-rich skarns. Coarse-grained, vuggy, garnet-rich skarns are in metasomatic contact with marble in many localities

and show no evidence of replacing pyroxene-rich skarn at the marble contact. Pyroxene skarn does not contact marble. Garnet skarns cut across and replace calc-silicate hornfels and skarnoid beds and form laterally extensive strata-bound replacement bodies in marble and hornfels adjacent to the pipe (Fig. 5). In many cases the light-colored, green grandite garnet skarns could not easily be distinguished from the light-colored, green idocrase garnet hornfels during un-

derground mapping and AX core logging; most of these contacts probably are gradational. Rocks were classified with confidence as skarn during underground mapping and core logging if they contained coarse-grained (green) garnet $\pm$ pyroxene with interstitial sulfides and/or obvious garnet veins.

With increasing elevation, sulfide-rich, garnet-bearing veins become common; however, coarse-grained garnet skarn with interstitial galena is present throughout the vertical exposures of the pipe (e.g., as the surface expression of the Essex pipe; Fig. 2). Sulfides mostly occur as disseminations in the skarn below the 500 level. Sulfide-rich veins commonly contain a few to 20 percent fine- to medium-grained euhedral garnet and are surrounded by an envelope of garnet $\pm$ idocrase skarn where they cut hornfels or marble (Eastman, 1980). Relations between these sulfide-rich veins and normal, sulfide-bearing skarn are problematic; the veins cut skarn but contain euhedral skarn minerals and are grossly transitional (with depth) to garnet-rich skarn (Fig. 5). We interpret these veins as representing a stage of hydrothermal activity which postdates the bulk of normal skarn formation but under conditions where garnet and idocrase continued to form. A few massive quartz-carbonate-sulfide $\pm$ garnet bodies are present as replacements of marble adjacent to sulfide-rich veins (Fig. 5); crosscutting relations indicate that these bodies were formed after the skarns, possibly contemporaneously with the sulfide-rich veins. Although sulfides, especially galena, commonly enclose or fill vugs and fractures in skarn minerals, unaltered garnet is present adjacent to sulfide throughout the pipe.

Very late veins (generally <0.3 m wide), with extremely coarse grained calcite and pyrite and with sporadic native gold and tellurides, are especially common along lithologic contacts and faults. These veins were generally not mined and are not shown in the maps and cross sections. Where the late quartz-calcite veins cut skarn, they are surrounded by poorly defined 0.1- to 1-m-wide envelopes of calcite-quartz-hematite alteration of the skarn.

The Defiance pipe is a steeply dipping body located 700 m southeast of the Essex pipe (Fig. 2). This part of the Darwin deposit is currently accessible only at the 400 and 570 levels, and consequently it was less well studied. On the 400 level it contains quartz, carbonate, bustamite, garnet, and retrograded pyroxene with massive to disseminated sulfides. Limited logging of AX drill core indicates that garnet-pyroxene skarns are present at deeper levels. Drill core also shows that a small body or bodies of granite porphyry (with quartz-K feldspar veinlets), porphyry matrix breccia, and skarn matrix breccia (which contains galena and sphalerite) occurs below the 1000 level. The granite porphyry and porphyry matrix breccia are surrounded by galena-sphalerite-bearing skarn. Above the 400

level the pipe horsetails into several quartz-carbonate-sulfide $\pm$ garnet veins which lie along the bedding of, and partly replace, garnet skarn (Hall and MacKevett, 1962; Fig. 2).

Reconnaissance logging and examination of >10,000 m of AX drill core and logging of 1,000 m of BX drill core suggests that underground and surface exposures of ore accessible in 1980-1982 are representative of the ore mined and sampled before 1970. If this is the case, then some generalizations can be made about the relative amounts of the various ore types present. In the Essex area, the bulk of ore (>75%) below the 200 level consisted of sulfides in skarn, with intergrown sulfide-garnet-pyroxene textures more common than obvious sulfide veins. Above the 200 level, sulfide-bearing skarns and sulfide-rich ($\pm$ garnet) veins are subequal in abundance. The Defiance pipe is dominated by sulfides disseminated in skarn below the 570 level, with highly retrograded skarn, sulfide-replaced marble, and sulfide-rich veins more common than simple sulfide-bearing skarn above the 400 level.

Skarn Mineralogy

The mineralogy of the Darwin Pb-Zn-Ag skarns is relatively simple, although there are complex mineral compositional patterns. The most abundant mineral is grandite garnet, with compositions ranging from 100 to 5 mole percent andradite (Fig. 6). Four generations of garnet have been identified, based on overgrowth textures, rare vein relationships, and optical and compositional properties (Figs. 6, 7). Several garnet types are typically present in the same sample and in many cases three generations are present in the same grain (Fig. 7A).

The earliest garnet (generation 1) possesses blotchy, irregular birefringence and typically occurs as cores to later garnet types. These garnets have compositions of Ad_{60-92} with 1 percent spessartine and show systematic enrichment in andradite component from core to margin. Blotchy birefringent garnets are surrounded by a narrow rim of yellowish, isotropic

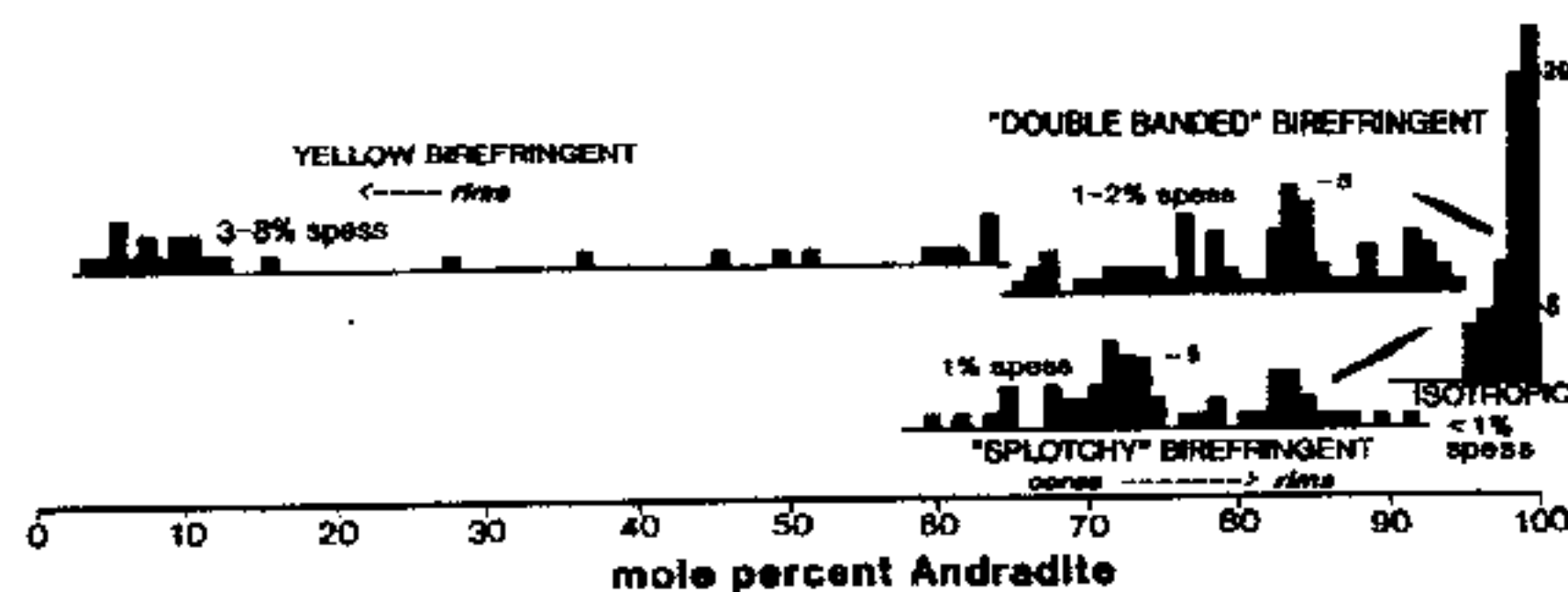


FIG. 6. Variations in composition of Pb-Zn skarn garnets, Darwin mine, based on electron microprobe analyses. The order of garnet types, as shown in the diagram, is consistently seen throughout the mine. All garnets have less than 1 percent combined almandine + pyrope contents; spessartine contents are as marked. Data from Eastman (1980) and this study.

(generation 2) garnet with compositions of Ad_{96-100} . Andradite garnet commonly exhibits incipient alteration to very fine grained opaque minerals. The third generation of garnet is banded birefringent, essentially identical in composition and appearance to the double-banded birefringent garnets of the Capote basin, Cananea district, Mexico, described by Meinert (1982). This generation (Fig. 7A) is characterized by narrow (.01-.002 mm) bands of alternating birefringent and nearly isotropic garnet, with alternating high and low iron contents. These garnets have compositions of Ad_{94-66} with 1 to 2 percent spessartine. The final (fourth) garnet generation is yellow and evenly birefringent. This garnet occurs as the final rims on banded birefringent garnets and more rarely as isolated grains in upper levels of the mine (Fig. 7B). These garnets have compositions of Ad_{65-5} with a systematic decrease in iron content rimward. Lowest iron, evenly birefringent garnets also contain a 5 to 7 percent spessartine component.

Garnets show complex relations with sulfides. Initial sphalerite and galena deposition apparently post-dated third generation banded birefringent garnet, as these sulfides commonly occur filling vugs between adjacent banded birefringent garnets, rather than as inclusions within these garnets. The banded birefringent garnets adjacent to interstitial sulfides show no signs of alteration, suggesting sulfides were stable with these garnets, but andradite cores to the banded birefringent garnets commonly exhibit incipient alteration to magnetite-calcite-quartz (Fig. 7C). Isolated grains of andradite garnet are commonly replaced by sulfides + quartz + calcite, even in deeper levels of the mine (Fig. 7D). Late, evenly birefringent, grossular-spessartine garnets, on the other hand, were deposited contemporaneously with sulfide in many cases; for example, as tiny (0.5 mm) garnets intergrown with sulfide, magnetite, quartz, calcite, and bustamite in the Defiance pipe (Fig. 7B). These late garnets also are present as envelopes around galena veins in calc-silicate hornfels. Garnet of all types is strongly altered, typically to fine-grained, chlorite-calcite-epidote-magnetite-pyrite, where adjacent to calcite-pyrite fissures.

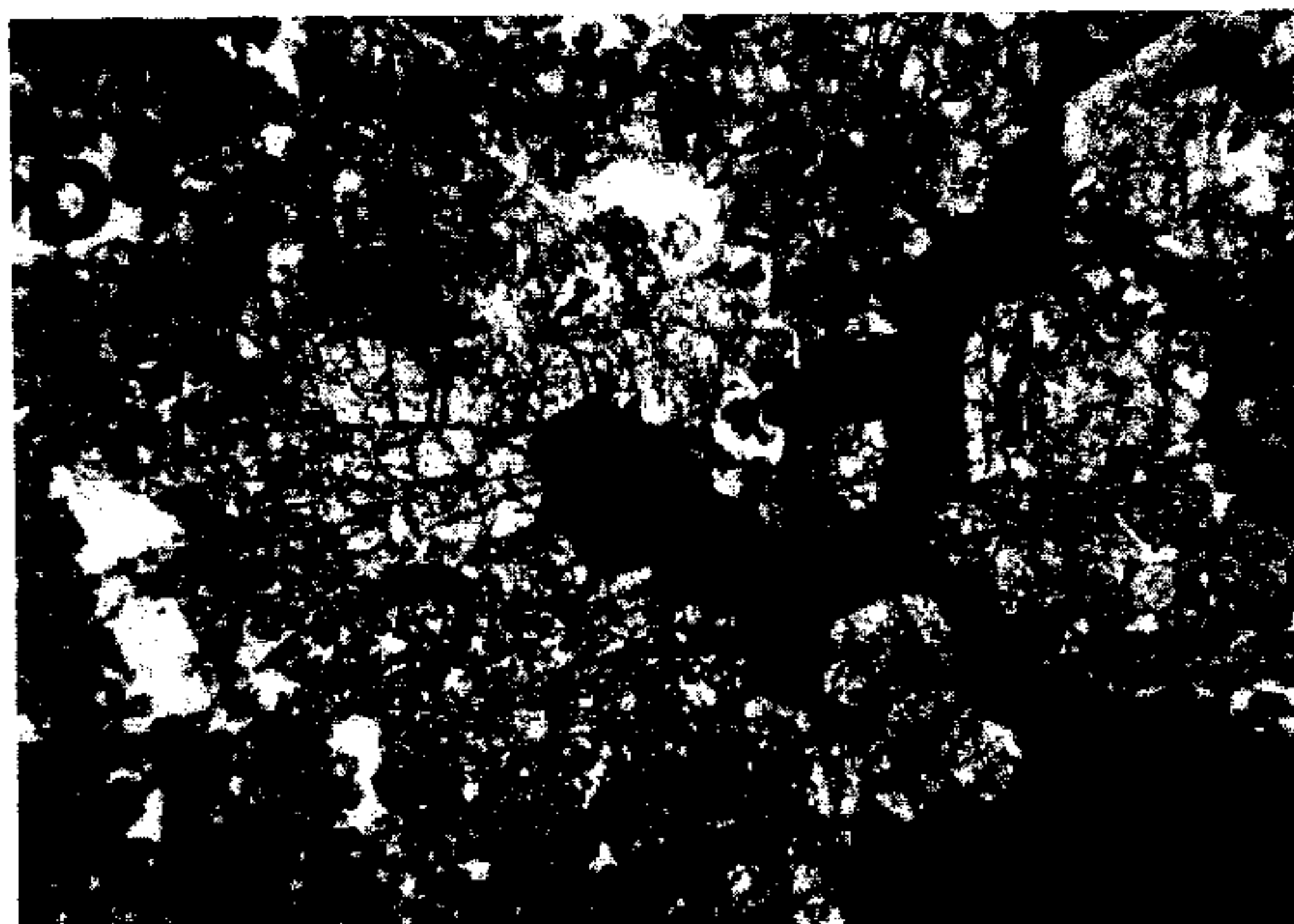
Pyroxene is much less common than garnet in presently known exposures of the Darwin skarns, and unlike garnet, pyroxene deposition probably predated the bulk of sulfide deposition. Massive pyroxene skarns, only currently known below the 500 level of the Essex pipe, contain 0.5- to 2-cm-long, bladed pyroxenes, partly replaced by garnet and sulfides (Fig. 7E). Pyroxene has not been identified in the Essex pipe Pb-Zn skarns above the 3A level, either because it has been totally replaced by garnet $\pm$ sulfide, or, more likely, because it never formed in the upper portions of the Essex pipe. In contrast, the Defiance pipe (400 level) contains small clots of isolated py-

roxene grains (with similar optical orientations) surrounded by murky carbonate + sulfide; this texture may indicate extensive retrograde alteration of an originally pyroxene-rich skarn pipe.

