Hunt et al., eds., 2012, Vertebrate Coprolites. New Mexico Museum of Natural History and Science, Bulletin 57.

EARLY PROCESSES IN THE FOSSILIZATION OF TERRESTRIAL FECES TO COPROLITES, AND MICROSTRUCTURE PRESERVATION

KURT HOLLOCHER[1] AND THOMAS C. HOLLOCHER[2]

[1] Geology Department, Union College, Schenectady, New York 12308, USA, email: hollochk@union.edu;
[2] Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02454, USA

Abstract—Carnivorous scat and herbivorous dung are so chemically labile and, in general, physically fragile, that they face a race between disintegration and preservation, and disintegration almost always wins. It is clear from the normally very short life times of feces that preservation processes must occur very early, perhaps on a scale of days to a few years. Early mineralization is critical and likely is commonly aided by burial and the onset of long-term anaerobic conditions. This slows decay and physical disruption, and places the material in contact with ground water, which can be a source of chemical components for mineralization. In addition to anaerobic stabilization, work over the past twenty years has established that the very bacteria active in tissue and feces decay can, under appropriate conditions, facilitate their mineralization. This process likely contributes to the preservation of dung, and we discuss an example of this process in the preservation of dinosaur dung. In the case of scat from carnivorous animals, an additional important factor is the dietary load of calcium and phosphate acquired chiefly from ingested bone. Some or much of these chemical components appear in scat as a microcrystalline apatite slurry which, with further crystallization, lends structural strength soon after scat deposition. The partially pre-mineralized state of scat gives it a preservational advantage, which probably explains why phosphatic coprolites greatly outnumber those derived from dung in the fossil record. We discuss two studies of phosphatic coprolites in which early apatite precipitation was important for their preservation. In one, later permineralization was complete. In the other, mineralization apparently ceased at an intermediate state, after complete precipitation of autochthonous apatite, but before subsequent permineralization or recrystallization. Rapid mineralization can preserve coprolites and some original interior structures in exquisite detail. With high-fidelity preservation, coprolites can provide a window, unavailable elsewhere, into the diets and digestive system characteristics of the producing animals.

INTRODUCTION

Coprolites, the term applied to fossilized feces, generally mimic the three-dimensional structure of the original feces, or preserve recognizable dietary structures within, or realize both characteristics. Indeed, coprolites are usually recognized in the field by their three-dimensional resemblance to modern examples of animal feces. In short, coprolites generally look like feces turned to stone (Matley, 1939a; Bradley, 1946; Sawyer, 1981, 1998; Chame, 2003; Ghosh et al., 2003; Northwood, 2005; Hunt et al., 2007; Wood et al., 2008; Duffin, 2009; Månsby, 2009; Farlow et al., 2010; Sardella et al., 2010; Sharma and Patnaik, 2010).

Feces in terrestrial environments are subject to rapid degradation, days to weeks in moist warm climates to a few years in dry ones, by aerobic bacteria, fungi, and mechanical processes. Because general shape and dietary content of feces are rarely preserved as coprolites, it is clear that processes stabilizing them must begin promptly and either block aerobic degradation or successfully compete against it. We will first discuss in general the factors that lead to coprolite preservation and some of the features that can be preserved, and then give as examples the results of studies on three quite different sets of coprolites in which some primary features are well preserved and which afford insight concerning early stabilizing processes.

The difficulties in developing mechanistic scenarios for coprolite formation are: 1) the fact that fossilization of feces is a rare event (Chin, 2002); 2) the need for early stabilization to halt or retard aerobic or mechanical degradation; and 3) the need to define subsequent diagenetic processes, such as permineralization and the degradation and loss of organic material (e.g., kerogenization, oxidation) that can take place over the geological lifetime of the specimen. An additional complexity is the fact that the feces of herbivorous animals (dung herein) are quite different in composition from those of carnivorous ones (scat herein). Although both types of feces contain a paste like binder comprised largely of bacteria and microbial biofilm ("extracellular biopolymers:" Decho, 2010, p. 137), dung is rich in undigested vegetable fiber whereas scat contains considerable amounts of dietary calcium phosphate in solution, as a micro- or nanocrystalline slurry, as undigested bone and teeth, or as all three, depending on the digestive physiology of the animal. The slurry consists of finely divided calcium phosphate minerals precipitated from supersaturated solution of calcium and phosphate largely derived from the digestive demineralization of bone and teeth (Fisher, 1981; Chin et al., 1998; Larkin et al., 2000; Chin, 2007a; Månsby, 2009; Farlow et al., 2010; Eriksson et al., 2011).

Another potentially significant factor is the form in which waste nitrogen is excreted. Mammals excrete urea, a water soluble compound, separately from feces, whereas most birds and lizards, and possibly dinosaurs, excrete or excreted uric acid, a highly insoluble compound that can become mixed with feces due to the anatomy of the cloaca as a common channel for excretion. Thus, in uric acid producers, feces contain an additional relatively insoluble organic compound rich in nitrogen. Though uric acid has been found in small amounts in some coprolites in an archeological context (Toker et al., 2005), we know of no work on uric acid as an early structural component in the coprolite literature.

The need for early stabilization is particularly pressing in the fossilization of dung, which is composed almost entirely of easily decomposed organic materials. Clearly, in this case, early mineralization must occur to preserve its original form and, potentially, traces of its internal organic inclusions. Without early mineralization, which must come almost entirely from external (e.g., ground water) sources, dung would be decomposed and disaggregated, or, if buried, would be reduced to thin organic laminae or entirely vanish. It is likely, therefore, that scat,

with its content of insoluble phosphate minerals from diet, and dung, lacking insoluble minerals, must experience quite different taphonomic processes shortly after their deposition in order to be preserved.

PHOSPHATIC COPROLITES

Origin of Phosphatic Coprolites

The great excess of dietary calcium and phosphate ingested by carnivorous animals beyond that required for growth is eliminated largely in feces. This excess is greatest in those that consume whole animals or bones with or in preference to tissue. Bone is demineralized in the very acidic stomach juices of some animals, and the solubilized calcium phosphate probably begins to precipitate in the intestines where the digestive contents experience a pH increase to 7 or 8 (Skoczylas, 1978). In the case of alligators in the wild, feces can contain 70% or more dry weight of minerals, chiefly carbonate hydroxyapatite, with minor amounts of calcium carbonate (Coulson and Hernandez, 1964). Most of this exists initially as a fine mineral slurry. A similar situation applies to hyenas, many of which can extensively demineralize bone (Larkin et al., 2000).

Any dissolved portion of the calcium and phosphate load of the scat precipitates within hours or days, particularly if allowed to dry. The scat at this stage can be durable, being comprised of an insoluble mineral matrix that helps support and maintain the external and internal structure. Larkin et al. (2000, p. 27) found that scat from the spotted hyena, fed a natural diet including bone, could be "trodden on forcibly" on a sandy substrate with little deformation, even when only 1 hour old or after having soaked in water for three weeks. Of course, in the case of animals that have a limited ability to digest bone, the slurry component in scat is accordingly diminished. Carnivorous animals can therefore produce scat containing crystallizing calcium phosphate that can quickly form a relatively insoluble mineral matrix of significant strength and durability.

The great advantage of phosphatic coprolites from carnivorous animals is that they come pre-mineralized at the outset, and then subsequently can experience varying degrees of diagenetic modification. We discuss below an example of a well-preserved phosphatic coprolite that never experienced diagenetic permineralization over some 65 Ma, and was preserved on the basis of its initial load of autochthonous apatite (Hollocher et al., 2010). This ability of scat to make use of dietary calcium phosphate as an early structural component probably explains why phosphate-rich (phosphatic) coprolites are overwhelmingly more abundant in the fossil record than those derived from dung, in spite of the fact that herbivorous animals occur in much larger numbers than carnivorous ones in nearly all ecosystems over great expanses of geological time (Chin, 2002).

Fluoride: A Ubiquitous Diagenetic Component in Ancient Phosphatic Coprolites

Most ancient phosphatic coprolites have incorporated considerable fluoride (Hubert and Panish, 2000; Pasteris and Ding, 2009). The range of fluoride concentrations in several analyzed phosphatic coprolites is 0.94-5.88% by weight (Gruner and McConnell, 1937; Bradley, 1946; Hollocher et al., 2005, 2010; Thiry et al., 2006). This compares with dry weight median fluoride contents of about 0.04% for bones of modern terrestrial herbivores (Field et al., 1976; Snioszek et al., 2008) and 0.25% for fresh and salt-water fish (Suga et al., 1983; Pinskwar et al., 2003). Fresh ground water has a median of about 0.2 ppm fluoride (White et al., 1963; Edmunds et al., 1987; Frape and Fritz, 1987; Gascoyne et al., 1987; Nordstrom et al., 1989). Because the original apatite mineral in bone is carbonate-hydroxyapatite (McConnell, 1970; Trueman and Martill, 2002; Elliott, 2002; Cho et al., 2003) with very little fluoride, the apatite in fresh phosphatic scat must have also been precipitated as low-fluoride carbonate-hydroxyapatite. Thus, for coprolites from terrestrial sediments, fluoride must have been picked up from ground water over geologic time as a diagenetic component.

The free energy for the apatite fluoridation reaction comes from the greater stability of francolite (carbonate-fluoroapatite) relative to carbonate-hydroxyapatite (Stearns, 1971). It is generally believed that this fluoridation is akin to solid state diffusion-ion exchange (Stearns, 1970, 1971) and involves very little, if any, recrystallization of apatite. On the other hand, Pasteris and Ding (2009) concluded that fluoride incorporation into apatite of horse tooth takes place by a process of dissolution and reprecipitation rather than diffusion through the crystal lattice. We believe that this study is not generally applicable to coprolite fluoridation because of the very high fluoride concentrations used, and other technical matters relating to the experimental and analytical conditions. It seems that fluoride diffusion into apatite occurs more slowly at high fluoride concentrations in solution because of the formation of a stable fluoroapatite surface layer (Stearns, 1970, 1971; de Leeuw, 2004). In addition, if fluoridation of apatite over geological time necessarily involved extensive dissolution and reprecipitation, it is difficult to understand how micrometer and smaller scale features could have been preserved in great detail in phosphatic coprolites.

PRESERVATION OF DUNG FROM HERBIVOROUS ANIMALS

As argued above, dung is less easily preserved as coprolites than scat of carnivores, and so is more rare (Chin, 2002). Although the dung of sheep and goats can have some mineral content (calcium oxalate: Badal and Atienza, 2007), that of most herbivores consists of easily degraded, finely commuted, partially digested vegetable material, plus bacteria and their secreted biofilm (Cheng et al., 1991). Rapid burial under wet, anaerobic conditions, is widely assumed to be critical for the fossilization of dung in most cases, though we know of no direct evidence of this other than sedimentary inference, wherein coprolites are generally found in environments where rapid burial was possible (fluvial and lacustrine environments: Sawyer, 1981; Currie et al., 1995, stomach contents; Chin and Gill, 1996; Ghosh et al., 2003; Kar et al., 2004; Prasad et al., 2005; Sharma, 2005; Farlow et al., 2010). Rapid burial also seems to be generally necessary for preservation of fossil bones (e.g., Hubert and Panish, 2000), though perhaps burial need not be quite so rapid as for dung.

