

Turning Pyrite Concretions Outside-In: Role of Biofilms in Pyritization of Fossils

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ABSTRACT: Studies integrating sedimentary geochemistry, diagenesis, and taphonomic experimentation provide new understanding about the development of pyrite concretions around organisms and the exceptional preservation of some nonmineralized tissues by pyrite crusts. As now interpreted, at least three factors influence the preservation of organisms by pyrite: 1) burial in a low oxygen environment or microenvironment; 2) ratio of sulfide ions to dissolved reactive iron in sediment pore waters; and 3) presence of reactive biofilms (microbial assemblages) associated with decaying organic material. Under low oxygen conditions, breakdown of organics allows for the release of sulfide ions into sediment pore waters, where they combine with reactive iron ions to form iron sulfides.

Pyrite often preserves biomineralized structures (primarily shells) through concretionary overgrowths, whereas non-biomineralized tissues (such as internal soft parts) are usually preserved by thin pyrite crusts. The extent of pyrite precipitation and the type(s) of organically produced material(s) preserved by FeS₂, seem to be related to the development of either reactive bacterial coatings that were in direct contact with decaying organic tissues or microbial assemblages (including bacteria and probably fungi) that formed halos around decaying organic tissues. Precipitation of pyrite to form a concretion apparently begins at multiple sites within a microbial halo, not just on the surface of the decaying mass.

INTRODUCTION

Among the more intriguing aspects of the fossilization process is preservation of soft tissues, chitinous coverings, or biomineralized structures by pyrite. This type of preservation is rather dogmatically referred to as replacement by pyrite in many geology textbooks. Studies integrating sedimentary geochemistry, diagenesis, and taphonomic experimentation, however, indicate that this notion of replacement is perhaps oversimplified because it fails to account for contrasts in the preservation of different types of organically produced structures. Moreover, it fails to account for factors influencing the formation of pyrite concretions as contrasted with the formation of thin pyrite crusts over organic structures.

Here, we present new information concerning the precipitation of sedimentary pyrite mediated by organic decay. This and other developing information (e.g., Schieber, 2002) provide the basis for an hypothesis that accounts for microbiological and geochemical factors leading to exceptional preservation of non-biomineralized tissues by means of pyrite. Also, preservation of biomineralized shells by

means of concretionary pyrite, without preservation of any associated non-biomineralized parts, is discussed. In addition to factors previously determined to play major roles in pyrite precipitation (e.g., burial of organics in low oxygen environments, and ratio of sulfide ions to dissolved reactive iron in sediment pore waters; e.g., Berner, 1970; Raiswell et al., 1988), pyrite precipitation seems to be strongly correlated with the development of microbial biofilms (Schieber, 2002). Such biofilms appear to have two forms that result in different patterns of pyrite precipitation. Bacteria-dominated biofilms apparently result in coating of tissues by thin pyrite crusts. Pyrite concretions (and sometimes pyrite rings) result from microbial assemblages that grow halos around decaying matter. Non-biomineralized parts of organisms are preferentially preserved by thin pyrite crusts, and non-biomineralized structures appear to be preferentially preserved by pyrite concretions.

Characterizing how pyrite has preserved fossils contributes at least two noteworthy advances: 1) a refined understanding of the conditions under which some exceptional

preservation of fossils has occurred (i.e., the rather unusual preservation of non-biomineralized tissues or so-called "soft parts;" e.g., Bartels et al., 1998; Stanley and Stürmer, 1987; Briggs et al., 1996; Grimes et al., 2002); and 2) a step toward more complete understanding of the precipitation of concretions in sedimentary strata. This work indicates that concretionary development is the result of rapid formation of an organic matrix surrounding a decaying mass. The presence of this decaying mass created a chemical microenvironment that induced precipitation of concretionary minerals. Crystal growth appears to have begun at multiple sites within the decaying mass, including the margin of the halo. The implication is that a pyrite concretion does not necessarily begin at the center and grow outward.

METHODS, MATERIALS, AND GEOCHEMICAL MODELS

Detailed study of sedimentary pyrite preserving fossils was carried out principally on specimens from the Alden Pyrite Bed (Ledyard Shale Member, Ludlowville Formation, Hamilton Group; Middle Devonian) of western New York (see Babcock and Speyer, 1987). The Alden Pyrite Bed, which ranges up to about 1.5 m in thickness, is one of the best developed pyrite beds in the Hamilton Group (Dick, 1982), and yields fossils representing a range of shallow marine organisms and body parts. Pyritization of fossils ranges from thin surficial coatings to round concretions that are typically less than 2 cm in diameter. Specimens were studied macroscopically, through sectioning, and via image enhancement (see Schieber, 2003) of sectioned specimens. For comparative purposes, taphonomic experiments were carried out on recently dead or frozen arthropods (horseshoe crabs and centipedes) in marine aquaria inoculated with microorganisms (see Babcock et al., 2000 and references therein). Finally, observational and empirical data were compared with geochemical models for pyrite precipitation.