Pyroxene associated with Pb-Zn skarn shows a narrow range of composition, Hd_{0-30} , with Fe/Mn ratios varying slightly around 2/1 (Fig. 8). Below the 600 level in the Essex pipe, pyroxene is enriched in iron from core to rim; above the 600 level pyroxene generally is depleted in iron from core to rim. Rare, late pyroxene, occurring with evenly birefringent yellow garnet, is nearly pure diopside.

Other nonsulfide minerals in the Pb-Zn skarns occur in several different modes. Fluorite (especially common in upper parts of the mine) and K feldspar are sporadically present in garnet-lined vugs. Widespread occurrence of fluorite is confirmed by analyses of skarn and hornfels grab samples (unpub. Anaconda Co. data), which indicate 550 to 16,000 ppm F. Wollastonite is common in the calc-silicate hornfels but is typically retrograded to fine-grained quartz + calcite where near Pb-Zn skarn veins. Idocrase also is common in the hornfels, is present in some Pb-Zn skarns (remnant metamorphic grains?), occurs in small amounts with bustamite, quartz, calcite, and grossularitic garnet in the Defiance pipe, and is locally present adjacent to sulfide veins in marble (Eastman, 1980). Epidote, chlorite, and actinolitic amphibole are common in the uppermost parts of the mine, formed by retrograde alteration of garnet and pyroxene near galena-sphalerite veins. Ilvaite is reported (Eastman, 1980) from pyrrhotite-bearing sulfide veins. Chlorite is common as an alteration product of garnet near calcite-pyrite veins.

As discussed in Czamanske and Hall (1975), the ore mineralogy at Darwin is dominated by sphalerite and slightly argentiferous galena. Galena in the upper parts of the mine is enriched in Ag, Sb, Bi, and Se relative to galena in deeper levels and contains sulfosalt inclusions, interpreted from thermal studies to be exsolution products. Bismuth-bearing galena and sulfosalt minerals are especially common; Bi contents of skarn grab samples range from 74 to 16,000 ppm (unpub. Anaconda Co. data). Late carbonate-quartz sulfide veins, with a poorly characterized distribution, contain tellurium-rich minerals, sulfosalts, and native gold. Pyrite is common in all the ore types; it appears to be earlier than galena. Pyrrhotite occurs in the western part of the Essex orebody, approximately 200 m from the main Darwin stock contact (as measured along cross sections E'-E and A'-A; Fig. 2). As noted by Eastman (1980), pyrite-pyrrhotite relations are complex in the western part of the Essex zone, with a paragenesis of (1) early pyrite, (2) hexagonal pyrrhotite, (3) pyrite + galena + sphalerite $\pm$ magnetite, (4) monoclinic pyrrhotite + porous pyrite. Chalcopyrite is present in deeper portions of the deposit.



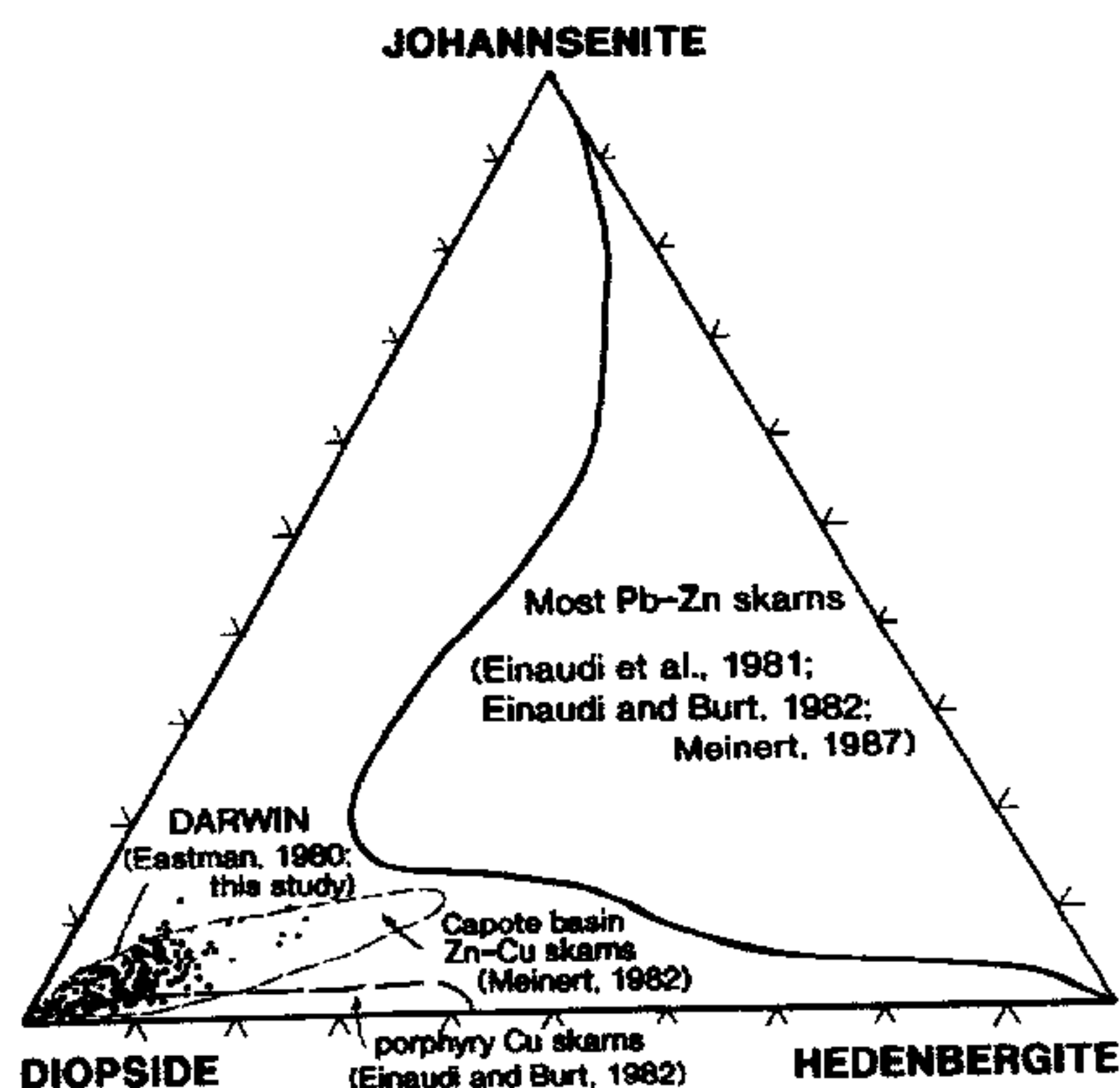


FIG. 8. Compositional variations in Darwin Pb-Zn skarn clinopyroxenes (98 electron microprobe analyses), in terms of the Mg (diopside), Fe (hedenbergite), and Mn (johannsenite) end members (mole %), relative to other skarns and skarn types. Note the low Jo + Hd contents (unusual for Pb-Zn skarns) and the sympathetic increase in Jo and Hd (not seen in porphyry Cu skarns). The Capote basin Zn-Cu skarns (Meinert, 1982) have clinopyroxenes with compositions similar to Darwin, but even those are less Mg rich than Darwin pyroxenes. Darwin data from Eastman (1980) and this study.

Tetrahedrite-tennantite and arsenopyrite are present in small amounts (skarn grab samples have As between 30 and 720 ppm), especially in upper parts of the deposit. Other rare and trace minerals are described by Czamanske and Hall (1975).

A generalized paragenetic diagram (Fig. 9) for the minerals at Darwin illustrates the series of metamorphic-skarn events and the complexities of the sulfide-silicate and sulfide-sulfide relationships for the main Pb-Zn ore event. This diagram differs from that of

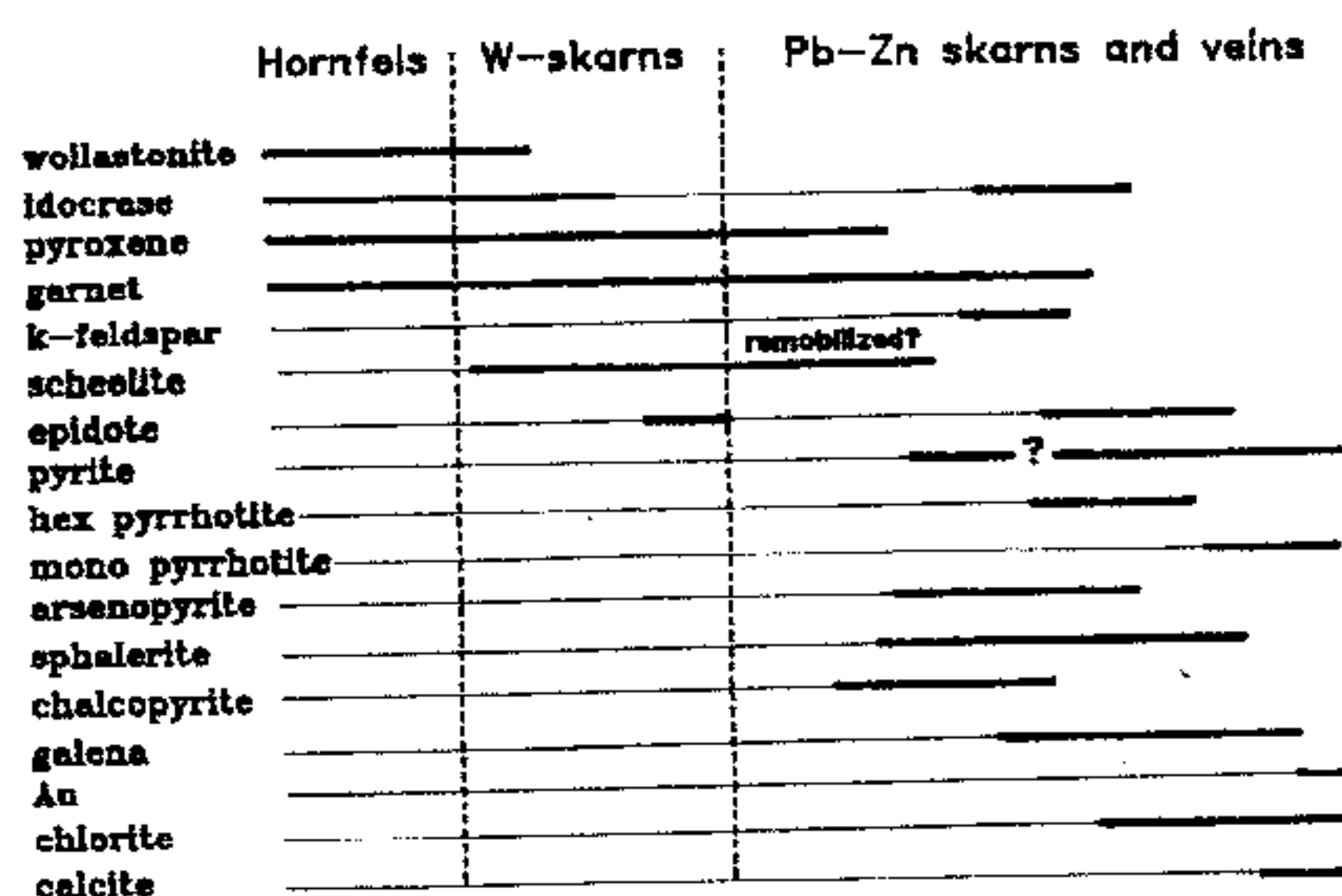


FIG. 9. Simplified paragenesis diagram for the Darwin ores.