Because there are generally no sources of mineral components on subaerially exposed surfaces, burial in a wet environment allows interaction between the coprolite precursor and ground water minerals. Burial thus exposes feces to ground water and sets up conditions suitable for mineralization by bacterial mediated or inorganic processes. Burial may be by sedimentation, such as deposition of new sedimentary layers by moving water, or possibly by trampling into a muddy substrate (Chin and Gill, 1996). In addition, burial protects the material from attack by coprophageous animals that can burrow into and disaggregate dung (Chin and Gill, 1996; Sharma and Patnaik, 2010), thus further increasing the likelihood of preservation. On some occasions, burial might not be immediately necessary if dung were deposited in water containing saturated or supersaturated concentrations of calcium carbonate or apatite (Chin and Gill, 1996; Hollocher et al., 2001; Matley, 1939b; Ghosh et al., 2003; Sharma et al., 2005; Thiry et al., 2006). Alternatively, if dung were deposited on wet ground, water evaporation and wicking of mineral-laden water upwards into the dung could provide another mechanism for its relatively rapid mineralization. Otherwise, slow advective flow and diffusion must suffice. Early exposure on the surface, prior to burial, can be indicated in coprolites by desiccation cracks (Ghosh et al., 2003) and attack by burrowing coprophageous animals such as dung beetles (Chin and Gill, 1996).

In some cases the internal structures of dung are not preserved at all, but instead the dung is entombed by fine-grained sediment, which forms a mold after the dung decomposes. When the mold is later filled with mineral material, the cast becomes the coprolite (or pseudo-coprolite). These casts, however, can delicately preserve external features such as overall shape and impressions of leaves and seeds (Harrison, 2011). In a rare example of an alternative to permineralization or high fidelity molds, fire can also help preserve coprolite precursors. In archeological

contexts, the use of dried dung for fuel is relatively common (Badal and Atienza, 2007). Incompletely burned dung is partially carbonized, making bacterial attack difficult and allowing preservation of fine-scale features for long periods of time.

BACTERIAL MEDIATION OF MINERALIZATION

Background

Whereas it has long been known that microorganisms are important for degrading once living materials, it has only recently been appreciated how important they are for the precipitation of minerals leading to fossil preservation (Briggs, 2003). The best known example of microbially mediated mineral precipitation is probably that of stromatolites. Stromatolites are layered structures made of carbonate minerals precipitated during photosynthesis in cyanobacterial mats (Dupraz et al., 2009).

A considerable body of experimental and observational literature makes clear that a variety of microorganisms (chiefly or entirely bacteria), which participate in decay of soft tissues and organic matter of bone, can also facilitate the mineralization of these decaying targets in the presence of suitable ions and at pH values around 7. In experiments, biofacilitated mineralization is typically detected within a few days to a few weeks at room temperature. Sterile controls and controls in which microbial growth and metabolism are blocked through use of a bacterial inhibitor either fail to show mineralization in the specimen being tested (Vasconcelos et al., 1995; González-Muñoz et al., 2003; Rivadeneyra et al., 2006; Sánchez-Román et al., 2008), or mineralization begins much later and proceeds much more slowly (Aloisi et al., 2006; Daniel and Chin, 2010).

There are numerous minerals that microorganisms are known to precipitate under natural conditions, including gypsum, calcite and aragonite, sulfides, apatite, siderite, Fe and Mn oxides and hydroxides, and clays (Jehl and Rougerie, 1995; Little et al., 1997; Fortin et al., 1997; Lucas and Prévôt, 1985, 1991; Cailleau et al., 2004; Kim et al., 2004; Omelon and Grynpas, 2008; McNamara et al., 2006, 2009). Experimental work, particularly the pioneering studies of Briggs and coworkers (Briggs and Kear, 1993; Briggs and Wilby, 1996; Briggs et al., 1993, 1995; Davis and Briggs, 1995), has helped define the conditions under which precipitation by microorganisms can take place for minerals such as calcite (Aloisi et al., 2006; Rivadeneyra et al., 2006; Daniel and Chin, 2010), dolomite (Vasconcelos et al., 1995; Sanchez-Roman et al., 2008), apatite (Hirschler et al., 1990), and barite (González-Muñoz et al., 2003).

Bacterial mediation of mineral precipitation can occur through a variety of mechanisms. These include production of intracellular and short range extracellular gradients in chemical concentration as a result of bacterial metabolism (e.g., pH: Decho, 2010; redox state: Fortin et al., 1997), degradation of cellular components to release key reactive materials (e.g., phosphate from nucleic acids and phospholipids to precipitate apatite: Hirschler et al., 1990; oxalic acid from metabolic products to sequester Ca for calcite precipitation: Calleau et al., 2004), and concentration of chemical components in extracellular polymeric capsids (Fortin et al., 1997; Aloisi et al., 2006; Dupraz et al., 2009; Decho, 2010). Metabolic production of carbon dioxide and its release into solution is a well known means of facilitating precipitation of carbonate minerals (e.g., Rivadeneyra et al., 1996, 2006; Pierre and Fouquet, 2007). It is also well established that the great variety of bacterial cell membrane pumps, channels, symports, and antiports can act to concentrate various materials into cells. In some cases, such as the ability of bacteria to concentrate the bases of weak acids (e.g., HF) in acidic environments, the critical factor is simply membrane permeability to uncharged weak acids plus action of a proton pump (Bhatnagar and Bhatnagar, 2000).

FACILITATION OF MINERAL PRECIPITATION IN PALEONTOLOGICAL MATERIALS

Bio-facilitated mineralization can occur at ion concentrations well below those that would be in saturation equilibrium with the solid mineral phase. This suggests that the microorganisms must either sequester critical ions (e.g., Ca^{2+}, PO_4^{3+}) internally or in adjacent biofilm (Fortin et al., 1997; Dupraz et al., 2009), release a critical component from digesting substrates (e.g., nucleic acid decomposition to release PO_4^{3+}: Lucas and Prévôt, 1985), or metabolically produce a critical component (e.g., CO_2: Pierre and Fouquet, 2007), or participate in two or three of these processes. These and other processes, such as change of local pH and redox state, conspire to achieve local mineral saturation and nucleation on some suitable substrate. Further precipitation can be expected to increase the size of crystals at nucleation sites (e.g., the "large globules" of calcite of Aloisi et al., 2006, p. 1018). Thus, bio-facilitated mineralization can apparently involve lowering the activation energy of nucleation in microenvironments (Fortin et al., 1997). It is interesting that in the mineralization of fresh bone, active decay greatly accelerated deposition of calcite from calcite-supersaturated solutions in experiments by Daniel and Chin (2010). In this case, microorganisms apparently had a kinetic effect rather than a free energy effect.

The presumed mechanisms of bio-facilitated mineralization described above allow for both intracellular and intercellular mineral deposition. The former would be expected to disrupt the internal workings of participating cells, and the latter would be expected to encapsulate cells and adjacent cellular biofilms, both of which assure cell death. Intracellular mineralization of bacteria (reviewed by Omelon and Grynpas, 2008) might be expected to fill intracellular space with something resembling a microcrystal or crystals bounded by the original cell wall or membrane. On the other hand, encapsulation by intercellular mineralization would be expected to confine cell residues to what might eventually become small sealed spaces, or microcavities, within the mineral mass (Bosak et al., 2004). Whether, after diagenesis, one could recognize which of these two possible modes of bacterial form preservation occurred depends on the fidelity of preservation. Based on the literature cited above, it would seem that extracellular precipitation is more common. Although pseudomorphs of bacteria in coprolites have been reported, it is rare that they contain, in addition, the recognizable carbonaceous remains of bacteria. We are aware of only one clear example of an ancient coprolite in which the carbonaceous residues of bacteria were identified, isolated and characterized, and were associated with the location of earliest mineralization (Hollocher et al., 2001).

The early deposition of iron minerals is of interest because local redox potential can be expected to control the oxidation state of iron and thereby its solubility near neutral pH. Fe^{2+} forms many readily soluble compounds, whereas Fe^{3+} forms few and exists in aqueous environments largely as a solid hydroxide or oxide. Thus, bio-facilitated precipitation of iron minerals might involve mobilization of iron as Fe^{2+} and its precipitation nearby as ferric compounds. In the case of pyrite (FeS_2), iron precipitation is from the ferrous state but depends upon the presence of sulfide (S^{2-}), a common metabolic product of sulfate-reducing bacteria under anaerobic conditions. Because both iron and organic sulfur are constituents of tissue, pyrite, at least in small amounts, might be expected to be a common component of coprolites. We discuss below an example of a coprolite that appears to contain autochthonous pyrite (Hollocher et al., 2005).

It is ironic that microorganisms that destroy biological tissues can simultaneously mineralize them and thereby preserve fine structural details for geologic periods of time. This means of preservation can involve a variety of different bacteria and requires an organic energy source, anaerobic conditions, and mineral ions in appropriate concentrations. Bacterially-facilitated mineralization stops when as much of the original biomass as possible has been converted into bacterial biomass.

IDENTIFICATION OF BACTERIAL AND OTHER MICROSTRUCTURES IN COPROLITES

Some microstructures preserved in coprolites are relatively uncontroversial. Among these are generally larger forms such as pollen (Scott, 1987, 2003; Yll et al., 2006; Villa et al., 2010), conodonts (Clark,

1989), fungi (Kar et al., 2004), plant cells and cuticle (Hollocher et al., 2001, 2005; Prasad et al., 2005), phytoliths (Prasad et al., 2005), hair (Farlow et al., 2010); seeds (Wood et al., 2008; Harrison, 2011); invertebrate parasites (Sardella et al., 2010); fish scales (Matley, 1939a; Northwood, 2005); bones and teeth (e.g., Matley, 1939a; Fisher, 1981; Chin et al., 1998; Hollocher et al., 2005; Farlow et al., 2010), and even soft tissues such as muscle (Briggs, 2003; Chin et al., 2003). These forms are either made of material different from the host coprolite matrix (e.g., organic material or silica instead of calcite or apatite), or have distinctive shapes or textures, such as seeds and bone.

More controversial and difficult to demonstrate are bacterial remains. During decay, the organic material of tissue is converted insofar as possible to bacteria, so it is not surprising that, at least occasionally, the bacteria themselves should become fossilized. Taylor and Krings (2005) reviewed some of the evidence for bacteria in the fossil record, and Bignot (1980) reviewed evidence and some of the different processes by which bacteria can leave fossil traces. Upon loss of their organic material, bacteria and endospores can leave behind cavities or molds. Bacteria can also form solution cavities on surfaces that approximate original bacteria sizes and shapes. Experiments have demonstrated mineral encasement of bacterial cells (Rivadeneyra et al., 1996, 2006; Fortin et al., 1997; Aloisi et al., 2006), though often mineral precipitation takes place at a short distance from the bacteria, rather than on or in them, thus leaving no distinctive fossil form (Hirshler et al., 1990; Jehl and Rougerie, 1995; Fortin et al., 1997; Little et al., 1997). Bosak et al. (2004) demonstrated the encasement of individual bacteria and bacterial clusters by calcite overgrowths, leaving a distinctive pattern of porosity that is recognizably different from porosity found in inorganic precipitates produced in sterile controls. In some cases, as with the fossilization of ancient feathers, the fine structure of the resulting carbonaceous film is that of bacteria and not of feather (Martill and Frey, 1995; but see Vinther et al., 2008).