The interaction of sulfide and reactive iron in controlling pyrite precipitation can be described using a double reservoir model (Helfferich and Katchalsky, 1970; Canfield and Raiswell, 1991; Raiswell et al., 1993). This model for bacterially mediated pyrite deposition describes the interaction between varying amounts of reactive iron and the sulfide released through bacterial sulfate reduction of organic structures having radii up to 50 μm (Raiswell et al., 1993). According to Canfield and Raiswell (1991), two variables



Figure 1: Centipede (*Scutigera*) decaying in water and surrounded by translucent bacterial-fungal halo. Length of specimen approximately 3 cm

control pyrite precipitation: 1) reactive iron content in the system; and 2) sulfide content in the system. Reactive iron is the amount of iron used in pyrite production as opposed to iron in the system as a whole (Raiswell et al., 1994). This iron may be introduced into a system through bacterially-catalyzed reduction of iron oxides (e.g., hematite) or iron oxyhydroxides (e.g., goethite, ferrihydrite, and lepidocrocite) by organic compounds (Jones et al., 1983; Lovely and Phillips, 1986a,b; Canfield, 1989), and the partial oxidation of iron sulfide minerals (Lord, 1980; Giblin and Howarth, 1984). Sulfide production, which influences the extent of pyrite precipitation around a decaying organism, is the result of bacterial dissimilation (Canfield and Raiswell, 1991). An increase in either of the reservoirs is expected to shift the deposition of pyrite toward the other reservoir. In the case of a decaying organic mass, the sulfide reservoir begins at the decaying organic mass and extends outward, whereas the reactive iron reservoir is in the surrounding sediment and associated pore water (Canfield and Raiswell, 1991). By using the flux of the two reservoirs, Canfield and Raiswell (1991) hypothesized that the three “types” of pyrite preservation outlined by Allison (1988) can be accounted for by: 1) precipitation of pyrite in the cellular pore spaces (permineralization); 2) precipitation of pyrite directly on the surfaces of the non-biomineralized body parts without preserving internal structure (mineral crusts); and 3) precipitation well outside of the boundary

of the organic material (mineral casts, molds, and concretions).

Here, the double reservoir model is emended to include the role of microbionts in mediating pyrite precipitation (Schieber, 2002), especially for decaying masses beyond the size constraints discussed by Raiswell et al. (1993). Biofilms help to explain the formation of both pyrite crusts and pyrite concretions, but not necessarily pyrite permineralization.

MODERN AND ANCIENT MICROBIOTA

The possibility of bacterial-fungal (or other microbial) interaction as a factor controlling pyritic macrostructure is supported based on results of SEM analysis of the cohesive and stable balloonlike structures (referred to here as microbial halos) that envelope decaying arthropods in laboratory experiments (Figs. 1, 2). Three-dimensional microbial halos develop around decaying organisms whether they are floating in water (Fig. 1), at the sediment sur-

face, or buried under sediment (Fig. 2). Scans of a microbial halo surrounding a decaying centipede (Fig. 1) show an anastomosing network of strands representing hyphae of a complex fungal mycelium (Fig. 3). Interspersed among the mycelia are small (0.5-2 μm) coccoid-shaped, gram-positive bacterial bodies (probably *Staphylococcus* or *Streptococcus*; Fig. 4).

Fungal mycelia that surround decaying organic matter in aqueous environments act as stabilizing media and substrates for the growth of interdependent, coherent microbial communities referred to as consortia (Cullimore, 2000). Modern microbial consortia can assume various forms, including crystallized structures such as nodules, crusts, rusticles, iron pans, stalactites, and stalagmites (Cullimore, 2000). An important product of microbial consortia is the accumulation of extracellular polymeric substances (EPSs), commonly referred to as “slime” (Cullimore, 2000). This slime acts as a three-dimensional pathway for the transport of recalcitrant accumulates such as ferric iron and nutrients such as nitrogen. Iron is a key component of EPSs

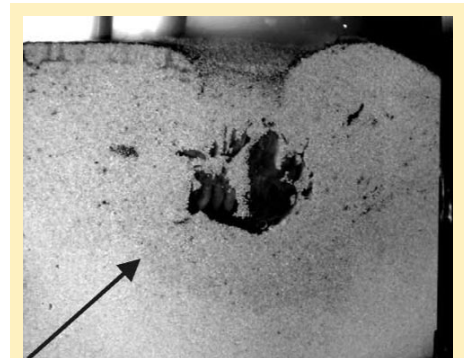


Figure 2 (top): Horseshoe crab (*Limulus*) decaying in sand and surrounded by dark bacterial-fungal halo (arrow). Length of halo approximately 8 cm.

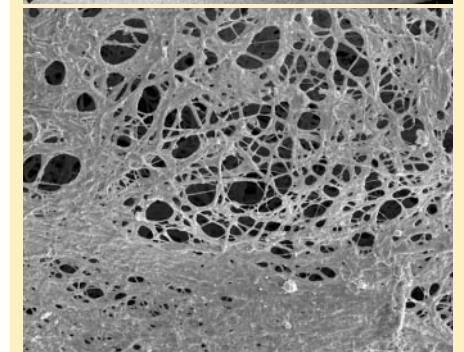


Figure 3 (middle): SEM image of network of fungal mycelia with interspersed bacterial cells extracted from halo surrounding specimen in Fig. 1. Length of bar scale 100 μm .