Hall and MacKevett (1962) largely in indicating a considerable overlap in time of formation between skarn (garnet, idocrase, epidote) and ore (pyrite, sphalerite, chalcoppyrite, galena). We attribute this difference in the diagrams to the availability of deep-level exposures and samples for this study and to our successful discrimination between metamorphic (hornfels-related) and metasomatic (skarn-related) calc-silicate minerals. Given that the development of hornfels accompanied intrusion of the Darwin stock (Hall and MacKevett, 1962; Eastman, 1980; Newberry, 1987), structural constraints indicate that third and fourth generation garnet and Pb-Zn ore deposition postdated formation of garnet in the calc-silicate hornfels by more than 20 Ma.

Mine-Scale Zonation Patterns

Constraints and limitations

Metal zoning studies in the Darwin mines are complicated by the fact that assays and production statistics reflect a combination of skarn, vein, and supergene-enriched ores. Ratios above the 3A level (Fig. 7A) are commonly based on supergene-enriched ores.

FIG. 7. Photomicrographs showing characteristic features of the Darwin skarns. A. Garnet from skarn on the 400 level, showing multiple growth events. Nonbanded, andradite core (generation 2) garnet with incipient alteration to magnetite + pyrite, surrounded by (generation 3A) banded rim, in turn rounded and surrounded by (generation 3B) new banded rim, finally surrounded by nonbanded, evenly birefringent (generation 4) garnet. Transmitted light, 0.35 mm field of view. B. Defiance pipe, 400 level. Detail of turbid calcite assemblage which has replaced pyroxene: sphalerite (gray), garnet (generation 4; dodecahedrons), and quartz (gray) in calcite (white). Crossed polars with condenser lens, 0.5 mm field of view. C. Garnet-sphalerite skarn, 400 level, Essex pipe: garnets with slightly altered cores (generation 2) and banded birefringent (generation 3) rims. Vugs formed by coalescing generation 3 garnets contain sphalerite with sulfidation "exsolution" pyrrhotite (blobs) and chalcoppyrite inclusions (rectangles). Sphalerite deposition in this sample postdates, but is in apparent equilibrium with, generation 3 garnet. Transmitted light with condenser lens, 1.5 mm field of view. D. Garnet-sphalerite skarn, 700 level, Essex pipe: generation 2 garnet (broken gray) partly replaced by sphalerite (dark gray), pyrite (black), and calcite (white). Generation 2 garnet is clearly unstable during sulfide deposition in this sample. Transmitted light, 5 mm field of view. E. Pyroxene skarn, 600 level, Essex pipe: coarse-grained euhedral pyroxene crystals partly replaced by sphalerite and galena (black). Crossed polars, 5 mm field of view.

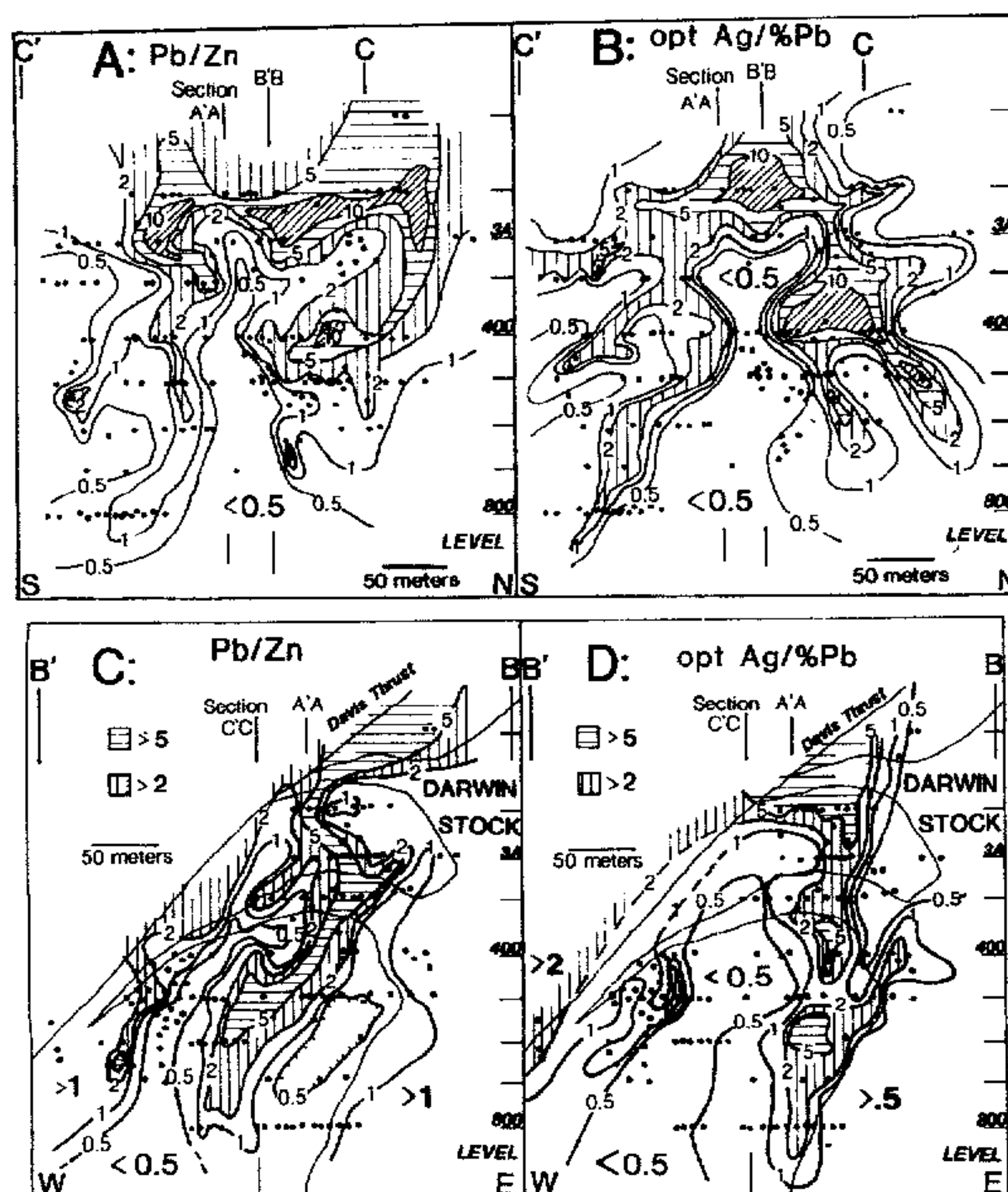


FIG. 10. North-south (A, B) and east-west (C, D) metal ratio cross sections for the Essex pipe. Pb and Zn are in percent, Ag is in troy ounces/short ton. Note the inverted cup morphology, centered on the skarn pipe (cf., Fig. 5), defined by metal ratios. Black dots represent location of data from unpublished assay maps, drill logs, and assay books, provided by the Anaconda Company.

If current exposures are representative, then the bulk of ore below the 3A level was from skarn or skarn-bearing vein material, but the information available does not permit a detailed analysis of metal ratios as a function of host rock.

Mineral, isotopic, and mineral compositional data have been derived from several published studies by several different authors. The data from these studies have been presented in several different mine cross sections. Detailed sample descriptions are not generally available for isotopic samples. Underground mapping and core logging in areas from which previously published studies were performed suggest that the bulk (more than 2/3) of previous samples from the Essex area was derived from skarn ores with the remainder primarily from garnet-bearing sulfide veins in skarn and hornfels. Virtually none of the previous samples represents the late pyrite-calcite event. Ores from the Defiance area are more difficult to categorize, given the limited amount of exposures available for this study. We suspect that the bulk of the previous

samples from the Defiance area was also taken from skarn.

Metal zoning—Essex pipe

Combined horizontal and vertical zoning in the Essex pipe is illustrated by metal ratio cross sections. Figure 10A and B shows metal zoning along north-south section C-C' and Figure 10C and D shows metal zoning along east-west section B-B' (both located in Fig. 2). Both Pb/Zn and Ag/Pb ratio contours describe an inverted cup morphology for highest values of these ratios. For example, the Ag/Pb contours are remarkably similar in both east-west and north-south views, both showing deep skirts of >2 (oz/ton/wt %) extending to roughly the 800 level on all sides. The inverted cup defined by metal ratios has a core of low values (<0.5 for both metal ratios) that corresponds with the center of the garnet-pyroxene skarn pipe (Fig. 5). The horizontal width of skarn in Figure 10 is approximately 80 to 120 m (note that Fig. 5 is drawn along the narrowest portion of the skarn body; cf.

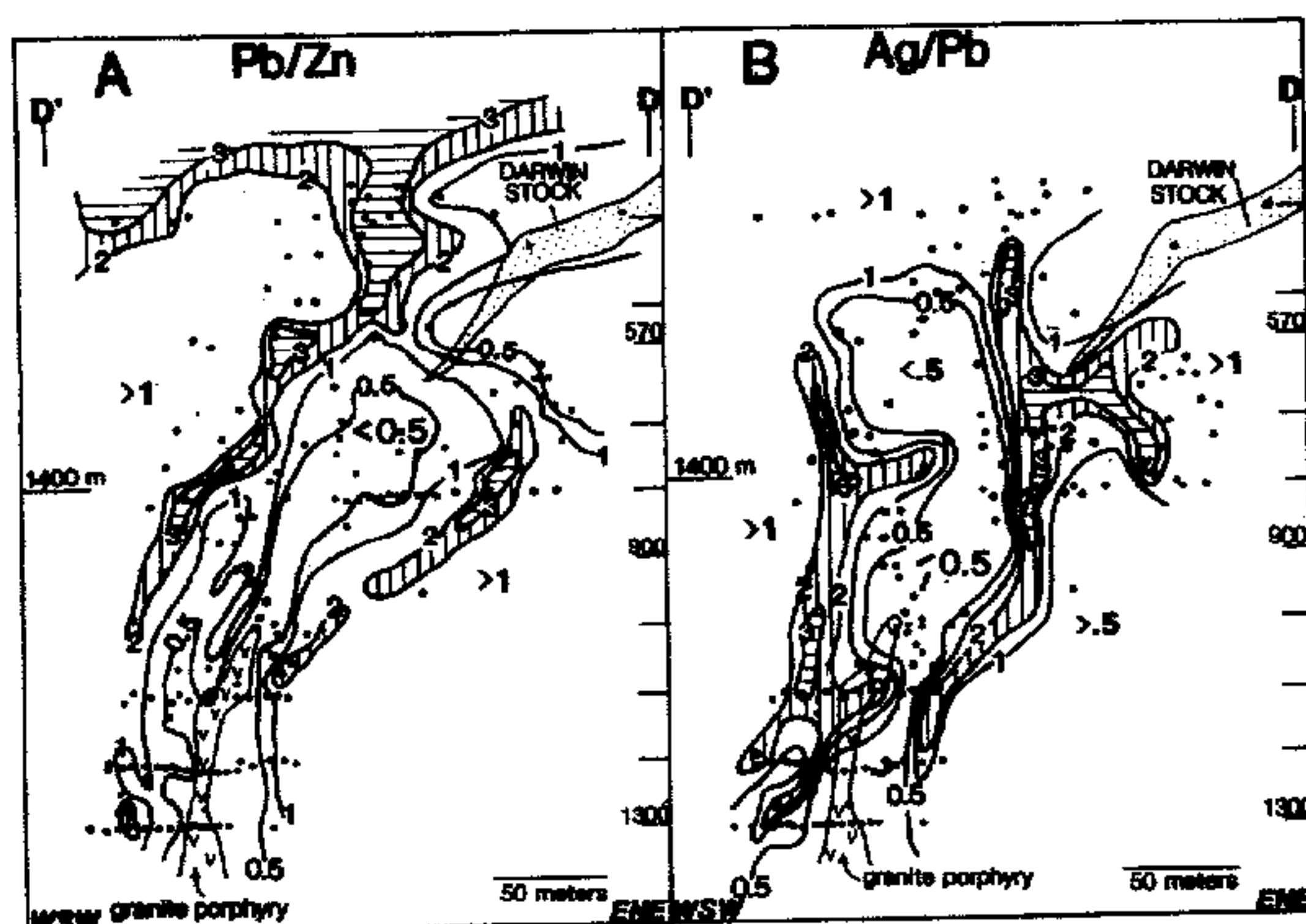


FIG. 11. Approximately east-west, Pb/Zn (A) and Ag/Pb (B) metal ratio cross sections through the Defiance pipe, below the 400 level. Units as in Figure 10. Note the inverted cup morphology to the metal ratios, centered on a granite porphyry plug. Location of granite porphyry determined from logging drill core; black dots represent location of data on metal ratios from unpublished assay maps, drill logs, and assay books, provided by the Anaconda Company.

Figs. 3 and 4), so that the zones of highest metal ratios in Figure 10 are commonly in skarn or the outer margins of skarn.

Within the Essex pipe, the high-grade ore stopes are located in areas with very high Ag/Pb and Pb/Zn ratios, and the bulk of ore mined was within the Ag/Pb and Pb/Zn >1 contours. The localization of high-grade ore is caused in part by supergene enrichment of Ag and Pb (Hall and MacKevett, 1962, p. 66) and in part by chemical-thermal zonation within the skarn pipe (see below). Although not noted by previous workers, stope cross sections of the Essex body outline an inverted cup morphology (cf. Czamanske and Hall, 1975, fig. 1), in agreement with the metal ratio sections.