The major difficulty in identifying actual fossil bacterial forms in natural samples is that many bacteria have generic shapes that can resemble things that were never living. This is particularly true for spherical bacteria (cocci), which can resemble spherulitic precipitates (Hirshler et al., 1990; González-Muñoz et al., 2003). Based on Bignot's review (Bignot, 1980), forms, for example, reported to be those of bacteria and cell nuclei by Bradley (1946), or of bacteria, amoeba, and virus by Loquin (1981), are questionable (but see Huldtgren et al., 2011). It is generally best to use multiple methods, such as light microscopy combined with SEM imaging, X-ray element mapping, and cathodoluminescence, to support a particular microstructural interpretation. It is particularly rare to unambiguously identify and isolate the organic residues of bacteria in ancient coprolites (Hollocher et al., 2001).

EXAMPLE 1: BIO-FACILITATED CALCITE MINERALIZATION OF ANCIENT DUNG

In order to establish that bio-facilitated mineralization was relevant to the taphonomy of an ancient coprolite, it is necessary to determine the loci of original microbes in the coprolite and to show that the loci of the earliest episode of mineralization are coincident with the microbial loci. We are aware of only one study in which this criterion is met (Hollocher, et al., 2001). This study was of calcareous coprolites attributable to an herbivorous Cretaceous dinosaur, likely the hadrosaur, *Maiasaura*. They are present in the Cretaceous Two Medicine Formation of Montana as dark gray to black masses, some of which have been heavily burrowed, probably by dung beetles and other invertebrates (Fig. 1A-B; also see Chin and Gill, 1996; Chin, 2007b).

These specimens afforded morphological, chemical, and contextual evidence for the presence of organic bacterial residues within the abundant plant residues that comprise much of the coprolites. The plant material was shown to be almost entirely finely commuted gymnosperm xylem (Chin and Gill, 1996), and the dark, kerogenized organic material is localized almost entirely within the capillary spaces of tracheids and ray cells of the xylem (Fig. 1C-D). Chin (2007b) argued that the disaggregated state and other features of the woody fragments in the coprolites arose chiefly as the result of ingestion and mastication of rotten wood, rather than as a consequence wholly of digestion.

As illustrated in Figure 1E, the organic material in tracheids is organized as discrete, dark, 0.5-2 μm particles encased in calcite crystals of similar size. At high magnification in transmitted light, the centers of the dark particles are brighter than their rims, a finding consistent with a distribution of the dark material as hollow spheres or shells; diffraction or lensing as a cause of this optical effect was ruled out. The dark organic material was isolated from the coprolites and shown to have characteristics, including chemical biomarkers, expected for kerogenized bacteria associated within a still somewhat elastic and cohering biofilm. Figure 1F shows a scanning electron micrograph of one of the dark particles that was partially released from the center of a tracheid in the coprolite by etching with the chelating agent ethylenediaminetetraacetate (EDTA). The object is carbonaceous, thin-walled and apparently hollow. We attribute the lack of rod-shaped residues to the partial disintegration of the original bacteria into spherical vesicles (Cheng et al., 1991) or to the preponderance of coccus-like bacteria in the original dung.

The lighter areas that surround dark tracheid channels (Fig. 1C-D) are the locations of what originally were the fibrous walls of xylem and ray cells now replaced by coarse-grained calcite that is almost entirely devoid of organic material. These thin sections thus present a kind of photographic negative of what one normally sees in thin sections of xylem, in which the capillary spaces of tracheids are empty and therefore optically bright and their fibrous walls are dark.

Calcite in this coprolite is cathodoluminescent, luminescing orange because of doping with variable amounts of Mn^{2+} (Waychunas, 1988). Cathodoluminescence helped to determine the history and sequential order of calcite deposition (Fig. 2). Figure 2A shows a transmitted light image of a woody fragment containing many tracheid capillaries darkened by black organic residues in microcrystalline calcite. Tracheid cell walls, fractures, and other void spaces are filled with coarse-grained calcite. In the cathodoluminescent image of the same field (Fig. 2B) the tracheid capillaries are darker than cell walls and void-filling calcite. This is because there is less Mn^{2+} in the dimly luminescing, very fine-grained calcite in the capillaries than elsewhere (demonstrated by electron probe X-ray mapping of manganese). Dim luminescence is not caused by the dark organic material itself, because luminescence comes from the outer 1 μm or less of the polished section surface, and the surface fraction of non-luminescent organic material is trivial. Fractures truncate many of the dark tracheid capillaries (arrows), showing that they were already mineralized at the time the fractures formed. The calcite in fractures is of the same generation as, and in fact forms continuous crystals with, the brightly luminescing calcite that replaced the tracheid walls. In some places (circled, Fig. 2A), the dark organic material of capillaries has been lost. However, the pattern of dimly luminescent calcite in the capillaries persists (circled, Fig. 2B). Figure 2C shows another example of a woody fragment that has lost almost all of its organic material, but in cathodoluminescence (Fig. 2D) the pattern of dimly luminescing tracheid capillaries is clear. These results show that loss of dark organic material (kerogenized bacterial residues) from capillaries in parts of some woody fragments occurred after initial mineralization of these capillaries. This loss of organic material did not also remove the calcite or perceptively change its cathodoluminescent properties.

The following picture emerges: Mineralization initiated early on, while bacteria within tracheid capillaries were metabolically active, with deposition of micron-scale calcite exactly within the capillaries. The sites of initial mineralization and recognizable bacterial colonies were coincident. The earliest calcite deposited in capillary spaces had low Mn^{2+} doping and thus low cathodoluminescence. Later, the fiber of tracheid cell walls was lost and replaced with brightly luminescing, coarse grained calcite, which also filled all cracks and voids. Some of the calcite in what were cell walls forms single, continuous crystals extending into

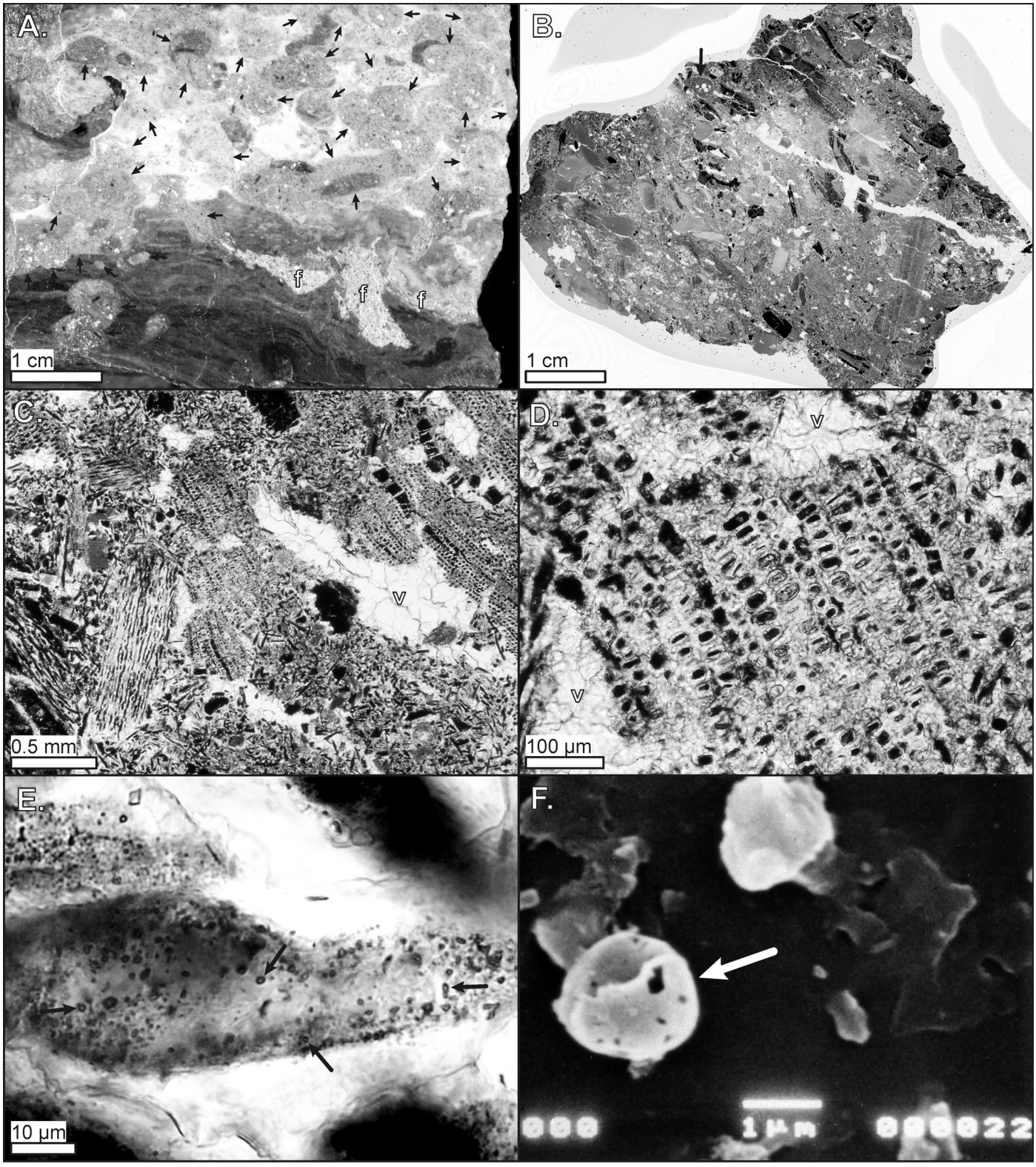


FIGURE 1. Blocky calcareous coprolite from the Two Medicine Formation (74-79 Ma) in Montana, thought to be from an herbivorous dinosaur, likely a hadrosaur. **A**, Red channel of an RGB color image of the cut surface of the coprolite, showing dark, organic-rich lower and lighter, oxidized upper portions. Several generations of burrows 1-6 mm in diameter penetrate the specimen (arrows), most of which are filled with silt and fine sand that is similar to the rock hosting the coprolite. Fractures (f) are filled with fine sand. **B**, Thin section of a dark, organic-rich part of the coprolite, showing numerous woody fragments and one burrow (arrow), and white calcite-filled fractures and other void spaces. **C-D**, Transmitted light images of thin sections made from organic rich parts of the coprolite, showing the loci of dark organic material in tracheid capillary channels and ray cells, in **C**, chiefly longitudinal orientation and **D**, transverse. Large clear areas are void-filling calcite (v). **E**, Magnified image of tracheids showing organization of the dark organic material into discrete particles 0.5-2 µm in diameter (some indicated by arrows) imbedded in fine-grained calcite. **F**, SEM secondary electron image of an organic vesicle partially released from a tracheid by etching using an EDTA solution. The thin, hollow organic shell resembles a bacterial cell wall or fragment thereof.