Metal ratios—Defiance pipe

Metal ratios for the Defiance pipe cross section below the 400 level (D-D', Fig. 11), show a pattern remarkably similar to that of the Essex body. Symmetrical zonation is present around a deep porphyry body, which is surrounded by low sulfide skarn matrix breccia that grades outward to ore-bearing skarn. The core of this pipe is defined by low Zn/Pb and Pb/Ag ratios, and an inverted cup morphology is defined by high (>2) Pb/Zn and Ag/Pb ratios. As in the Essex area, high values for Pb/Zn above the 400 level in the Defiance body partly reflect supergene enrichment.

Mineral zoning—Essex pipe

Mineral zonation in the Essex pipe is clearly seen in the distribution of both sulfide and nonsulfide minerals. A cross section (A-A') through the Essex skarn

zone (Fig. 12) is used to illustrate several types of mineral zoning patterns around the central skarn pipe as defined by geologic mapping (Figs. 3, 4, and 5) and by metal ratio studies (Fig. 10).

Galena/sphalerite ratios, based on underground mapping, core logging, and hand specimen and polished section examination (Fig. 12A) show that the skarn pipe has a zinc-rich core and a lead-rich periphery. Galena/sphalerite ratios are not clearly defined outside of the orebody, where abundances of both these minerals are low relative to pyrite and pyrrhotite, and the relative proportions of galena to sphalerite might be low on the fringes of the orebody. These mineralogical ratios are in agreement with the Pb/Zn ratios defined by ore grades and support the hypogene origin of the metal zoning pattern within the pipes. The more economic zones in the mine are defined by high sulfide abundance together with high galena/sphalerite ratios (0.5–3), generally found in the upper parts of the deposit.

Chalcopyrite in the Essex pipe skarn occurs both as isolated grains and commonly as very fine grained, subhedral, and oriented grains in sphalerite. Estimated abundance of chalcopyrite in sphalerite has been contoured (Fig. 12B); these data, combined with the distribution of samples containing chalcopyrite as separate grains, define a copper-rich core to the orebody. Hall (1971) presented data for Cu content of sphalerite; these data also outline a copper-rich core to the orebody. The Cu data also are consistent with limited Cu assays, which indicate values up to 0.65 percent Cu in deeper parts of the mine (in comparison to typical grades of $<0.2\%$ Cu for the ores). The cop-

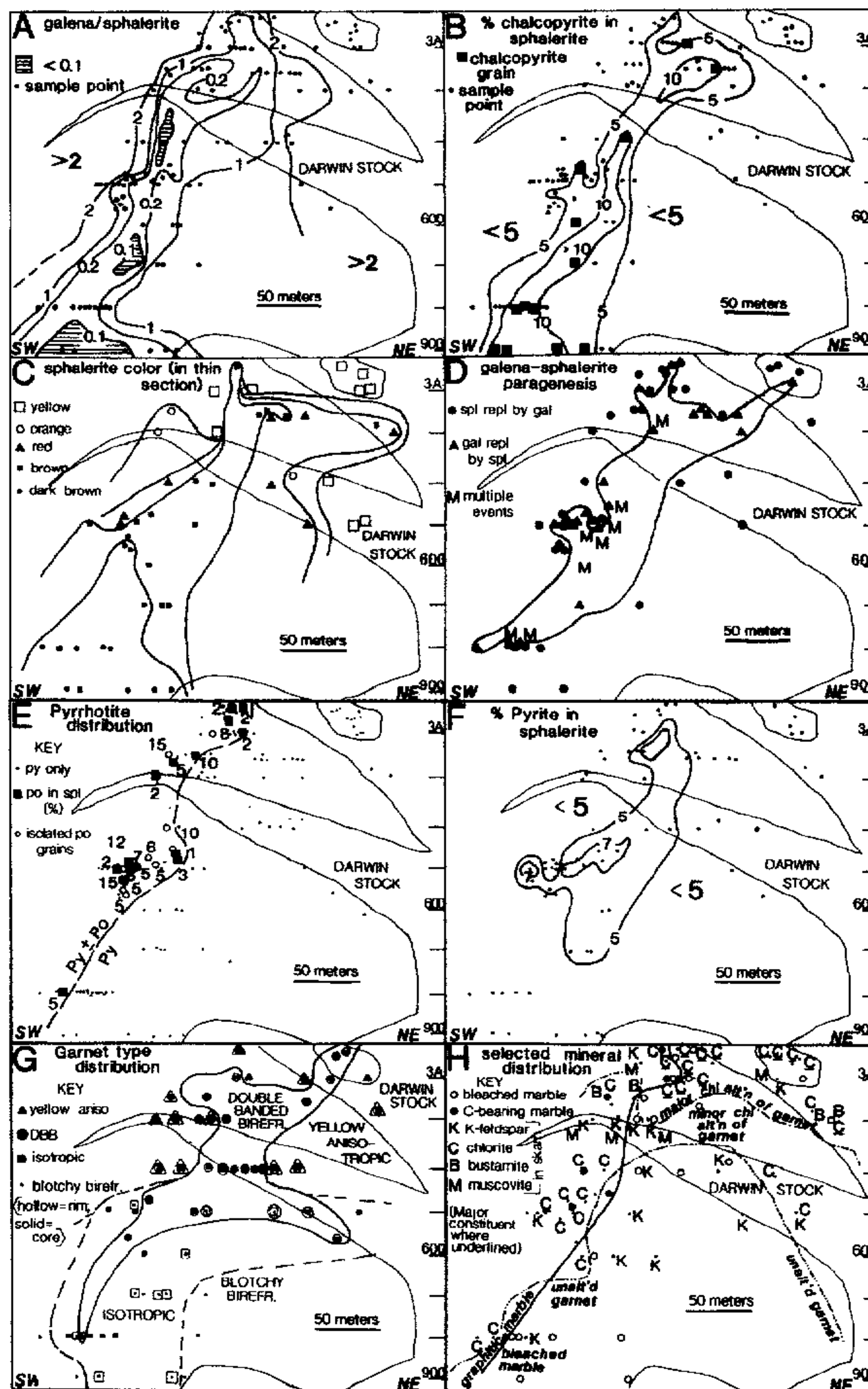


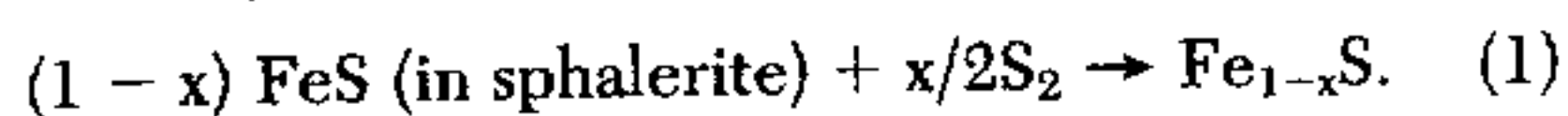
FIG. 12. Mineralogical variations along cross section A'-A (Figs. 2 and 5) in the Essex pipe, based on thin section, polished section, and hand specimen studies. Data points located within 50 m of the cross-section line were projected onto that line, so that the lateral distribution of skarn samples is greater than the lateral extent of skarn shown in Figure 5. A. Galena/sphalerite ratio (note correspondence between the low galena-sphalerite core and the low Pb/Zn ratios of Fig. 10C). B. Chalcopyrite distribution, showing a high chalcopyrite core similar in location to the low galena-sphalerite zone. C. Sphalerite color (thin section transmitted light). D. Galena-sphalerite paragenesis. E. Pyrrhotite distribution. F. Distribution of pyrite inclusions in sphalerite. G. Distribution of garnet types and garnet zoning. Each shape within a composite symbol represents a different garnet type, with the zoning as seen in thin section replicated in the composite symbol. Note the restriction of major andradite (isotropic) garnet to the lower parts of the pipe. H. Distribution of selected nonsulfide minerals, showing boundary

per-rich core (Fig. 11B) corresponds closely with the zone of lowest Pb/Zn ratios in the ore (Fig. 11A).

Sphalerite color changes within the ore zone; sphalerite in the deep, central, part of the mine is dark colored, whereas sphalerite in upper and high fringe parts of the skarn is pale colored (Fig. 11C). Individual grains are not color zoned. Comparison with compositions determined by electron microprobe indicates that this pattern only partly reflects variations in combined iron, manganese, and cadmium content of sphalerite; another important factor might be sulfur content (Scott and Barnes, 1972).

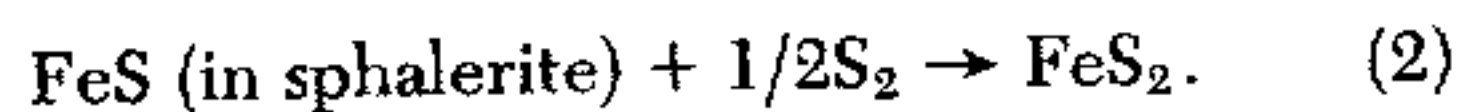
Polished section study of crosscutting and inclusion textures involving galena and sphalerite indicates that in a central zone multiple periods of ore deposition led to complex relative ages, whereas in peripheral zones and at depth, sphalerite was replaced by galena (Fig. 12D). This depositional history is consistent with Hall and MacKevett (1962) and Eastman (1980), who report galena generally younger than, but commonly overlapping with, sphalerite.

Pyrrhotite is present locally in the west part of the Essex orebody as individual grains and as minute inclusions in sphalerite. The contact between pyrrhotite-bearing and pyrrhotite-absent assemblages is roughly parallel to the main Darwin stock contact (Fig. 12E), as noted by Rye et al. (1974). Within the pyrrhotite-bearing zone, however, there is no apparent spatial trend to the abundance of pyrrhotite inclusions in sphalerite. The origin of these pyrrhotite inclusions is unclear; they may represent sulfidation as represented by an equation like



If this is the case, sphalerite was altered after initial precipitation by a hydrothermal fluid with a relatively higher sulfur fugacity.

The distribution of fine-grained pyrite inclusions in sphalerite is more regular, as there appears to be a core zone in the upper parts of the Essex orebody in which sphalerite contains a high abundance of pyrite inclusions (Fig. 11F). Such inclusions may represent further sulfidation, as represented by



The locus of highest abundance of iron sulfide inclusions in sphalerite (Fig. 12E and F) is fundamentally based on the original locus of Fe-rich sphalerite (see below) combined with the locus of flow of later sulfidizing hydrothermal fluids.

Unreplaced marble beds are common beyond the

margins of the Essex skarn pipe and some of these are located between the skarn and the Darwin stock (Figs. 4 and 5). The marble close to the stock is bleached, whereas marble far from the stock contains disseminated graphite (Fig. 12H). This distribution pattern suggests that bleaching and other contact metamorphic effects occurred during intrusion of the Darwin stock (Eastman, 1980); subsequently both bleached and unbleached marble was overprinted by the Pb-Zn skarn hydrothermal system. Eastman (1980) noted that rare graphite in the Essex skarn is restricted to a zone located >150 m west of the main Darwin stock contact. The spatial coincidence of unbleached marble (Fig. 12H), graphite in skarn, and pyrrhotite-bearing ores (Fig. 12E) suggests that progressive reduction of the ore fluid by reaction with organic matter in the distal carbonate rocks controlled the deposition of pyrrhotite and graphite in skarn.

Silicate minerals also show systematic patterns around the core of the orebody. Garnet generations (cf. Fig. 7A) are systematically zoned (Fig. 12G), with the earliest garnet being characteristic of the lowermost skarn in the Essex pipe and the youngest garnet characteristic of the upper and upper peripheral parts of the skarn. Garnet with final banded birefringent rims outlines the central skarn core and yellow birefringent garnet characterizes the upper parts of the Essex pipe away from the central core.

K feldspar is a trace constituent in skarn above the 600 level, where it commonly fills vugs between garnet grains and is in textural equilibrium with sulfides and fluorite. Fine-grained, texturally late, muscovite-quartz alteration of the K feldspar in skarn is erratic but limited to the uppermost part of the orebody, above the 400 level (Fig. 12H). A similar pattern is seen for chlorite-calcite-iron oxide alteration of garnet and for bustamite alteration of pyroxene (Fig. 12H), which both are concentrated at the top and periphery of the Essex orebody. These patterns indicate that lower temperature, postskarn alteration, dominated by hydrolysis and sulfidation, was concentrated in the upper and peripheral parts of the system and suggest that conditions (T - f_{O_2} - X_{CO_2}) remained within garnet ($\pm$ K feldspar) stability in the lower central portions of the skarn pipe.

Zoning of mineral compositions—Essex pipe

Due to the highly complex zoning of individual garnet grains (Figs. 6 and 7A), the deposit-wide zoning of garnet compositions is also highly complex. Given the range of garnet compositions observed in

between bleached and unbleached marble at a location near the pyrite-pyrrhotite boundary of 12E, presence of K feldspar throughout the skarn above the 600 level, restriction of major alteration of garnet to the upper and marginal parts of the Essex pipe. Data (some of the pyrite, pyrrhotite, and chalcopyrite abundance data) from Eastman (1980) and this study (remaining data).