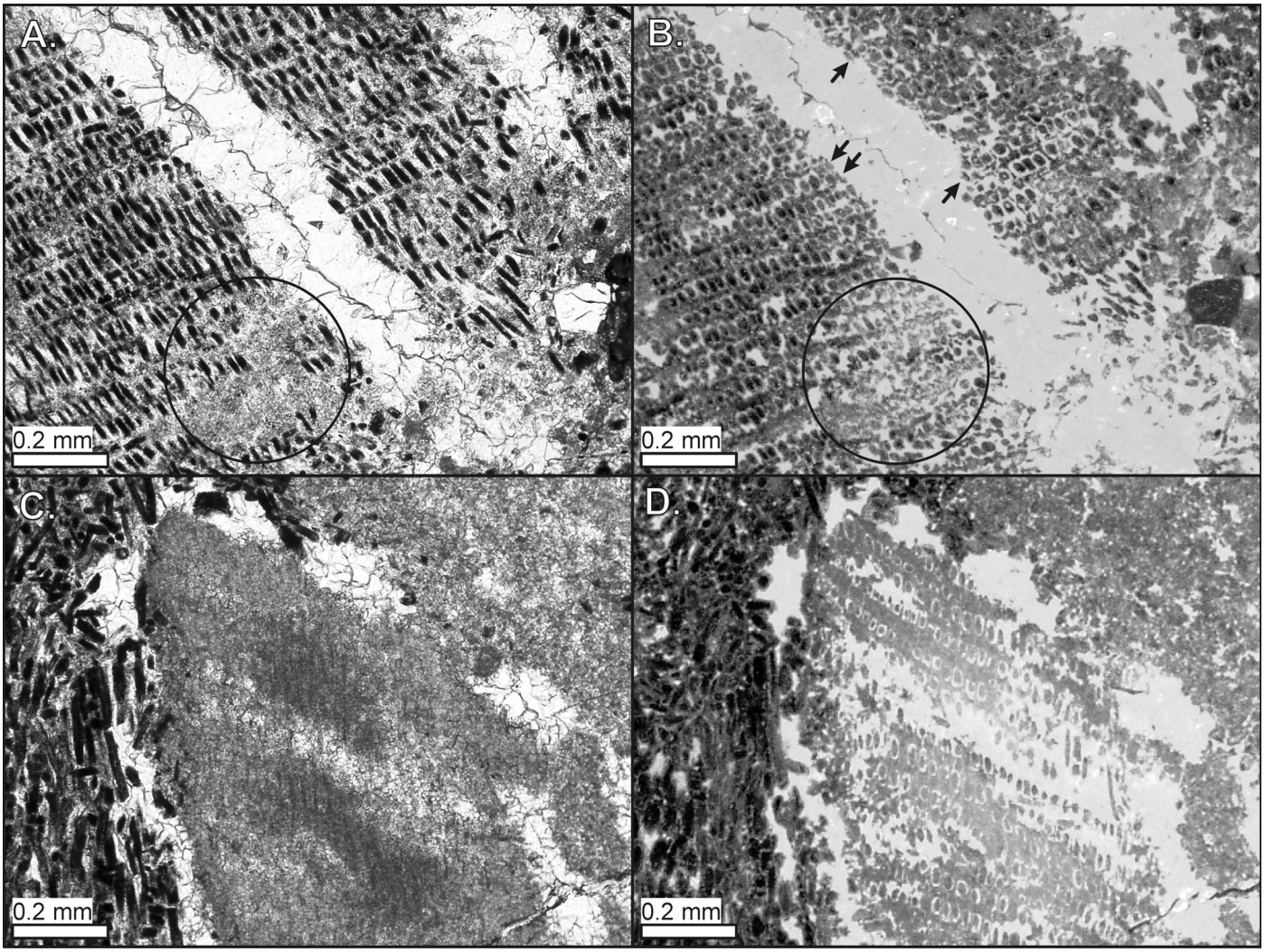


FIGURE 2. Paired transmitted light and cathodoluminescence micrographs of the same thin section as in Figure 1C-E. **A**, Transmitted light image, showing dark, organic-rich tracheid centers in a woody plant fragment. Some of the fragments are cut by calcite-filled fractures. The circled area shows a patch where organic matter has been lost from a fragment. **B**, Cathodoluminescence image of the same field as A. Arrows point to dark (dimly luminescent) tracheid centers cut by the fracture. Circled area shows dark tracheid centers, visible by their weak cathodoluminescence where none are clearly visible in transmitted light (A). C-D, similarly show the ability of cathodoluminescence to highlight tracheid centers after loss of their organic material. **C**, Transmitted light image of a highly disrupted woody plant fragment (left) containing abundant dark organic material, and another fragment (center) lacking obvious tracheid structures. **D**, Cathodoluminescence image of the same field as C, clearly showing dark (faintly luminescing) tracheid centers where none had been visible in C. Note that in transmitted light images (A, C) the view is through the entire 30 μm thin section thickness, whereas in cathodoluminescence images (B, D) the light comes from the outer 1 μm or less of the polished thin section surface. That is why some tracheid centers, depending on their angle with respect to the section surface, appear to be longer in transmitted light than in cathodoluminescence images.

fractures and other void spaces with no change in luminescent brightness or other discontinuity. This demonstrates that cell wall and void-filling calcite were precipitated in the same continuous episode.

In addition to the cathodoluminescence results, electron microprobe X-ray mapping showed that phosphorous, indicative of small amounts of apatite, was located exclusively within tracheid capillaries. Thus the loci of bacterial colonies, earliest calcite, and apatite are all coincident in this 75 Ma old Cretaceous coprolite. This is the expected signature of bio-facilitated mineralization. It is unlikely that later stages of calcite deposition were facilitated by bacteria, because the amount of calcite involved was massive and not localizable to any recognizable bacterial organic residues.

During digestion in extant cellulose fermenting animals, plant stem capillaries are colonized with bacteria (Cheng et al., 1991), and we presume the same situation would have applied in herbivorous dinosaurs. Surely, in the original dung, bacteria must have been ubiquitous. One question about the taphonomy of this coprolite concerns why kerogenized bacterial residues were found in what originally were capillary spaces and not throughout the coprolite volume. One possibility is that bio-facilitated mineralization was sufficiently delayed such that the xylem fragments had lost much of their original load of microorganisms, except for those colonies confined and protected within capillary spaces. Alternatively, the micro-environment of tracheid capillaries might have been continuously anaerobic and conducive to bacterial mediated mineralization, whereas more aerobic conditions elsewhere in the dung discouraged mineralization. This might afford protection of capillary bacteria by differential mineral encapsulation. The second scenario requires, however, that major oxygen concentration gradients must have been maintained over very small distances for long periods of time. In either case, mineralization soon encapsulated bacterial colonies in tracheid capillaries, thus preserving some of their organic material from diagenetic destruction.

EXAMPLE 2: RAPID EARLY MINERALIZATION AND DIAGENESIS OF PHOSPHATIC COPROLITES

Detailed mineralogical analyses have proved useful to demonstrate that ancient phosphatic coprolites underwent a process of early precipitation of dietary phosphate, followed by subsequent permineralizing diagenetic events. Hollocher et al. (2005), in a study of Late Triassic coprolites from the Ischigualasto Formation of Argentina, showed that the earliest discernible event in mineral deposition was the crystallization of apatite as small crystals having brownish pigmentation derived from included organic material. These crystals were initially very fine-grained and randomly oriented, but during growth developed into radiating feathery columns (Fig. 3A). The growing columns pushed aside organic material, concentrating it at column tips. Mn^{2+} also increased in concentration toward apatite column tips, as indicated by the brightness of its yellow cathodoluminescence (Barbarand and Pagel, 2001).

Altogether these are the characteristics expected of rapid crystallization with initial high nucleation density from a supersaturated solution, followed by progressively slower, more directional growth as the degree of supersaturation decreased. Although it is possible that bacteria facilitated apatite precipitation, there is no direct evidence, contrary to the case of Example 1, above. At this early stage, the incipient coprolite would have been composed of a mass of small apatite crystals and organic material, much of which would have been bacteria. Later, some additional apatite precipitated as well-formed, larger, individual crystals, generally on the edge of voids and solid inclusions in the coprolite (Fig. 3B). These crystals generally lack organic pigmentation. The crystal habit and size of later apatite is characteristic of slow crystal growth from a depleted reservoir at low degrees of supersaturation, possibly in the absence of biological mediation (Bosak et al., 2004).

Pyrite, and hematite produced by later oxidation of pyrite, are associated closely with the matrix organic material and with small undigested bone shards (Fig. 3C). The likelihood that hematite is secondary is indicated by the presence of hematite rimming irregular, corroded-looking pyrite grains. The largest pyrite cluster in the thin section is found near the center of a shard of cancellous bone. From the proximal loci of bone, pyrite, and early apatite deposits, it is likely that pyrite was deposited more or less contemporaneously with early apatite, possibly from sulfide produced by endogenous sulfate-reducing bacteria. The presence of pyrite, and the abundance of organic material out to the coprolite margin, indicates that its environment became anoxic soon after deposition.

Burrowing animals attacked these coprolites during or after precipitation of early apatite, as indicated by the fact that backfilled burrows contain coherent fragments of coprolite matrix in addition to abundant, externally-derived sand grains. Burrowing took place prior to calcite permineralization, as indicated by the texture of void-filling calcite in the burrows that is identical to that found in internal void spaces such as gas bubbles. Finally, calcite and glauconite were deposited in open spaces that included gas bubbles and other voids, cracks, and residual channelways not previously filled with apatite or organic material.

Figure 3E shows a large void space, probably originally a gas bubble, filled with calcite and green glauconite. With reference to the cathodoluminescent image of the same field (Fig. 3F), calcite void filling began with non-luminescing, inward-coarsening calcite (layer 1c), more inwardly-coarsening calcite, but with layers having different luminescence (2c), a layer of glauconite (3g), and lastly the center of the void was filled with homogeneously luminescing calcite that contains abundant fluid inclusions (4c). The orange luminescence varies with concentration of the Mn^{2+} luminescence activator in calcite, which tends to vary with the redox state of local ground water (Mason and Moore, 1982; Retallack, 1997). In oxidizing waters manganese is in the form of Mn^{3+} and Mn^{4+}, which form insoluble minerals. In reducing waters, manganese is reduced to its soluble Mn^{2+} state, which can be incorporated into growing calcite. On this basis the ground water that precipitated calcite is interpreted to have been initially oxidizing (layer 1c). The oxidizing conditions at this stage are clearly very different from the earlier history of the coprolite, during which time pyrite was precipitated and considerable organic material preserved. This episode of oxidizing groundwater may also have been the time when some of the smaller pyrite grains were oxidized to hematite. The ground water then went through an episode of variable redox states (2c), precipitating calcite layers having variable luminescent brightness. Glauconite precipitation (3g) signifies a dramatic change in local ground water chemistry, and some glauconite growth seems to have been at the expense of pyrite (Fig. 3C). Finally, possibly after a considerable period of time, reducing ground water deposited the last void-filling calcite (Fig. 3F, layer 4c). Thin trails (t) of bright calcite luminescence amongst the darker apatite matrix are interpreted to be the filled channel ways through which water gained access to void spaces.

Following precipitation of endogenous apatite, the porous scats, or incipient coprolites, resisted collapse or disintegration and retained their cylindrical shapes. Later permineralization with calcite and glauconite made them solid, dense, and durable. Because of the excellent state of preservation of endogenous bone and other inclusions, and the delicate and distinctive crystal habits of apatite, we think that little or no recrystallization of matrix apatite could have occurred over some 230 Ma. This study showed that crystallization of dietary minerals occurred early in the coprolites' histories, resulting in a partially mineralized structure making up a considerable volume fraction of the whole form. Later, void spaces were permineralized with calcite and glauconite to form dense, fully mineralized coprolites.