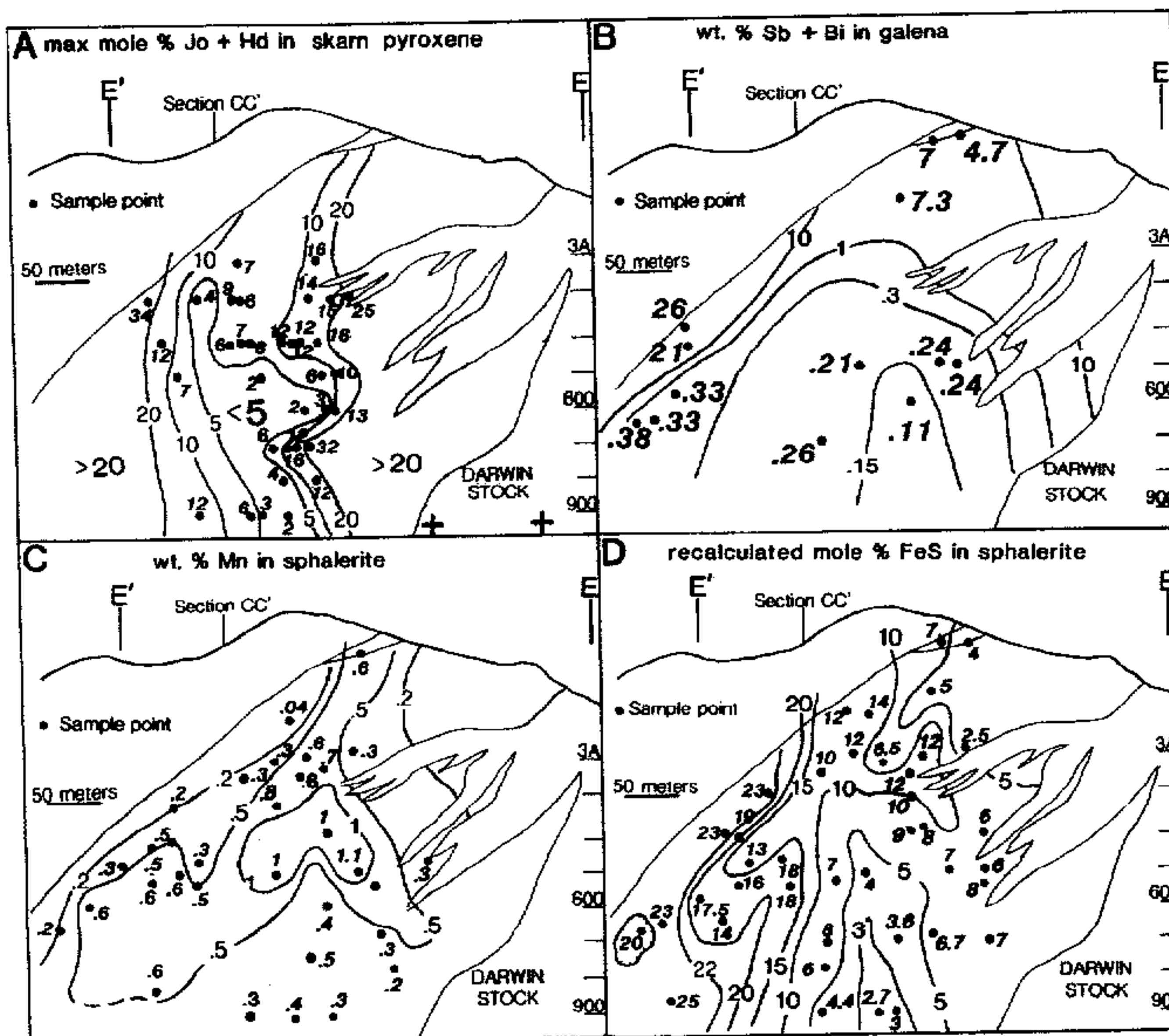


FIG. 13. Distribution of mineral compositions along cross section E-E, Essex pipe. The data are all consistent with zoning around a central skarn pipe, with some perturbations related to higher graphite contents in marbles on the west side of the pipe. A. Maximum mole percent johannsenite (Jo) + hedenbergite (Hd) components in skarn clinopyroxene (electron microprobe analyses). B. Average wt percent Bi + Sb contents in galena (microprobe analyses and atomic absorption analyses of high-quality mineral separates). C. Wt percent Mn in sphalerite. D. Estimated mole percent FeS in sphalerite prior to sulfidation (see text), based on (a) electron microprobe analyses adjusted for inclusion pyrrhotite and pyrite and (b) atomic absorption analyses of mineral separates. Data from Hall and MacKevett (1962), Hall (1971), Czamanske and Hall (1975), Eastman (1980), and this study [most of the sphalerite and pyroxene electron microprobe analyses].

a single grain, average compositions show no recognizable patterns. The restriction of the second generation yellow isotropic garnet to lower portions of the Essex skarn pipe, however, (Fig. 12G) indicates that andradite garnet is restricted in distribution and is only abundant in lower parts of the Essex pipe.

Pyroxene also shows complex zoning patterns (e.g., Newberry, 1987) but a narrower range in composition than that of garnet within a single sample. Maximum hedenbergite (Hd) + johannsenite (Jo) content in pyroxene shows a simple pattern (Fig. 13A), increasing progressively away from the deep core zone where pyroxene is close to diopside in composition.

Compositional zoning of galena (Fig. 13B), based on the data of Hall (1971) and Czamanske and Hall (1975), indicates that galena became increasingly enriched in Sb + Bi with increasing distance from the deep core of the pipe. In conjunction with the py-

roxene and chalcopyrite data, this indicates that the hydrothermal fluid became relatively enriched in Sb, Bi, Fe, and Mn and relatively depleted in Mg and Cu with distance from its source.

Average manganese content of sphalerite is also zoned (Fig. 13C), with an initial upward and outward increase from the deep center of the pipe and a return to low Mn contents at the fringes of the pipe. This pattern bears some similarity to the pattern of Mn in pyroxene (Fig. 13A) in terms of the initial outward increase in Mn; lower temperatures on the fringe of the pipe (see below) may have restricted MnS solubility in sphalerite, causing the low Mn characteristic of the skarn fringe.

The interpretation of analytical data on the iron content of sphalerite is complicated by the presence of very fine grained pyrite and pyrrhotite inclusions (cf. Fig. 12E and F). Iron contents determined by

bulk chemical techniques for sphalerite separates (Hall, 1971) include the iron sulfide blebs, but electron microprobe analyses do not. If it is accepted that the Fe sulfide inclusions in sphalerite resulted from sulfidation alone (as argued above)—with no addition of Fe—than the bulk Fe/Zn ratios of these composites represent the original (presulfidation) sphalerite compositions. Therefore, the original bulk compositions of inclusion-bearing sphalerite grains were estimated from electron microprobe analyses in conjunction with estimated modal abundance of Fe sulfide inclusions, and these were used to indicate the original hydrothermal zoning pattern. This recalculation results in small increases in the FeS content and is quantitatively important only in those areas with >5 vol percent iron sulfide inclusions in sphalerite (cf. Fig. 12E and F). Compositions for no other minerals were treated in this way because there is no petrographic evidence that the late sulfidation event caused changes in mineral composition for other minerals considered here.

Zoning of recalculated sphalerite compositions is partially asymmetric with respect to the pipe core (Fig. 13D). There is a general increase in recalculated mole percent FeS upward and toward the periphery of the pipe (Fig. 13D), although the increase in FeS from the core toward the pluton is much less than that from the core away from the pluton. Additionally, a zone of lower iron sphalerite appears in the uppermost levels of the Essex pipe.

Compositional variations in sphalerite, recalculated to reflect initial depositional environments (Fig. 13D), can be interpreted in terms of the sulfidation state of hydrothermal fluids, because the iron content of sphalerite in equilibrium with an iron sulfide is a function of temperature and fugacity of sulfur (Scott and Barnes, 1971). Thus, iron content of sphalerite increased as sulfidation state decreased upward and toward the periphery of the pipe. The decrease in sulfidation state from the core toward graphitic marble (away from the pluton) was much greater than that from the core toward the pluton, reflecting the lower sulfidation-oxidation environment that also stabilized pyrrhotite rather than pyrite. The upward decrease in sulfidation is reversed in the uppermost levels (above 3A level; Fig. 7A), where low iron sphalerite reflects relatively high sulfidation states. If this sphalerite was deposited during main-stage Pb-Zn mineralization and if the recalculation of sphalerite compositions to reflect main-stage conditions was valid, then the high-level sphalerite signals a spatial reversal toward higher sulfidation states relative to deeper and lateral trends. Because this area is spatially coincident with the locus of extensive retrograde alteration of garnet and pyroxene (Fig. 13H), it also is possible that the low iron content of sphalerite reflects late sulfidizing fluids that were appreciably cooler and/or more oxidized than deeper and earlier fluids.

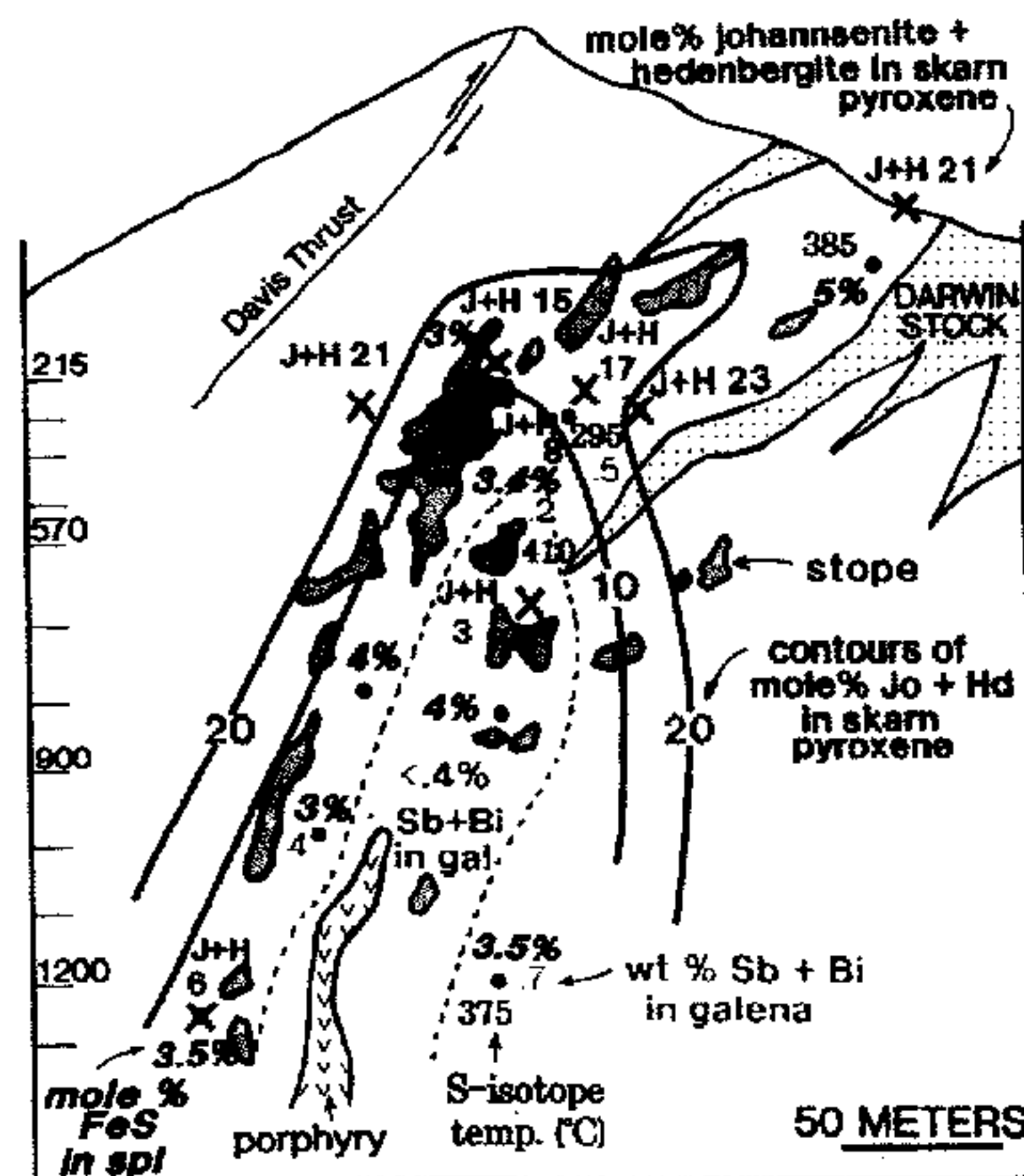


FIG. 14. Cross section through the Defiance pipe (section D'-D, Fig. 11), showing progressive outward zoning of (a) maximum Jo + Hd component in clinopyroxene and (b) wt percent Bi + Sb in galena, similar to shape of Pb/Zn > 1 metal ratio zone (Fig. 11A). Also shown are average FeS contents of sphalerite and S isotope-based temperature estimates, which show little variation. Major stope locations (taken from unpub. Anaconda Company maps) are marginal to the porphyry plug and show an inverted cup morphology. Analytical data from Hall and MacKevett (1962), Hall (1971), Rye et al. (1974), Czamanske and Hall (1975), Eastman (1980) [most sphalerite and pyroxene microprobe analyses], and this study. Abbreviations: Hd = hedenbergite, Jo = Johannsenite.

Zoning of mineral compositions—Defiance pipe

Limited data for mineral compositions from the Defiance pipe (Fig. 14) is compatible with the data presented for the Essex pipe. Iron + manganese contents of pyroxene increase upward and outward, as do the Bi + Sb contents of galena. Pyroxene compositional isopleths are concordant with metal zoning and are symmetrically distributed above the granite porphyry plug. Sphalerite shows virtually no compositional variation, however, indicating minimal changes in the sulfidation state despite major changes in the pyroxene compositions.

Zoning of sulfur isotope ratios

Three galena samples and one sphalerite from the deep central core of the Essex pipe were analyzed for sulfur isotope ratios for this study (Table 1) in order to complement the coverage of Rye et al. (1974), particularly in the deep central core of the Essex pipe. Samples were selected, crushed, and then handpicked under a binocular microscope. The combined data set is illustrated in Figure 15A, where $\delta^{34}\text{S}$ values of galena are interpreted as zoned around the

TABLE 1. Sulfur Isotope Data from the Essex Pipe, Darwin Deposit

Sample no.	Level	$\delta^{34}\text{S}$ gl	$\delta^{34}\text{S}$ spl	$\Delta\text{spl-gl}$	T°C
Dar1	600	+1.3	+2.8	1.5	420
Dar2	900	+2.1			
Dar3	600	-2.0			

Analyses performed at Geochron Labs, Cambridge, Massachusetts; fractionation factors from Ohmoto and Rye (1979); samples plotted in Figure 15

Abbreviations: gl = galena, spl = sphalerite

skarn pipe defined by mineral, metal, and mineral compositional zoning (Figs. 5, 10, 12, and 13). The $\delta^{34}\text{S}$ values of galena are highest in the central, deep part of the pipe and decrease outward and upward, although the core to margin zoning is greatest on the west side of the pipe. The $\delta^{34}\text{S}$ values of sphalerite from Rye and Ohmoto (1974) also are interpreted as zoned around a central core; $\delta^{34}\text{S}$ values of galena are employed here because Rye et al. (1974) present a wider spatial distribution of galena than of sphalerite data.

In contrast to the pattern for the Essex pipe, sulfur isotope ratios from the Defiance pipe show only minor variations (Rye et al., 1974). Values decrease upward in a relatively systematic manner, e.g., the $\delta^{34}\text{S}$ value for pyrite changes gradationally from 4.4 per mil at the 1200 level to 2.0 per mil near the surface. The available data are insufficient to define a horizontal zonation.

Thermal zoning

In order to verify the data of previous workers, additional temperature estimates were made for this study employing sphalerite-arsenopyrite compositional geothermometry (3 samples; Table 2) and sphalerite-galena sulfur isotope thermometry (1 sample; Table 1). Arsenopyrite-sphalerite temperatures were estimated from electron microprobe analyses of arsenopyrite and sphalerite grains from coexisting arsenopyrite-sphalerite-pyrite (or pyrrhotite) assemblages. One of these samples contained pyrrhotite blebs and these were included in the estimate of original sphalerite composition. The calculations used the intersections of arsenopyrite compositional isopleths (Kretschmar and Scott, 1976) with sphalerite compositional isopleths (Scott and Barnes, 1971) on a log f_{S_2} vs. temperature diagram.

Temperatures derived from S isotope fractionation (Rye et al., 1974; and this study), phase homogenization (Czamanske and Hall, 1975), and arsenopyrite geothermometry (this study) all are compatible with thermal zoning around the Essex pipe. Despite the variety of techniques employed, all temperature estimates are $>350^\circ\text{C}$ in the core of the skarn pipe and $<300^\circ\text{C}$ on the margins of the skarn (Fig. 15B). There appears to be a small vertical thermal gradient and a large horizontal thermal gradient. The fact that temperatures estimated from sphalerite-arsenopyrite-iron sulfide equilibria, which reflect presulfidation conditions, are compatible with temperatures estimated from phase homogenization and sulfur isotope fractionation (Fig. 15B), suggest that the latter estimates also reflect presulfidation conditions.

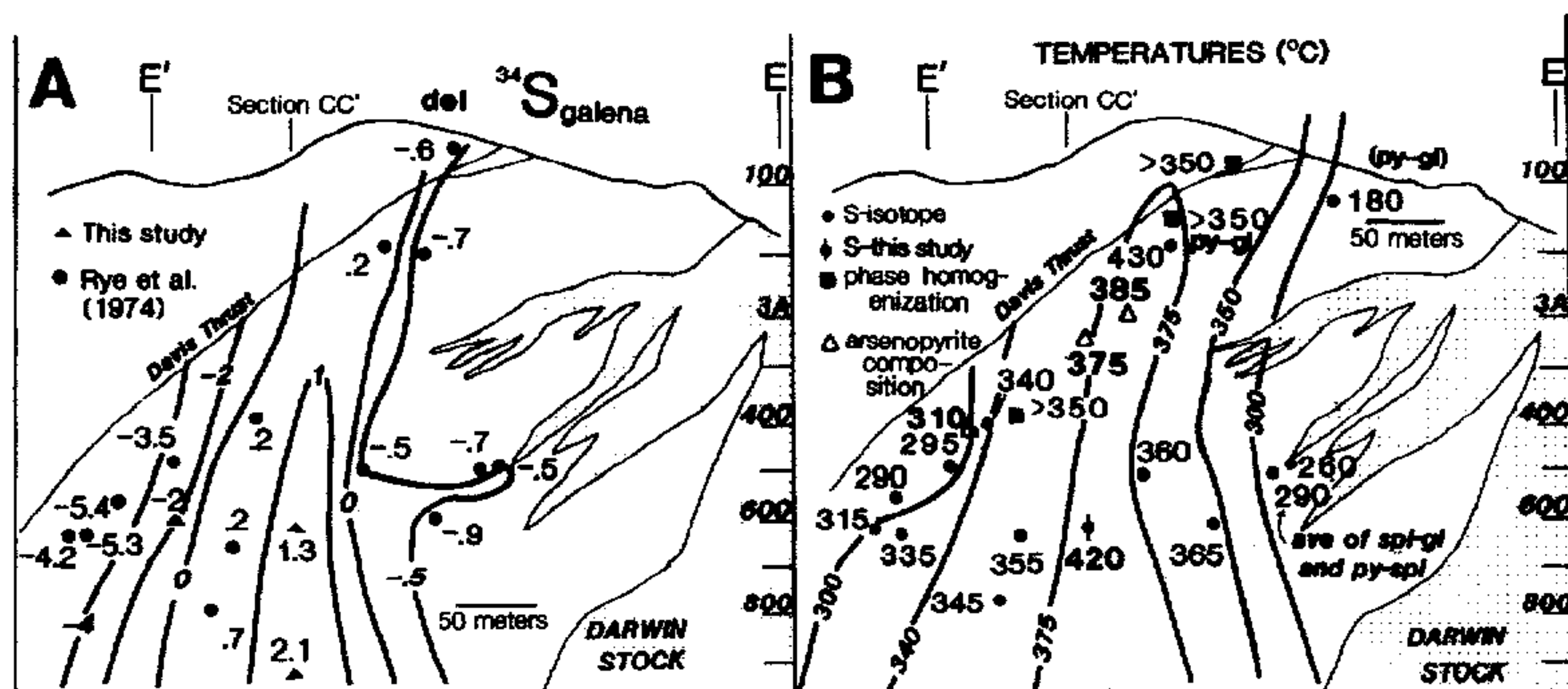


FIG. 15. A. Distribution of sulfur isotope ratios in galena. B. Distribution of sulfide depositional temperatures for cross section E-E in the Essex pipe. Sulfur isotope ratios from Rye et al. (1974) (with sample locations from Rye and Ohmoto, 1974; and Czamanske and Hall, 1975) and this study. Temperature estimates based on (1) S isotope ratio fractionation between sphalerite and galena, unless noted (from Rye et al., 1974, and this study), (2) minimum temperatures for rehomogenization of exsolved sulfosalts (Czamanske and Hall, 1975), and (3) compositions of coexisting sphalerite and arsenopyrite (this study).

TABLE 2. Data for Calculation of Arsenopyrite-Sphalerite Temperatures¹

Sample no.	87 Arsenopyrite	87 Sphalerite	40 Arsenopyrite	40 Sphalerite	82 Arsenopyrite	82 Sphalerite
N ²	4	4	6	3	3	3
Fe	35.25 (.04) ³	5.58 (.32)	35.31 (.36)	7.55 (.22)	35.47 (.15)	6.62 (.44)
Zn	0.05 (.02)	60.54 (.54)	0.02 (.02)	58.13 (.35)	0.02 (.01)	59.45 (.47)
Mn	0.02 (.01)	0.28 (.04)	0.01 (.01)	0.52 (.04)	0.02 (.01)	0.28 (.03)
As	43.50 (.13)	0.0 (0)	42.48 (.29)	0.0 (0)	43.93 (.21)	0.0 (0)
S	21.04 (.10)	33.12 (.07)	21.55 (.28)	33.41 (.41)	20.33 (.11)	33.30 (.18)
Total ⁴	99.91	99.52	99.37	99.61	99.77	99.65
Mole% FeS		9.8 (.5)		19 ⁵ (.2)		11.6 (.6)
Mole% As	31.03 (.03)		30.27 (.19)		31.60 (.07)	
Temp ⁶	375 (5)°C		310 (10)°C		385 (5)°C	

¹ Electron microprobe analyses (in wt %) performed using Cameca microprobe at Washington State University

² N = number of spot analyses for that sample

³ One standard deviation in parentheses

⁴ Electron microprobe analyses in Eastman (1980) indicate approximately 0.5 wt percent Cd is typically present in Darwin sphalerite

⁵ Based on presence of 7 vol percent pyrrhotite inclusions

⁶ Uncertainty from microprobe analyses only

Comparison of isotherms determined by the above techniques to the locations of major stopes in the Essex zone (Fig. 16) suggest that a close correlation existed between temperature and ore deposition; ore was deposited in the temperature interval from 375° to 300°C. The pattern of isotherms also is similar to patterns of mineral composition, metal ratios, and mineral distribution, suggesting a common thermal control.

Isotopic temperatures from the Defiance skarn pipe (Fig. 14) also are high (>375°C). A sample yielding an anomalously low temperature (295°C) represents a zone of major calcite-quartz sulfide alteration (as indicated by underground mapping), whereas the other samples are from sulfide-bearing skarn (sample descriptions in Hall and MacKevett, 1962, p. 69).

Hence, the higher and lower temperature samples reflect temperatures of skarn formation and skarn destruction, respectively, rather than a time-independent thermal zonation. As all the data are from the central part of the pipe or the bedded skarn extension (cf. Hall and MacKevett, 1962), the data cannot resolve a horizontal thermal zonation. The locus of major ore deposition, as indicated by locations of major stopes, shows a bell-shaped pattern centered on the porphyry body (Fig. 14) similar to that seen for the Essex pipe. Although definitive temperature data are not available, by analogy with the Essex pipe, the distribution of ore shoots in the Defiance pipe may have been controlled by thermal patterns.

Discussion

Metal zoning

Metal zoning in the Essex pipe (Fig. 10) is dominated by an upward and outward increase in Pb/Zn, similar to that observed in other lead-zinc skarns (e.g., Einaudi et al., 1981; Shimizu and Iiyama, 1982; Yun and Einaudi, 1982; Meinert, 1987; Megaw et al., 1988), followed by a reversal on the outer margins, where relatively low Pb/Zn ratios are characteristic of pyrite- and/or pyrrhotite-rich assemblages low in both Pb and Zn. Similar outward changes in Pb/Zn ratios have been observed by Loucks and Petersen (1988).