EXAMPLE 3: RAPID EARLY MINERALIZATION OF A PHOSPHATIC COPROLITE WITHOUT DIAGENETIC PERMINERALIZATION

Hollocher et al. (2010) provided a clear demonstration of the structural importance of dietary minerals in coprolites of carnivorous animals in the study of a low-density coprolite from the 65 Ma Hell Creek Formation of eastern Montana. This coprolite was highly porous on millimeter to nanometer scales, with a void volume of about 50% based on density. It consists almost entirely of carbonate fluoroapatite (francolite) and detrital grains. As far as could be seen by optical microscopy, SEM imaging, X-ray diffraction, and cathodoluminescence, the coprolite entirely lacked recrystallized apatite or void-filling permineralization. It contained well-preserved organic residues of spores and pollen (Fig. 4A), leaf cuticle (Fig. 4B), high fidelity mineral impressions of seeds (Fig. 4C), and thin organic residues of open plant cells and cell walls (Fig. 4D). Because carnivorous animals are not generally thought of as eating plants, these may represent incidentally consumed plants on the ground surrounding the prey, or possibly gut contents of the prey. Most of the francolite matrix is microcrystalline and consists mostly of blocky to granular apatite crystallites, typically <50 nm across. These form some disordered regions, but are largely organized into hollow and filled spheres 0.5-3 μm in diameter. Some of the filled spheres have shell-shaped gaps (4E). There are also larger, relatively rare spherulites up to 20 μm across made of needle-shaped apatite crystals radiating from central nucleation points (Fig. 4F).

The larger crystalline spherulites are indicative of rapid crystallization from supersaturated solution, but they may actually post-date crystallization of the nanocrystalline matrix. Here, again, precipitation may have been facilitated by bacteria, but unfortunately there is no evidence either way. The hollow and hollow-shell spheres were interpreted as pseudomorphs of organic particles, probably including fecal bacteria or derived vesicles thereof that existed in the original scat. Any organic material that might have helped to organize spheres in the matrix was subsequently lost during diagenesis. Rare, stubby hexagonal apatite prisms 1-3 μm across are also found (Fig. 5A) and are believed to have formed as the last crystalline components at low degrees of supersaturation, though it is possible that they are very minor diagenetic recrystal-

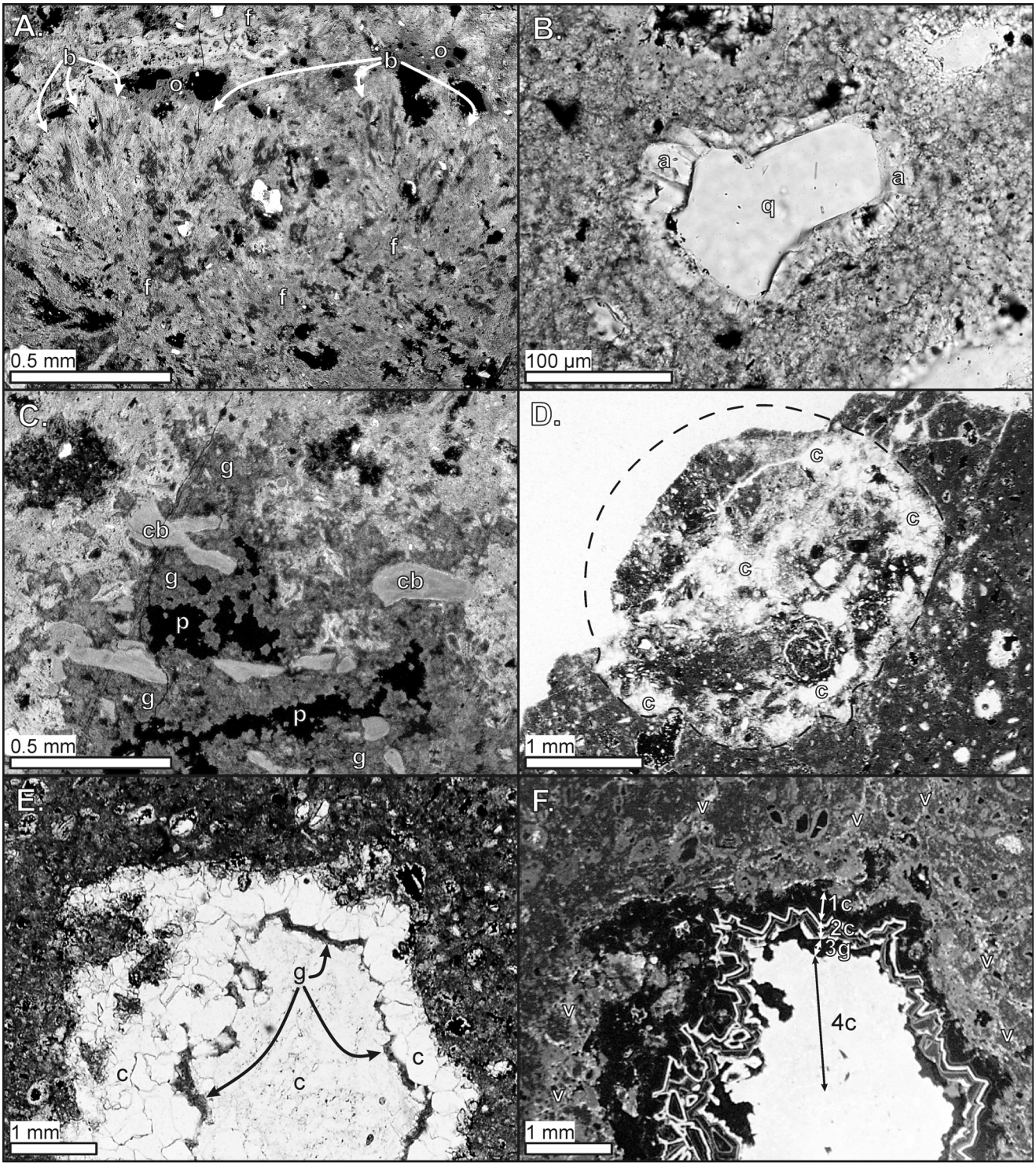


FIGURE 3. Thin section photomicrographs of a phosphatic coprolite from the 228 Ma Triassic Ischigualasto Formation of Argentina. **A**, Blue channel of a color RGB image showing the coprolite matrix: fine-grained apatite (f) progressing to radiating feathery apatite columns (b) where white arrows show column tips that pushed aside organic material (o). Black grains are hematite, probably after pyrite, and white grains are detrital silicates. **B**, Detrital quartz grain (q) surrounded by well-formed, clear, colorless apatite crystals (a). **C**, Blue channel of a color RGB image showing an undigested but heavily eroded cancellous bone fragment (cb), with pyrite (p) occupying the originally organic-rich interior. The pyrite is surrounded by secondary green glauconite (g). Surrounding the bone is light-colored matrix of fine-grained and radiating, columnar apatite, and various inclusions. **D**, Blue channel of a color RGB image showing an invertebrate burrow outlined by a black dashed line. About half of the burrow is backfilled with fragments of the phosphatic coprolite matrix and colorless sand grains, and the rest was void space that was filled with late calcite (c). **E**, Large void filled with layers of calcite (c) and glauconite (g), and surrounded by the phosphatic coprolite matrix and various inclusions. **F**, Red channel of a color RGB cathodoluminescence image of the same field of view as E, showing the variable luminescence of the void filling calcite. Narrow calcite veins (v) were probably the channel ways through which water that precipitated calcite and glauconite accessed the coprolite interior. 1c, 2c, 3g, and 4c represent four sequential stages of void infill layers of calcite and glauconite (see text).

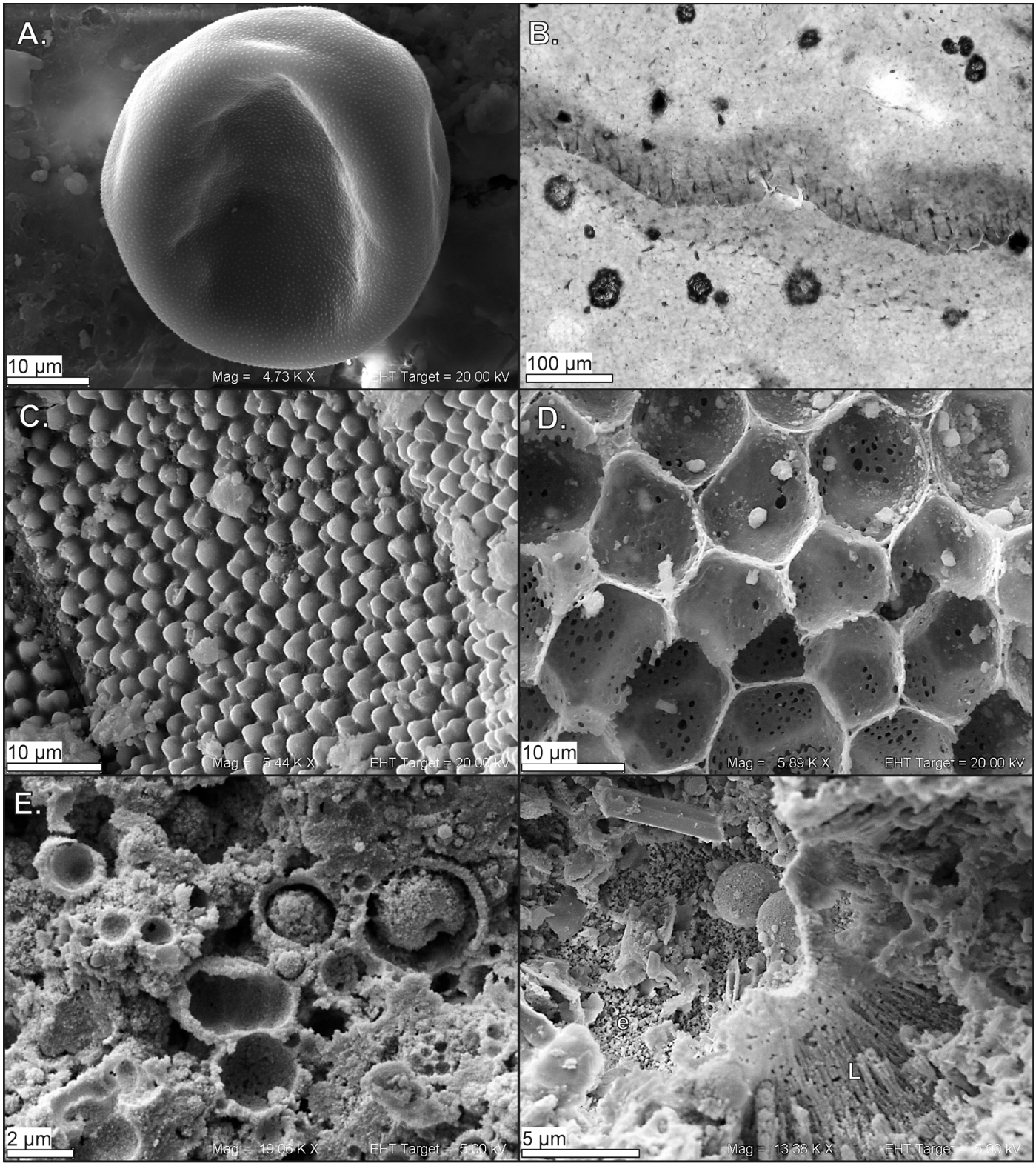


FIGURE 4. Phosphatic coprolite from the 65 Ma Late Cretaceous Hell Creek Formation of eastern Montana. **A** and **C-F** are secondary electron SEM images, and **B** is a transmitted light image. **A**, Pollen grain released by EDTA etching of coprolite chips. **B**, Thin section photograph of organic residue of plant cuticle, probably from a leaf, on which numerous trichomes 20-30 µm long can be seen. **C**, Mold of the surface of a small seed exposed on a fractured coprolite surface. **D**, Relatively intact plant cell walls made of original organic material and exposed on a fractured surface. **E**, Spherulites, 0.5-3 µm in diameter, on a fractured coprolite surface. Note that some are completely hollow spheres, whereas others are filled but commonly have an empty shell-shaped gap near their periphery. **F**, Large spherulite composed of radiating needle-shaped apatite crystals, seen end-on (e), and lengthwise (L).

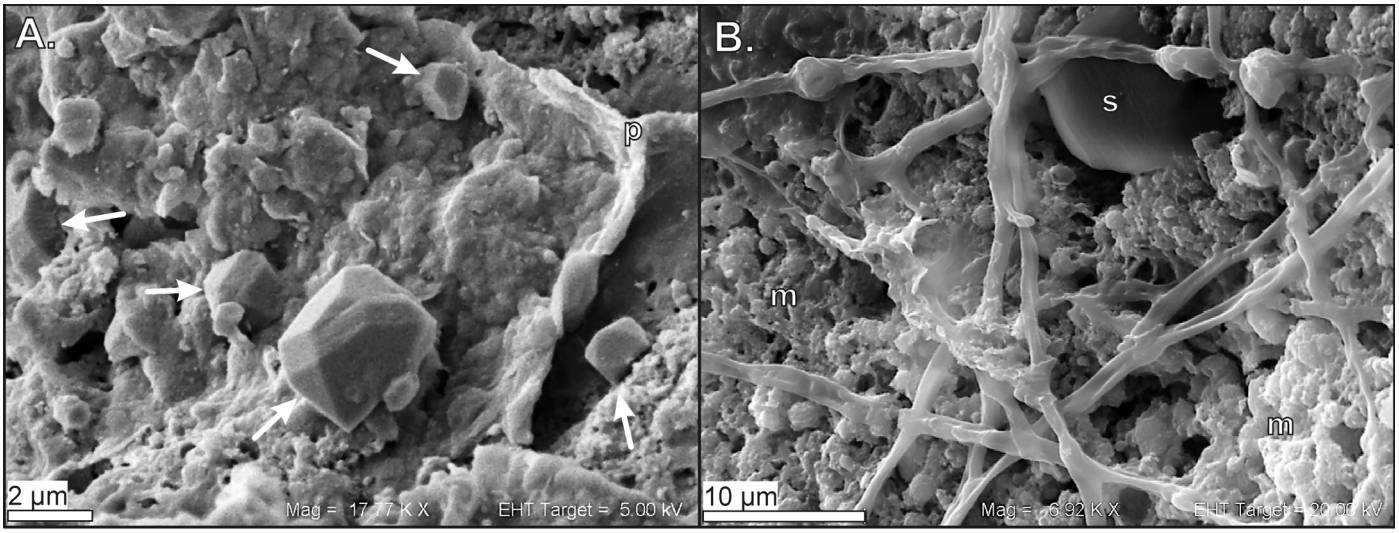


FIGURE 5. Secondary electron SEM images of fractured surfaces of the same coprolite in Figure 4. **A**, Small but well-faceted apatite crystals (white arrows), thought to be among the last apatite to have crystallized in this coprolite. The ridges meeting at a point, p, are the remnant cell walls of three adjacent plant cells. **B**, Fungal hyphae comprised of organic, not mineral, material as determined from element maps, and may not be ancient. Detrital silicate grain (s), and phosphatic matrix (m). The chip for B was etched with EDTA solution prior to SEM imaging.

lization products. This coprolite was invaded by fungal hyphae (Fig 5B). Because the hyphae are made of organic material and not mineralized, they may be modern rather than ancient. The preservation of delicate plant residues over geological time, within a matrix of micro- to nanocrystalline apatite, shows that apatite recrystallization could not have been significant following its original deposition.

The fact that the siltstone matrix immediately adjacent to the coprolite is essentially devoid of apatite shows that the coprolite's apatite could not have been derived from ground water and must have been autochthonous and surely dietary. Overall, study of this coprolite shows that dietary calcium phosphate can provide sufficient structural strength alone, without secondary permineralization, to maintain structural integrity in fluvial sediments for tens of millions of years. The early deposition of apatite derived from dietary calcium phosphate is the process that gives scat of carnivorous animals a great preservational advantage over dung from herbivorous ones.

CONCLUSIONS

Not all coprolites are of a quality to allow the kinds of microscopic, chemical, and mineralogical discoveries described in the three examples above. Processes, such as early decomposition of organic material, compaction by overburden, diagenetically-induced recrystallization of minerals, and dissolution of autochthonous minerals and residual organic material, with or without replacement, can make clear interpretations difficult.

A relevant and interesting question is whether the precipitation or crystallization of dietary calcium phosphate in the scat of carnivorous animals can be facilitated or accelerated by fecal bacteria during decay of organic components. Such a process seems intuitively likely, and experiments demonstrate that bacteria can promote apatite precipitation in some circumstances (Lucas and Prévôt, 1985; Hirschler et al., 1990), but we know of no direct evidence to the point in actual coprolites or realistic experimental models. This matter might be addressed by making a mineralogical examination of, for example, alligator scat, as it ages in order to determine the kinetics of mineral precipitation and crystal growth, and the physical relationships between bacteria and crystallizing minerals. Studies of other low density coprolites (Sawyer, 1981) might also be fruitful, because they are likely to be largely unrecrystallized and free of void-filling secondary minerals. If bio-facilitated apatite mineralization occurs in scat, that would show it enjoys a double taphonomic advantage over that for dung from herbivorous animals, in the sense that the mineral material upon which the bacteria would operate is already present and need not be garnered from ground water.

At this stage in the study of coprolites, we have some understanding of two processes, bio-facilitated mineralization and precipitation of dietary calcium phosphate, that appear to be important early events in the conversion of dung and scat into coprolites, followed in some cases by diagenetic permineralization. Many details of these processes, however, remain to be elucidated, and it is likely that other early stabilizing processes remain to be discovered.

ACKNOWLEDGMENTS

We would like to thank Alex Bartholomew, Karen Chin, and John Hubert for their helpful suggestions and comments. We thank the Museum of the Rockies, the Museum of Natural Sciences at the National University of San Juan, and Fort Peck Paleontology, Inc., Fort Peck, Montana, for access to the specimens and for providing support at dig sites, and the Worldwatch Institute for support of field work in Argentina. We thank all coauthors on our previous papers for keeping our investigations oriented toward topics of paleontological interest. We also thank Union College for supporting analytical work, and the National Science Foundation, grant MRI0619578, for support of SEM instrumentation.

REFERENCES

Aloisi, G., Gloter, A., Krüger, M., Wallmann, K., Guyot, F. and Zuddas, P., 2006, Nucleation of calcium carbonate on bacterial nanoglobules: Geology, v. 34, p. 1017-1020.

Badal, E. and Atienza, V., 2007, Análisis microscópico de coprolitos de hervbívoros hallados en contextos arqueológicos; *in* Molera, J., Farjas, J., Roura, P. and Pradell, T., eds., Avances en Arqueometría: Actas del VI Congreso Ibérico de Arqueometría: Girona, Spain, Universitat de Girona, p. 283-293.

Barbarand, J. and Pagel, M., 2001, Cathodoluminescence study of apatite crystals: American Mineralogist, v. 86, p. 473-484.

Bhatnagar, M. and Bhatnagar, A., 2000, Algal and cyanobacterial responses to fluoride: Fluoride, v. 33, no. 2, p. 55-65.

Bignot, G., 1980, A la recherché des bacteries fossils: Bulletin Trimestriel De La Société Géologique De Normandie Et Des Amis Du Muséum Du Havre, v. 67, no. 2, p. 15-41.

Bosak, T., Souza-Egipsy, V., Corsetti, F. and Newman, D., 2004, Micrometer-scale porosity as a biosignature in carbonate crusts: Geology, v. 32, p. 781-784.

Bradley, W.H., 1946, Coprolites from the Bridger Formation of Wyoming: their composition and microörganisms: American Journal of Science, v. 244, p. 215-239.

Briggs, D.E.G., 2003, The role of decay and mineralization in the preservation of soft-bodied fossils: Annual Reviews of Earth Planetary Sciences, v. 31, p. 275-301.

Briggs, D.E.G. and Kear, A.J., 1993, Fossilization of soft tissue in the laboratory: Science, v. 259, p. 1439-1442.

Briggs, D.E.G. and Wilby, P.R., 1996, The role of the calcium carbonate-calcium phosphate switch in the mineralization of softbodied fossils: Journal of the Geological Society of London, v. 153, p. 665-668.

Briggs, D.E.G., Kear, A.J., Martill, D.M. and Wilby, P.R., 1993, Phosphatization of soft-tissue in experiments and fossils: Journal of the Geological Society of London, v. 150, p. 1035-1038.

Briggs, D.E.G., Kear, A.J., Baas, M., De Leeuw, J.W. and Rigby, S., 1995, Decay and composition of the hemichordate *Rhabdopleura*: Implications for the taphonomy of graptolites: Lethaia, v. 28, p. 15-23.

Cailleau, G., Braissant, O., Dupraz, C., Arango, M. and Verrecchia, E., 2004, Biologically induced accumulations of CaCO3 in orthox soils of Biga, Ivory Coast: Catena, v. 59, p. 1-17.

Chame, M., 2003, Terrestrial mammal feces: a morphometric summary and description: Memórias do Instituto Oswaldo Cruz, Rio de Janeiro, v. 98, supplement 1, p. 1-12.

Cheng, K.-J., McAllister, T.A., Kudo, H., Forsberg, C.W. and Costerton, J.W., 1991, Microbial strategy in feed digestion; in Ho, Y.W., Wong, H.K., Abdullah, N. and Tajuddin, Z.A., eds., Recent Advances on the Nutrition of Herbivores: 3rd International Symposium on the Nutrition of Herbivores, Malaysian Society of Animal Production: Kuala Lampur, Vinlin Press, p. 181-187.

Chin, K., 2002, Analyses of coprolites produced by carnivorous vertebrates: Paleontological Society Papers, v. 8, p. 43-50.

Chin, K., 2007a, Thin section analysis of lithified coprolites (fossil feces): Microscopy and Microanalysis, v. 13, p. 504-505.

Chin, K., 2007b, The paleobiological implications of herbivorous dinosaur coprolites from the Upper Cretaceous Two Medicine Formation of Montana: why eat wood?: Palaios, v. 22, p. 554-566.

Chin, K. and Gill, B.D., 1996, Dinosaurs, dung beetles, and conifers: Participants in a Cretaceous food web: Palaios, v. 11, p. 280-285.

Chin, K., Tokaryk, T.T., Erickson, G.M. and Calk, L.C., 1998, A king-sized theropod coprolite: Nature, v. 393, p. 680-682.