The pattern of Ag/Pb zoning is similar to that of Pb/Zn, in that an upward and outward increase in Ag/Pb is observed in the highly mineralized portions of the pipe, followed by a reversal to lower ratios on the fringes. Similar zonal patterns have been described by Megaw et al. (1988) for several skarns and replacements in northern Mexico. At Darwin, the location of highest Ag/Pb ratios reflects the presence of paragenetically younger, Ag-rich galena (Hall,

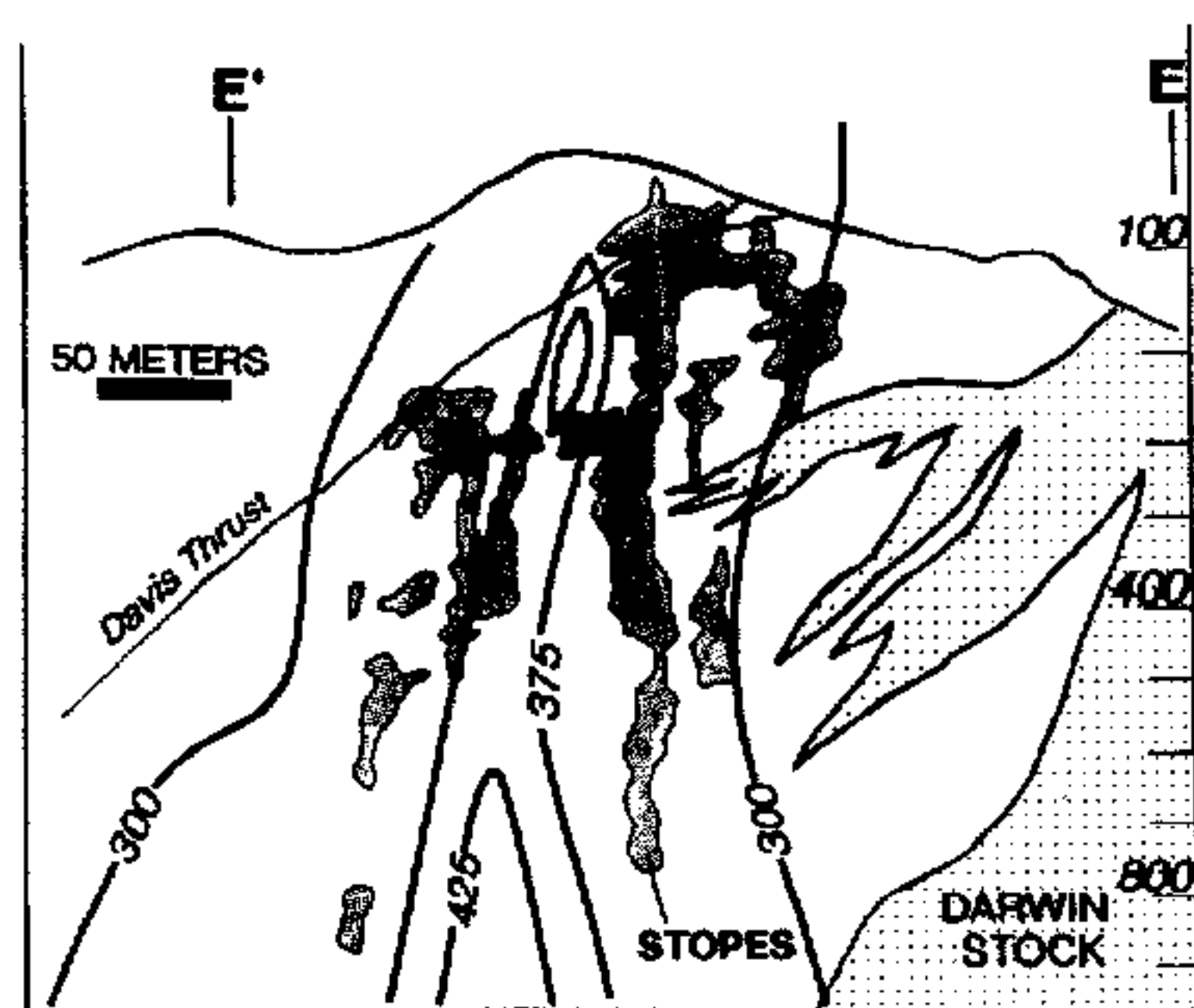


FIG. 16. Distribution of stopes (from unpub. Anaconda Co. maps) and sulfide mineral isotherms (from Fig. 15B) for the E-E cross section of the Essex pipe, illustrating (1) symmetrical zoning of stopes around the pipe core, and (2) localization of most stopes in the area between the 375° and 300°C isotherms.

1971; Czamanske and Hall, 1975) which tends to occur outside the core of the pipe (Fig. 12D).

Mineral zonation

Perhaps the key observation concerning minerals and their distribution at Darwin is that the Darwin deposit is truly a skarn, rather than a series of "massive replacement bodies in silicated limestone" (Rye et al., 1974, p. 468). Sulfide mineral as well as metal ratio patterns mimic (and are partly caused by) silicate mineral distribution patterns, e.g., distribution of garnet types and distribution of pyroxene compositions. Furthermore, the paragenetic relations between sulfides and silicates indicate that during sulfide deposition, the hydrothermal fluid evolved through a range of physiochemical conditions from those appropriate for garnet + pyroxene and then garnet stability, to those in which both garnet and pyroxene were hydrolyzed.

Mineralizing pluton

Metal, mineral, and mineral compositional zoning, as well as isotopic zoning, suggest that a vertical locus of upwelling hydrothermal fluids was located about 150 m from the main contact with the Darwin stock and that these fluids flowed both toward and away from the stock. On this basis, a genetic tie between the Pb-Zn-Ag skarns and the Darwin pluton can be ruled out. Furthermore, structural evidence (Newberry, 1987) that indicates the Darwin Pb-Zn skarns postdate the Darwin pluton by at least 20 Ma also rules out a genetic link to a deeper off-shoot of the Darwin stock. Major and trace element compositions of the Darwin stock greatly differ from those of the deep porphyry body at the Defiance pipe (Newberry, 1987), which suggests the deep porphyry body is unrelated to the Darwin stock.

The problem of determining the mineralizing pluton is not unique to the Darwin skarn. There is, unfortunately, nothing about the spatial proximity of pluton to skarn which guarantees a genetic relationship, especially in districts where multiple plutonic events are known to have occurred. For example, the Cirque Lake stock is coincidentally next to (north of) the MacTung W skarn, N.W.T., but zoning of quartz vein densities, alteration, and mineralization point to a hidden plutonic source at depth south of the deposit (Atkinson and Baker, 1986).

Temperatures of ore deposition

Rye et al. (1974) determined isotopic temperatures for the Essex zone that ranged from 365° to 255°C and stated that the uncertainties in sampling and isotopic techniques could not explain the observed variations in isotopic temperatures. These authors concluded that spatial variations in depositional temperatures for sphalerite-galena ores probably did exist

and chose a median temperature of $325^{\circ} \pm 55^{\circ}\text{C}$. Rye et al. (1974) did not attempt to place their temperature estimates into a thermal zoning context (and they downplayed temperature decline as a cause of ore deposition), but they recognized that "near the intrusion on the east fringe of the mineralized zone, the isotopic temperatures for some unknown reason are low" (p. 474). The present study explains this apparent anomaly; if all the temperature estimates based on sulfur isotope fractionation, phase homogenization, and sphalerite-arsenopyrite compositions are compiled in a single cross section, and if the temperature estimates are taken at face value, a thermal zoning pattern for the main stage of ore deposition emerges that is consistent with the zoning of mineral assemblages, mineral compositions, and metal ratios. This overall zonal pattern is centered on a vertical skarn pipe located west of the Darwin stock.

That S isotope-based temperatures are compatible with the arsenopyrite-sphalerite and the phase homogenization temperatures (Fig. 15B) suggest that the S isotope fractionations also reflect presulfidation equilibrium temperatures. Lack of isotopic equilibration of sphalerite at the lower temperatures of sulfidation ($<250^{\circ}\text{C}$) is suggested by the fact that much of the pyrrhotite present (Eastman, 1980) is the monoclinic polymorph (stable below 254°C ; Kissen, 1974), but sulfur isotope temperatures from the pyrrhotite zone (Rye et al., 1974) are consistently in the vicinity of 300°C . Although the sulfidation reactions described require addition of new sulfur to the sphalerite to precipitate the tiny inclusions of pyrrhotite or pyrite, the amount of added sulfur, and hence potential change in bulk sulfur isotope ratio of the sphalerite (assuming the presulfidation sulfur in sphalerite does not isotopically reequilibrate), is small. For example, if sulfidation of a sphalerite results in precipitation of 5 modal percent pyrite (a typical upper limit seen at Darwin), and the added sulfur is in equilibrium with the new inclusion pyrite at 300°C (at which temperature $\Delta_{\text{pyrite-sphalerite}}$ is about 1‰), addition of the new sulfur results in an increase in the $\delta^{34}\text{S}$ value for the altered (composite) sphalerite grain of about 0.05 per mil—well within analytical uncertainties.

The temperature distribution pattern illustrated in Figure 15B may represent a time-integrated pattern; i.e., temperature estimates from sulfides in the core of the deposit represent earlier deposited skarn-associated ores, whereas the temperature estimates from the margin of the deposit are from sulfides deposited at a time when the entire deposit had cooled to lower temperatures. This is a viable hypothesis; but the gradational change in temperatures measured from pipe core to margin might argue against it. Although we have not seen either the bulk of the samples which were submitted for S isotope studies or

the precise sampling locations, our underground mapping in the vicinity of previous sample locations suggests that the bulk of the samples taken were from skarn-associated ores. Consequently, we suspect that the thermal distribution of Figure 15B represents a snapshot of temperatures present in the deposit during the main stage of sulfide deposition.

Regardless of the precise temperature distribution, much of the sulfide deposition took place at temperatures in excess of 375°C, probably in the presence of a strong lateral thermal gradient. At an $X_{\text{CO}_2} < 0.02$ (computed by Rye et al., 1974), pressure < 0.5 kbar (indicated by aplite geobarometry; Newberry, 1987; and by 20% FeS sphalerite with pyrite-pyrrhotite; Hall and MacKevett, 1962), and oxidation state (see below) between hematite-magnetite and nickel-nickel oxide, grandite garnet is stable to at least 350°C (Taylor and Liou, 1978). This is consistent with the petrographic data (e.g., Fig. 7B) that suggests that much of the sulfide was deposited with or in equilibrium with garnet skarn. A strong lateral thermal gradient (Fig. 15B) suggests that sulfide deposition was not isothermal, as is also suggested by the observed variations in sulfide-silicate relations (e.g., Fig. 12H). Indeed, the thermal patterns suggest that the main stage of sulfide deposition took place over a temperature range from $>400^\circ$ to $<300^\circ\text{C}$.

Conditions of sulfide deposition and deposit formation

The similarities in characteristics of both the Essex and Defiance pipes suggest that an integration of data from both pipes is a valid approach in establishing a generalized model for skarn sulfide pipes in the Darwin district. Sphalerite compositional patterns (Figs. 13D and 14) from this study and S isotope variations from Rye et al. (1974) and this study can be used to estimate changes in pH, f_{O_2} , and f_{S_2} during ore deposition (Fig. 17). Sulfide deposition took place over a range of temperatures, from $>400^\circ$ to $<300^\circ\text{C}$. However, because variations in mineral $\delta^{34}\text{S}$ values are far more sensitive to changes in pH and oxidation state than to temperature in the 300° to 400°C range (Ohmoto, 1972), an isothermal pH-log f_{O_2} diagram can be employed as a first approximation to track fluid evolution (Fig. 17). Most parameters chosen (temperature, total sulfur, etc.) are the same as those employed by Rye et al. (1974) to facilitate comparison.

The initial fluid was either of magmatic derivation or was in equilibrium with granitic rocks at high temperatures, because of the high salinities of ore fluids (>24 wt % NaCl equiv; Rye et al., 1974), the presence of a quartz porphyry plug at depth under the Defiance pipe, and the presence of high-temperature skarn minerals at depth in both pipes. A bulk fluid $\delta^{34}\text{S}$ value of 5 per mil is within the magmatic range for fluids in equilibrium with I-type or magnetite series grani-