Chin, K., Eberth, D.A., Schweitzer, M.H., Rando, T.A., Sloboda, W.J. and Horner, J.R., 2003, Remarkable preservation of undigested muscle tissue within a Late Cretaceous tyrannosaurid coprolite from Alberta, Canada: Palaios, v. 18, p. 286-294.

Cho, G., Wu, Y. and Akerman, J., 2003, Detection of hydroxyl ions in bone mineral by solid state NMR spectroscopy: Science, v. 300, p. 1123-1127.

Clark, N., 1989, Carboniferous coprolitic bacteria from the Ardross Shrimp Bed, Fife: Scottish Journal of Geology, v. 25, no. 1, p. 99-194.

Coulson, R.A. and Hernandez, T., 1964, Biochemistry of the Alligator: Louisiana State University Press, Baton Rouge, 138 p.

Currie, P.J., Koppelhus, E.B. and Muhammad, A.F., 1995, "Stomach" contents of a hadrosaur from the Dinosaur Park Formation (Campanian, Upper Cretaceous) of Alberta, Canada; *in* Sun, A. and Wang, Y., editors, Sixth Symposium on Mesozoic Terrestrial Ecosystems and Biota, 1995, Short Papers: Beijing, China Ocean Press, p. 111-114.

Daniel, J. and Chin, K., 2010, The role of bacterially mediated precipitation in the permineralization of bone: Palaios, v. 25, p. 507-516.

Davis, P.G. and Briggs, D.E.G., 1995, Fossilization of feathers: Geology, v. 23, p. 783-786.

Decho, A.W., 2010, Overview of biopolymer-induced mineralization: what goes on in biofilms?: Ecological Engineering, v. 36, no. 2, p. 137-144.

de Leeuw, N.H., 2004, Resisting the onset of hydroxyapatite dissolution through the incorporation of fluoride: Journal of Physical Chemistry B, v. 108, 1809-1811.

Duffin, C., 2009, "Records of warfare…embalmed in the everlasting hills:" a history of early coprolite research: Mercian Geologist, v. 17, no. 2, p. 101-111.

Dupraz, C., Reid, R.P., Braissant, O., Decho, A., Norman, R.S. and Visscher, P., 2009, Processes of carbonate precipitation in modern microbial mats: Earth Science Reviews, v. 96, p. 141-162.

Edmunds, W.M., Kay, R.L.F., Miles, D.L. and Cook, J.M., 1987, The origin of saline groundwaters in the Carnmenellis Granite, Cornwall (U.K.): further evidence from minor and trace elements; *in* Fritz, P. and Frape, S.K., eds., Saline Water and Gasses in Crystalline Rocks: Geological Association of Canada, Special Paper 33, p. 127-143.

Elliott, J., 2002, Calcium phosphate biominerals; in Kohn, M., Rakovan, J. and Hughes, J., eds., Phosphates-Geochemical, Geobiological, and Materials Importance: Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, v. 48, p. 427-453.

Eriksson, M.E., Lindgren, J., Chin, K. and Månsby, U., 2011, Coprolite morphotypes from the Upper Cretaceous of Sweden: novel views on an ancient ecosystem and implications for coprolite taphonomy: Lethaia, v. 44, p. 455-468.

Farlow, J., Chin, K., Argast, A. and Poppy, S., 2010, Coprolites from the Pipe Creek Sinkhole (Late Neogene, Grant County, Indiana, U.S.A.): Journal of Vertebrate Paleontology, v. 30, p. 959-969.

Field, R., Kruggel, W. and Riley, M., 1976, Characteristics of mechanically deboned meat, hand separated meat, and bone residue from bones destined for rendering: Journal of Animal Science, v. 43, p. 755-762.

Fisher, D.C., 1981, Crocodilian scatology, microvertebrate concentrations, and enamel-less teeth: Paleobiology, v. 7, p. 262-275.

Fortin, D., Ferris, F. and Beveridge, T., 1997, Surface-mediated mineral development by bacteria; *in* Banfield, J. and Nealson, K., eds., Geomicrobiology: Interactions Between Microbes and Minerals: Mineralogical Society of America, Reviews in Mineralogy, v. 32, p. 161-180.

Frape, S.K. and Fritz, P., 1987, Geochemical trends of groundwaters from the Canadian Shield; *in* Fritz, P. and Frape, S.K., eds., Saline Water and Gasses in Crystalline Rocks: Geological Association of Canada, Special Paper 33, p. 19-38.

Gascoyne, M., Davison, C.C., Ross, J.D. and Pearson, R., 1987, Saline groundwaters and brines in plutons in the Canadian Shield; in Fritz, P. and Frape, S.K., eds., Saline Water and Gasses in Crystalline Rocks: Geological Association of Canada, Special Paper 33, p. 53-59.

Ghosh, P., Bhattacharya, S., Sahni, A., Kar, R., Mohabe, D. and Ambwani, K., 2003, Dinosaur coprolites from the Late Cretaceous (Maastrichtian) Lameta Formation of India: isotopic and other markers suggesting a C3 plant diet: Cretaceous Research, v. 24, p. 743-750.

González-Muñoz, M., Fernández-Luque, B., Martínez-Ruiz, F., Chekroun, K., Arias, J., Rodríguez-Gallego, M., Martínez-Cañamero, M., Linares, C. and Paytan, A., 2003, Precipitation of barite by Myxococcus xanthus: Possible implications for the biogeochemical cycle of barium: Applied and Environmental Microbiology, v. 69, p. 5722-5725.

Gruner, J.W. and McConnell, D., 1937, The problem of the carbonate-apatites: the structure of francolite: Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie, v. 97, p. 208-215.

Harrison, T., 2011, Coprolites: Taphonomic and paleoecological implications; *in* Harrison, T., ed., Paleontology and Geology of Laetoli: Human Evolution in Context, v. 1, Geology, Geochronology, Paleoecology and Paleoenvironment, Vertebrate Paleobiology and Paleoanthropology: Springer Science, p. 279-292.

Hirschler, A., Lucas, J. and Hubert, J-C., 1990, Apatite genesis: a biologically induced or biologically controlled mineral formation process?: Geomicrobiology Journal, v. 7, p. 47-56.

Hollocher, T.C., Chin, K., Hollocher, K. and Kruge, M.A., 2001, Bacterial residues in coprolite of herbivorous dinosaurs: role of bacteria in miner-

alization of feces: Palaios, v. 16, p. 547-565.
Hollocher, K., Alcober, O.A., Colombi, C.E. and Hollocher, T.C., 2005, Carnivore coprolites from the Upper Triassic Ischigualasto Formation, Argentina: chemistry, mineralogy, and evidence for rapid initial mineralization: Palaios, v. 20, p. 51-63.
Hollocher, K., Hollocher, T. and Rigby, J.K., Jr., 2010, A phosphatic coprolite lacking diagenetic permineralization from the Upper Cretaceous Hell Creek Formation, northeastern Montana: importance of dietary calcium phosphate in preservation: Palaios, v. 25, p. 132-140.
Hubert, J. and Panish, P., 2000, Sedimentology and diagenesis of the dinosaur bones exposed at Dinosaur Ridge along Alameda Parkway in the Morrison Formation (Upper Jurassic), Morrison, Colorado: The Mountain Geologist, v. 37, no. 2, p. 73-90.
Huldtgren, T., Cunningham, J., Yin, C., Stampanoni, M., Marone, F., Donoghue, P. and Bengtson, S., 2011, Fossilized nuclei and germination structures identify Ediacaran "animal embryos" as encysting protists: Science, v. 334, p. 1696-1699.
Hunt, A.P., Lucas, S.G., Spielmann, J.A. and Lerner, A.J, 2007, A review of vertebrate coprolites of the Triassic with descriptions of new Mesozoic ichnotaxa: New Mexico Museum of Natural History and Science, Bulletin 41, p. 88-99.
Jehl, C. and Rougerie, F., 1995, Phosphatogenése en atolls Polynésiens: la filiation mattes cyanobactériennes-phosphorites: Oceanologica Acta, v. 18, p. 79-93.
Kar, R.K., Sharma, N. and Kar, R., 2004, Occurrence of fossil fungi in dinosaur dung and its implication on food habit: Current Science, v. 87, p. 1053-1056.
Kim, J., Dong, H., Seabaugh, J., Newell, S.W. and Ebert, D.D., 2004, Role of microbes in smectite-to-illite reaction: Science, v. 303, p. 830-832.
Larkin, N., Alexander, J. and Lewis, M., 2000, Using experimental studies of recent faecal material to examine hyaena coprolites from the West Runton Freshwater Bed, Norfolk, U.K.: Journal of Archaeological Science, v. 27, p. 19-31.
Little, B., Wagner, P. and Lewandowski, Z., 1997, Spatial relationships between bacteria and mineral surfaces; *in* Banfield, J. and Nealson, K., eds., Geomicrobiology: Interactions Between Microbes and Minerals: Mineralogical Society of America, Reviews in Mineralogy, v. 32, p. 123-159.
Locquin, M.V., 1981, Amibes, bacteries, bacteriophages et virus fossils: Traveux du Laboratoire de Micropaléontologie, no. 9, p. 213-225.
Lucas, J. and Prévôt, L., 1985, The synthesis of apatite by bacterial activity: mechanism: Sciences Géologiques Memoirs, v. 77, p. 83-92.
Lucas, J. and Prévôt, L.E, 1991, Phosphates and fossil preservation; *in* Allison, P. and Briggs, D., eds., Taphonomy, Releasing the Data Locked in the Fossil Record: New York, Plenum Press, p. 389-409.
Martill, D. and Frey, E., 1995, Colour patterning preserved in Lower Cretaceous birds and insects: the Crato Formation of N.E. Brazil: Neues Jahrbuch für Geologie und Paläontologie, Monatshefte 1995, p. 118-128.
Månsby, U., 2009, Late Cretaceous coprolites from the Kristianstad Basin, southern Sweden [M.S. thesis]: Lund, Lunds Universitet, Geologiska Institutionen Centrum för Geobiosfärsvetenskap, 18 p.
Mason, B. and Moore, C.B., 1982, Principles of Geochemistry, 4th ed.: New York, John Wiley and Sons.
Matley, C., 1939a, On some coprolites from the Maleri Beds of India: Records of the Geological Survey of India, v. 74, p. 530-534.
Matley, C., 1939b, The coprolites of Pijdura, Central Provinces: Records of the Geological Survey of India, v. 74, p. 535-547.
McConnell, D., 1970, Crystal chemistry of bone mineral: Hydrated carbonate apatites: American Mineralogist, v. 55, p. 1659-1669.
McNamara, M., Orr, P., Kearns, S., Alcalá, L., Anadón, P. and Peñalver-Mollá, E., 2006, High-fidelity organic preservation of bone marrow in ca. 10 Ma amphibians: Geology, v. 34, p. 641-644.
McNamara, M., Orr, P., Kearns, S., Alcalá, L., Anadón, P. and Peñalver-Mollá, E., 2009, Soft-tissue preservation in Micene frogs from Libros, Spain: insights into the genesis of decay microenvironments: Palaios, v. 24, p. 104-117.
Nordstrom, D.K., Ball, J.W., Donahoe, R.J. and Whittemore, D., 1989, Groundwater chemistry and water-rock interactions at Stripa: Geochimica et Cosmochimica Acta, v. 53, p. 1727-1740.
Northwood, C., 2005, Early Triassic coprolites from Australia and their palaeobiological significance: Palaeontology, v. 48, p. 49-68.
Omelon, S. and Grynpas, M., 2008, Relationships between polyphosphate chemistry, biochemistry and apatite biomineralization: Chemical Reviews, v. 108, p. 4694-4715.
Pasteris, J. and Ding, D., 2009, Experimental fluoridation of nanocrystalline apatite: American Mineralogist, v. 94, p. 53-63.
Pierre, C. and Fouquet, Y., 2007, Authigenic carbonates from methane seeps of the Congo deep-sea fan: Geo-marine Letters, v. 27, p. 249-257.
Pinskwar, P., Jezierska-Madziar, M. and Golski, J., 2003, Fluoride in bone tissue of fish sampled from the old Warta reservoirs near Lubon and Radzewice, Poland: Fluoride, v. 36, no. 3, p. 185-188.
Prasad, V., Strömberg, C., Alimohammadian, H. and Sahini, A., 2005, Dinosaur coprolites and the early evolution of grasses and grazers: Science, v. 310, p. 1177-1180.
Retallack, G.J., 1997, Dinosaurs and dirt; *in* Wolberg, D.L, Stump, E. and Rosenberg, G., eds., Dinofest International, proceedings of a symposium held at Arizona State University: Academy of Natural Sciences, Philadelphia, p. 345-359.
Rivadeneyra, M.A., Ramos-Cormenzana, A., Delgado, G. and Delgado, R., 1996, Process of carbonate precipitation by *Deleya halophila*: Current Microbiology, v. 32, p. 308-313.
Rivadeneyra, M.A., Delgado, R., Párraga, J., Ramos-Cormenzana, A. and Delgado, G., 2006, Precipitation of minerals by 22 species of moderately halophilic bacteria in artificial marine salts media: influence of salt concentration: Folia Microbiologica, v. 51, p. 445-453.
Sánchez-Román, M., Vasconcelos, C., Schmid, T., Dittrich, M., McKenzie, J., Zenobi, R. and Rivadeneyra, M., 2008, Aerobic microbial dolomite at the nanometer scale: implications for the geologic record: Geology, v. 36, p. 879-882.
Sardella, N., Fugassa, M., Rindel, D. and Goñi, R., 2010, Paleoparasitological results for rodent coprolites from Santa Cruz Province, Argentina: Memórias do Instituto Oswaldo Cruz, Rio de Janeiro, v. 105, no. 1, p. 33-40.
Sawyer, G.T., 1981, A study of crocodilian coprolites from Wannagan Creek quarry (Paleocene-North Dakota), Ichnofossils II: Scientific Publications of the Science Museum of Minnesota, New Series, v. 5, no. 2, p. 1-29.
Sawyer, G.T., 1998, Coprolites of the Black Mingo Group (Paleocene) of South Carolina: Transactions of the American Philosophical Society, New Series, v. 88, no. 4, p. 221-228.
Scott, L., 1987, Pollen analysis of hyena coprolites and sediments from Equus Cave, Taung, Southern Kalahari (South Africa): Quaternary Research, v. 28, p. 144-156.
Scott, L., Fernández-Jalvo, Y., Carrión, J. and Brink, J., 2003, Preservation and interpretation of pollen in hyaena coprolites: taphonomic observations from Spain and southern Africa: Palaeontologia Africana, v. 39, p. 83-91.
Sharma, K.M. and Patnaik, R., 2010, Coprolites from the Lower Miocene Baripada beds of Orissa: Current Science, v. 99, p. 804-808.
Sharma, N., Kar, R.K., Agarwal, A. and Kar, R., 2005, Fungi in dinosaurian coprolites from the Lameta Formation (Maastrichtian) and its reflection on food habit and environment: Micropaleontology, v. 51, p. 73-82.
Skoczylas, R., 1978, Physiology of the digestive track; *in* Gans, C. and Gans, K.A., eds., Biology of the Reptilia: Academic Press, London, v. 8, p. 589-717.
Snioszek, M., Telesinski, A., Musik, D. and Zakrzewska, H., 2008, Comparative analysis of fluoride content in sheep mandibles from archeological excavations in Szczecin according to individual age and time of being deposited in soil: Journal of Elementology, v. 13, p. 675-684.
Stearns, R.I., 1970, Incorporation of fluoride by human enamel: I. Solid-state diffusion process: Journal of Dental Research, v. 49, p. 1444-1451.
Stearns, R.I., 1971, Incorporation of fluoride by human enamel: II. An exothermic chemical process: Journal of Dental Research, v. 50, p. 1575-1579.

Suga, S., Taki, Y. and Wada, K., 1983, Fluoride concentration in the teeth of perciform fishes and its phylogenetic significance: Japanese Journal of Ichthyology, v. 30, no. 1, p. 81-93.

Taylor, T.N. and Krings, M., 2005, Fossil microorganisms and land plants: associations and interactions: Symbiosis, v. 40, p. 119-135.

Thiry, J., Galbois, J. and Schmitt, J.-M., 2006, Unusual phosphate concretions related to groundwater flow in a continental environment: Journal of Sedimentary Research, v. 76, p. 866-870.

Toker, N.Y., Onar, V., Belli, O., Ak, S., Alpak, H. and Konyar, E., 2005, Preliminary results of the analysis of coprolite material of a dog unearthed from the Van-Yoncatepe Necropolis in Eastern Anatolia: Turkish Journal of Veterinary and Animal Science, v. 29, p. 759-765.

Trueman, C.N. and Martill, D.M., 2002, The long-term survival of bone: the role of bioerosion: Archaeometry, v. 44, p. 371-382.

Vasconcelos, C., McKenzie, J., Bernasconi, S., Grujic, K. and Tien, A., 1995, Microbial mediation as a possible mechanism for natural dolomite formation at low temperatures: Nature, v. 377, p. 220-222.

Villa, P., Goñi, M., Bescós, G., Grün, R., Ajas, A., Carlos, J., Pimienta, G. and Lees, W., 2010, The archaeology and paleoenvironment of an Upper Pleistocene hyena den: an integrated approach: Journal of Archaeological Science, v. 37, p. 919-935.

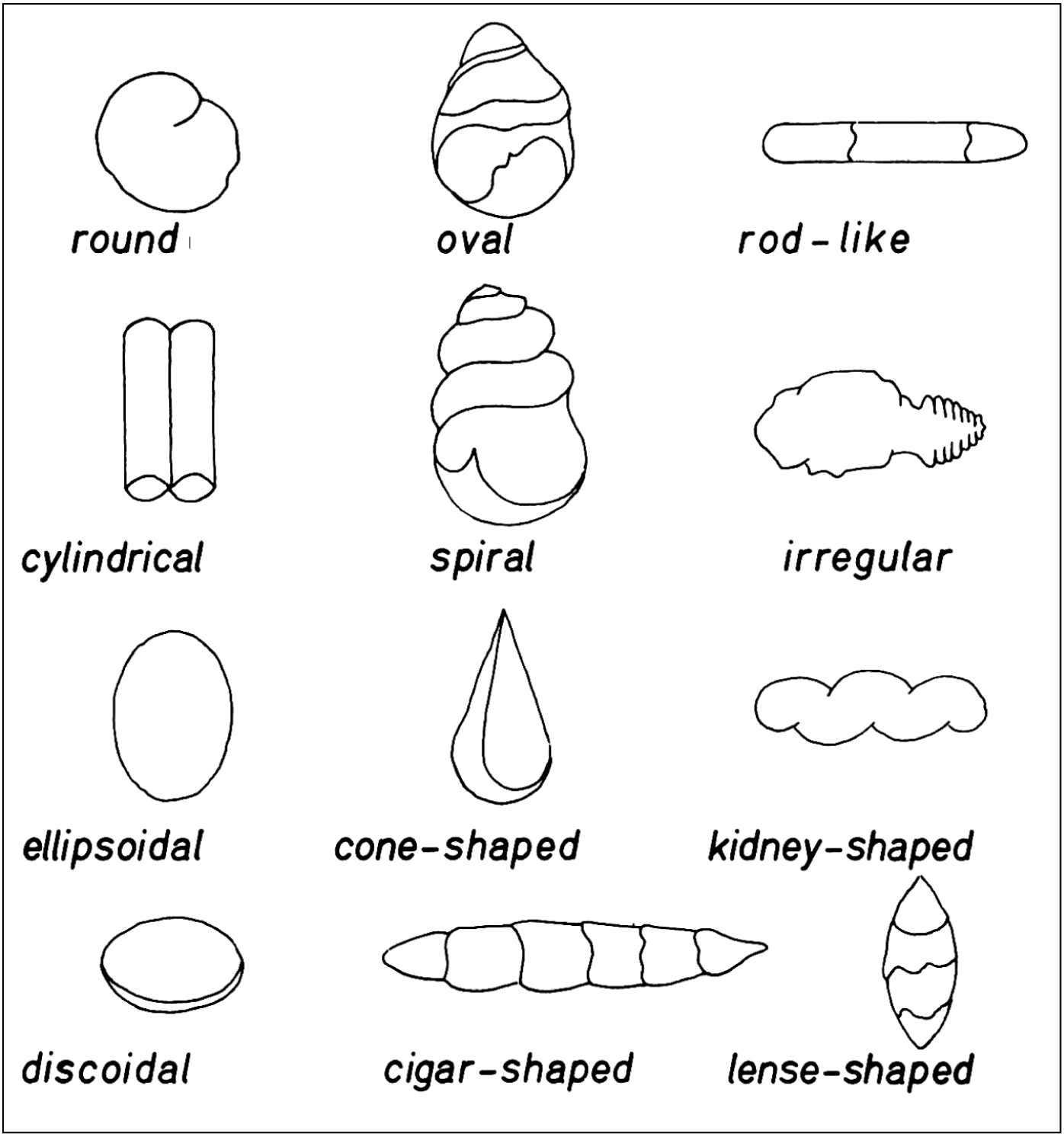
Vinther, J., Briggs, D., Prum, R. and Saranathan, V., 2008, The colour of fossil feathers: Biology Letters, v. 4, p. 526-529.

Waychunas, G.A., 1988, Luminescence, X-ray emission and new spectroscopies; *in* Hawthorne, F.C., ed., Spectroscopic Methods in Mineralogy and Geology: Mineralogical Society of America, Reviews in Mineralogy, v. 18, p. 639-698.

White, D.E., Hem, J.D. and Waring, G.A., 1963, Chapter F. Chemical composition of sub-surface waters; *in* Fleischer, M., ed., Data of Geochemistry, 6th ed.: U.S. Geological Survey Professional Paper 440-F, 67 p.

Wood, J., Rawlence, N., Rogers, G., Austin, J., Worthy, T. and Cooper, A., 2008, Coprolite deposits reveal the diet and ecology of the extinct New Zealand megaherbivore moa (Aves, Dinornithiformes): Quaternary Science Reviews, v. 27, p. 2593-2602.

Yll, R., Carrión, J., Marra, A. and Bonfiglio, L., 2006, Vegetation reconstruction on the basis of pollen in Late Pleistocene hyena coprolites from San Teodoro Cave (Sicily, Italy): Palaeogeography, Palaeoclimatology, Palaeoecology, v. 237, p. 32-39.



Classification of coprolites (from Häntzchel et al.).