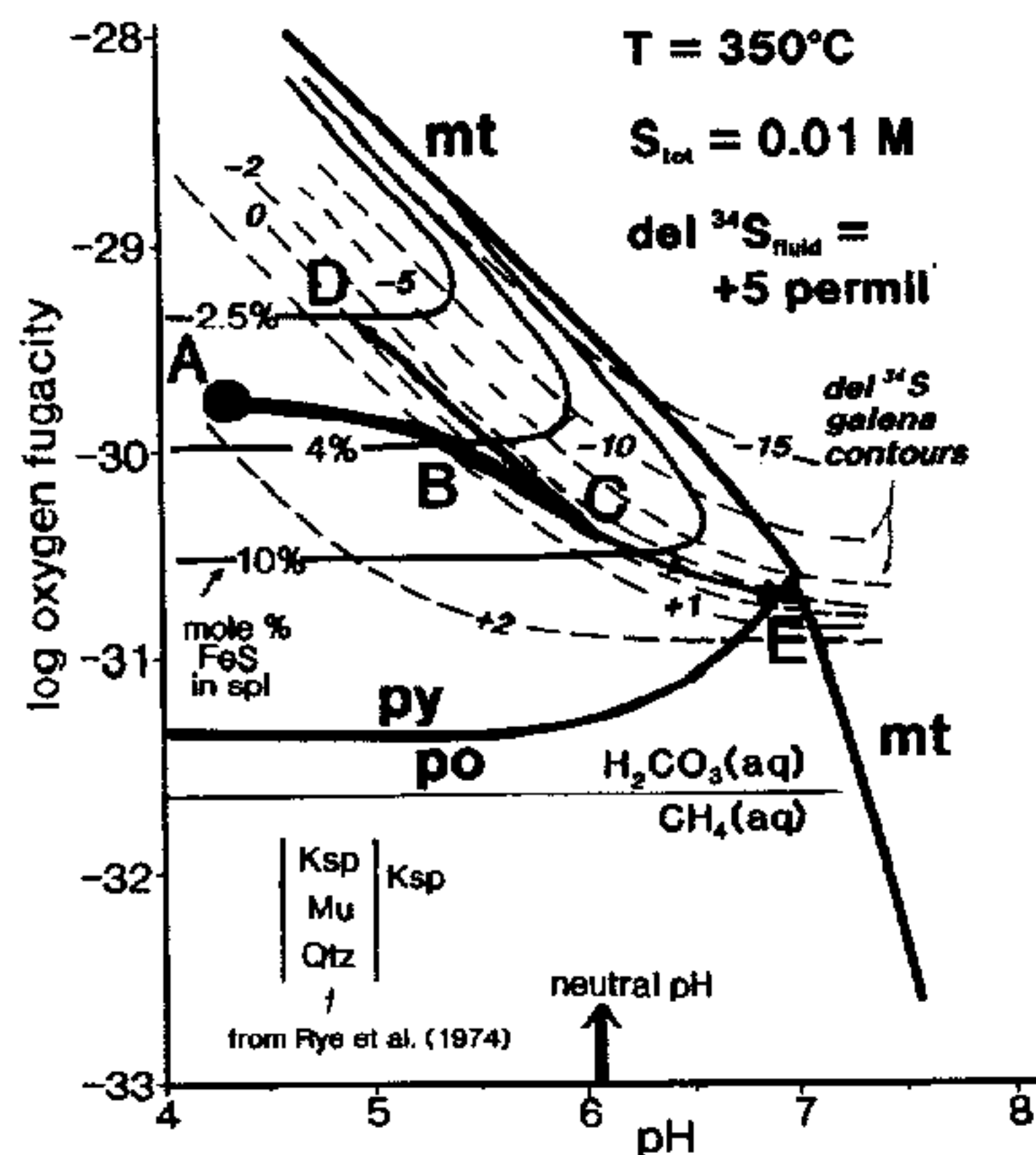


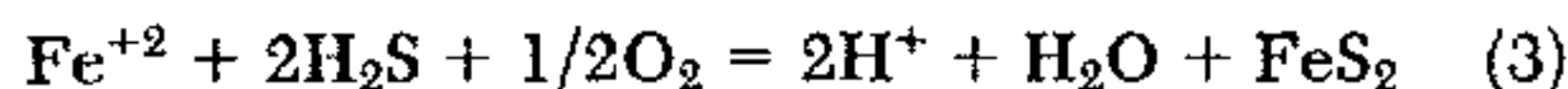
FIG. 17. Log f_{O_2} -pH diagram (350°C) modified from Rye et al. (1974) showing simplified vertical and lateral chemical evolution of the Essex pipe ore-forming fluids, based on sphalerite compositions (Fig. 13D) and sulfur isotope ratios (Fig. 15A). This isothermal diagram is a gross simplification of the fluid evolution, as the data in Figure 15B clearly indicate a $>125^\circ\text{C}$ variation in fluid temperature between the pipe core and margins. Sulfur isotope ratio isopleths (modified from Rye et al., 1974) are for galena in equilibrium with a fluid containing 0.01 M sulfur and with a bulk $\delta^{34}\text{S}$ value of 5 per mil. Locations of sulfide oxide field boundaries are somewhat different (although the diagram topology is maintained) using most recently published log K 's; this diagram is retained to permit direct comparison with results presented by Rye et al. (1974). Some curves were calculated using the computer program of Ripley and Ohmoto (1979). Letters A to E represent estimated fluid conditions for various parts of the deposit, discussed in text. Abbreviations: Ksp = K feldspar, mt = magnetite, mu = muscovite, po = pyrrhotite, py = pyrite, qtz = quartz, spl = sphalerite.

toids at oxidation states between nickel-nickel oxide and hematite-magnetite (Ohmoto and Rye, 1979). As pyrrhotite is not present in the deepest workings (but low iron sphalerite + pyrite is present), the oxidation state of the initial fluid was above that of pyrite-pyrrhotite-magnetite. Interaction of this fluid with micaceous hornfels (Fig. 5) would have set the initial pH at less than 5 (minimum required for muscovite-K feldspar-quartz stability at 350°C for the fluid composition as derived from fluid inclusions by Rye et al., 1974). On cooling at constant composition from high temperature to 410° to 430°C (the highest sulfide depositional temperatures determined in this study) such a fluid would precipitate galena with a $\delta^{34}\text{S}$ value of approximately 2 per mil, sphalerite with a $\delta^{34}\text{S}$ value of approximately 3.5 per mil (values estimated using data in Ohmoto, 1972), and with an

iron content of about 3 mole percent (solid circle labeled "core" in Fig. 16).

The first appearances of K feldspar in the Essex skarn at the 600 level, decrease in galena and sphalerite $\delta^{34}\text{S}$ values to about 1 and 3 per mil, respectively, and slight increase in iron content of sphalerite to about 4 mole percent are consistent with fluid evolution to a slightly lower oxidation state and an appreciably higher pH (point B, Fig. 17). Neutralization and slight reduction of the sulfide-depositing fluids are likely consequences of reaction with the pyroxene-bearing skarn and slightly graphitic marble present below the 600 level (Essex pipe). A major portion of the sulfide in this part of the skarn occurs as replacement of iron-poor pyroxene (Fig. 7E).

Above the 600 level (Essex pipe) garnet skarn with minor pyroxene is common, and pyroxene skarn is rare. Fluids traveling up and to the east from the skarn pipe core toward the stock (at the 600 level) followed a path of decreasing oxidation state and increasing pH, as indicated by sphalerite compositions (Fig. 13D) and decreasing S isotope ratios (Fig. 15A) to neutral pH for that temperature (point C, Fig. 17). Increase in pH is a logical consequence of interaction with carbonates, but the appreciable decrease in oxidation state is not (given the low graphite content this marble), unless pH is chemically linked to f_{O_2} . One possible link is precipitation of pyrite from an H_2S -predominant solution:



for which an increase in pH yields a decrease in $\log f_{\text{O}_2}$.

Lower iron sphalerite in the uppermost part of the Essex pipe (east side) together with little change in S isotope ratios (Fig. 15A) requires both oxidation and pH decrease, that is, a reversal in the overall trend (path C→D, Fig. 17). Decrease in pH is consistent with sericite-quartz alteration of K feldspar and chlorite alteration of garnet in the upper part of the skarn (Fig. 12H). Rye et al. (1974) indicate that hydrothermal fluids responsible for (late) carbonate deposition were not purely of magmatic derivation; perhaps mixing of such nonmagmatic fluids with the upwelling skarn-forming fluids resulted in oxidation. Oxidation could cause a decrease in pH (especially at temperatures below 300°C) by partial conversion of the weak acid H_2S to the strong acid H_2SO_4 .

Hydrothermal fluids in the Essex pipe flowing from the core to the west (path B→E, Fig. 17) follow a path similar to the east-flowing fluids, but the high graphite content of the marbles to the west of the pipe caused a greater decrease in oxidation state (equilibrium with graphite was not attained, however). The presence of unreplaced carbonate on both sides of the Essex pipe (e.g., Fig. 5) indicates that

reaction with carbonate alone did not produce the high pH characteristic of fluids in the western pyrrhotite-pyrite zone. Here again, a coupled f_{O_2} -pH reaction, such as in eq (3), probably caused pH to increase as f_{O_2} decreased. The importance of a pyrite-precipitating reaction is suggested by the lack of further increase in pH (i.e., no magnetite-only zone) once pyrrhotite becomes the predominant iron sulfide. Variations in sulfur isotope ratios over short distances in the pyrrhotite-magnetite-pyrite zone (Fig. 15A) probably were caused by minor fluctuations in the fluid oxidation state (as suggested by fluctuations between pyrite, magnetite, and pyrrhotite stability in this zone; Eastman, 1980).

The data available for the Defiance pipe permit an interpretation broadly similar to that of the Essex pipe. Most notably, although there are major variations in pyroxene and galena compositions in the Defiance pipe (Fig. 14), variations in sphalerite composition (Fig. 14) and sulfur isotope ratios (Rye et al., 1974) are quite small. Compositions of sphalerite in located samples vary from 3 to 3.5 percent FeS at depth to 5 percent FeS near the surface, compatible with an oxidation state decrease similar to that seen in the mid-deeper parts of the Essex pipe. Sulfur isotope ratios from galena and sphalerite show no systematic variations, but the values (Rye et al., 1974) of +0.9 to -0.3 (galena) and 3 to 1 (sphalerite) are similar to those seen in the lower and central parts of the Essex pipe. The absence of major variations in sphalerite compositions and isotopic ratios in the Defiance pipe partly reflects limited sampling outside of the pipe core region (Fig. 14) and partly reflects the lack of graphite in host carbonate rocks around the Defiance pipe (as indicated by surface and underground mapping).

The model presented here hypothesizes that fluids were derived from a source below the central part of the Essex orebody and not from the adjacent Darwin stock. Hence, the absence of mineralization and appreciable alteration in the Darwin stock is a consequence of the lack of genetic connection between the Darwin stock and the ores. The absence of Pb-Zn skarns east of the Darwin stock (Fig. 1) is related to the absence of granite porphyry bodies in that area. Further, the distal nature of Pb-Zn skarns (Einaudi et al., 1981) is reaffirmed, as the orebodies extend outward from a deeper source, unexposed at present in the Essex pipe, but seen at the Defiance pipe. Finally, the relatively low temperatures of ore fluids (<400°C) can be reconciled with a magmatic source, given that (1) the most likely source lies at depth below the orebodies, (2) the source was a high F granite with a composition near the ternary eutectic (hence, a solidus temperature of about 550°C; Newberry, 1987), and (3) the ore fluids cooled as they rose and moved outward.

Comparison with other Pb-Zn skarns

Pb-Zn skarns are typically characterized by pyroxene with high to very high Fe + Mn contents (Einaudi et al., 1981), very unlike those seen at Darwin (Fig. 8). High Mg contents in Pb-Zn skarn pyroxenes are considered indicative of proximity to the fluid source (e.g., Meinert, 1987), which is compatible with a granite porphyry body seen deep in the Defiance pipe. Lack of evolution to high Fe-Mn contents in Darwin skarn pyroxene may be related to the apparent instability of pyroxene in the aluminous environment at Darwin or to the relatively deep level of erosion.

Symmetric (and similar) distributions of isotherms, metal ratios, and stopes (Figs. 10, 15B, and 16), and asymmetric-inconsistent patterns of pH- f_{O_2} changes (Fig. 17) around the skarn core at the Essex pipe suggest metal deposition took place at least partly due to temperature decrease. The Darwin deposit appears to have a much greater thermal gradient than observed in other Pb-Zn skarns; $<50^{\circ}\text{C}/\text{km}$ for Providencia, Mexico (Sawkins, 1964) and $23^{\circ}\text{C}/\text{km}$ (regional gradient) for Groundhog, New Mexico (Meinert, 1987) relative to the $100^{\circ}\text{C}/100\text{-m}$ lateral gradient for Darwin. Based on data from the above studies, Megaw et al. (1988) concluded that fluid cooling is not a major control on mineralization in Mexican Pb-Zn skarn manto deposits, as Rye et al. (1974) concluded about Darwin. However, because it is nowhere demonstrated that the pattern of sampling has succeeded in isolating the factor of time, i.e., that the measured temperatures all reflect the same instant of time, it is unlikely that any of the studies (including this one) have measured a true thermal gradient. If one accepts the data at face value, there is still a problem in comparing the values inasmuch as the two thermal gradient studies cited above are gradients along the fluid conduit, not perpendicular to the fluid conduit. Meinert (1987) showed a dike to marble thermal gradient of 35° to 50°C over 5 to 20 m; a higher gradient than that seen at Darwin, although a lower absolute decrease in temperature. Two points can be made (1) it is not clear that any author has presented a true thermal gradient for a Pb-Zn skarn, hence the potential effects of solution cooling on metal deposition in the Pb-Zn skarn environment are not yet established; and (2) the geometry of isotherms in Pb-Zn skarns probably varies considerably. The latter effect is not only important in developing chimney vs. manto morphology (Megaw et al., 1988) but developing Pb-Zn skarn morphology and zonation patterns.

Conclusions

The Darwin deposit illustrates several characteristics of skarn deposits and several problems inherent in skarn studies.

1. The Darwin Pb-Zn-Ag deposit fits in the continuum between skarn deposits and carbonate-hosted Pb-Zn-Ag deposits. Metal deposition in the Darwin deposit clearly began after some, but not all, calc-silicate deposition, as indicated by skarn with interstitial sulfides, sulfide-rich veins which contain and/or are enveloped by garnet, sulfide-quartz-carbonate veins associated with destruction of garnet, and sulfide veins and replacements in marble. Thermal gradients, pressure of formation, and longevity of individual fluid flow conduits, among other variables, probably determine the degree of spatial proximity of skarn and nonskarn ores in a given district.

2. Coincidence of zoning patterns for skarn silicates and for Pb-Zn-Ag ores at Darwin indicates that although ore and gangue were not deposited simultaneously, they belong to the same evolving hydrothermal system, and they should be treated as a single entity.

3. Because sulfur isotope fractionation factors are relatively insensitive to temperature in the 300° to 400°C range, metal deposition at Darwin has been treated as a simple, essentially isothermal process. In detail the process was complex, probably took place over a temperature decrease of $>125^{\circ}\text{C}$, and probably involved complex (Fig. 15) but interrelated changes in solution temperature, pH, oxidation state, and major element chemistry.

4. This study illustrates the difficulty in assigning a skarn to a mineralizing pluton. The spatial proximity of pluton and skarn, although taken by many as prima facie evidence for cause and effect, is, in itself, not very compelling evidence for a genetic link.

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