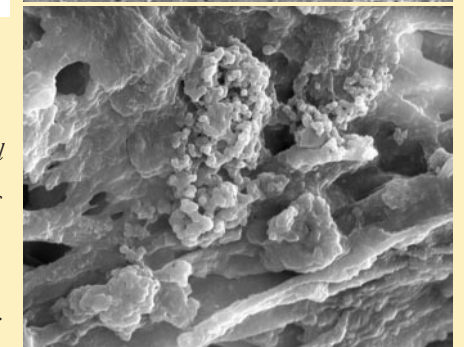


Figure 4 (bottom): SEM image of bacterial cells within the microbial consortium illustrated in Fig. 3. Length of bar scale 10 μm .

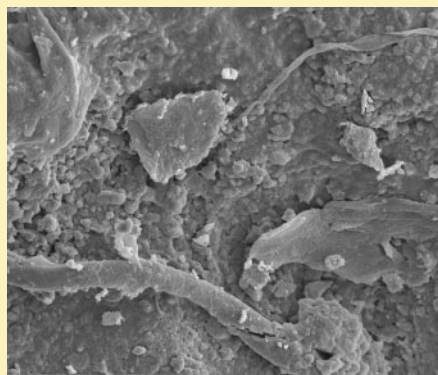


Figure 5: SEM image of pyrite crust over soft parts associated with the siphuncle of an orthocone nautiloid showing probable fungal hyphae (strandlike structures) and bacteria (round structures); from the Alden Pyrite Bed (Ledyard Shale Member of Ludlowville Formation; Devonian) of western New York. Length of bar scale 70 μm .

because some bacterial respiration mechanisms rely upon it. The presence of iron-binding agents, called siderophores (Madigan et al., 1997), in some bacteria make the formation of a consortium beneficial to those bacteria lacking in efficient iron-binding proteins. They allow iron to be transported throughout microbial communities (Madigan et al., 1997), which is an important prerequisite for the formation of FeS₂.

We interpret microbial halos that surround decaying organic matter within sediment as precursors of concretions. Darkened halos observed to surround decaying horseshoe crabs (Fig. 2) consist of fungal hyphae that surround and enshroud grains of sediment. The halos are so cohesive that extracting samples without disturbing the surrounding sediment can be difficult. Under SEM and EDX analysis, the dark halos appear to be largely bacterial in composition and not due to the presence of iron monosulfide or manganese hydroxide.

SEM analyses of pyritized mollusks from the Alden Pyrite Bed reveal minute strands and beadlike structures (Fig. 5) that closely resemble microbionts observed in the halos surrounding organisms decaying in aqueous laboratory experiments. The strands are inferred to be pyritized fungal hyphae (although the possibility that some may be cyanobacterial strands cannot be ruled out at present), and the beadlike structures are interpreted as coccoid bacteria. Similar structures observed previously from sedimentary rocks (e.g., Southam et al., 2001; Schieber, 2002; Grimes et al., 2002; Schieber and Arnott, 2003) likewise have been associated with the decay of animals or plants. Preservation of bacterial cells, and by implication, also soft

internal tissues in pyrite tends to occur in rather sheltered areas (e.g., linings of the chambers of orthocone nautiloids; cover photo). Pyritized areas have a honeycomb texture that is different from the surrounding pyritic matrix. This texture is similar to that observed in carbonized Oligocene feathers and interpreted as having a biofilm origin (Davis and Briggs, 1995).

BIOFILM RESPONSE PATTERNS IN PYRITIZED FOSSILS

The composition of microbial consortia involved in the decay of organic tissues seems to play a major role in the style of pyritization of fossils. Bacteria-dominated consortia lead to pyrite crusts and are preferentially associated with non-biomineralized tissues, whereas microbial consortia dominated by extensive networks of microbes (presumably fungal hyphae and bacteria) lead to pyrite concretions. Also, a relationship exists between the types of microbial consortia and the extent to which integrity of the decaying organisms is maintained within the resulting fossils: tissues preserved by crusts seem to have been more susceptible to development of blow-out structures resulting from gas release during decay

than were structures preserved by network-supported microbial consortia.

Bacteria-dominated (fungi-depleted) sheets surrounding decaying organic matter probably responded differently to gas release than did larger, presumably mycelium-supported, microbial consortia. In order to study the different effects of biofilms influencing preservation style, images of cut and polished pyritized fossils were enhanced using Adobe Photoshop (see Schieber, 2003). In examples where points of rupture associated with gas release have been studied, pyritization was evidently associated with bacterial sheets lacking significant strands or networks of microbes. Pressure associated with gas buildup in response to decay was not well accommodated in the relatively non-elastic bacteria-dominated sheets. The more elastic, network-supported microbial halos were better at accommodating gas pressure. As a result, rupture was more common in decaying organisms covered by bacteria-dominated sheets (cover photo). In specimens having more extensive microbial networks, biofilms were probably more stable and able to distribute gas release more evenly over the circumference of the consortium. This may have been an important step in the formation of a concretion (Fig. 6) around a decaying organic nucleus.

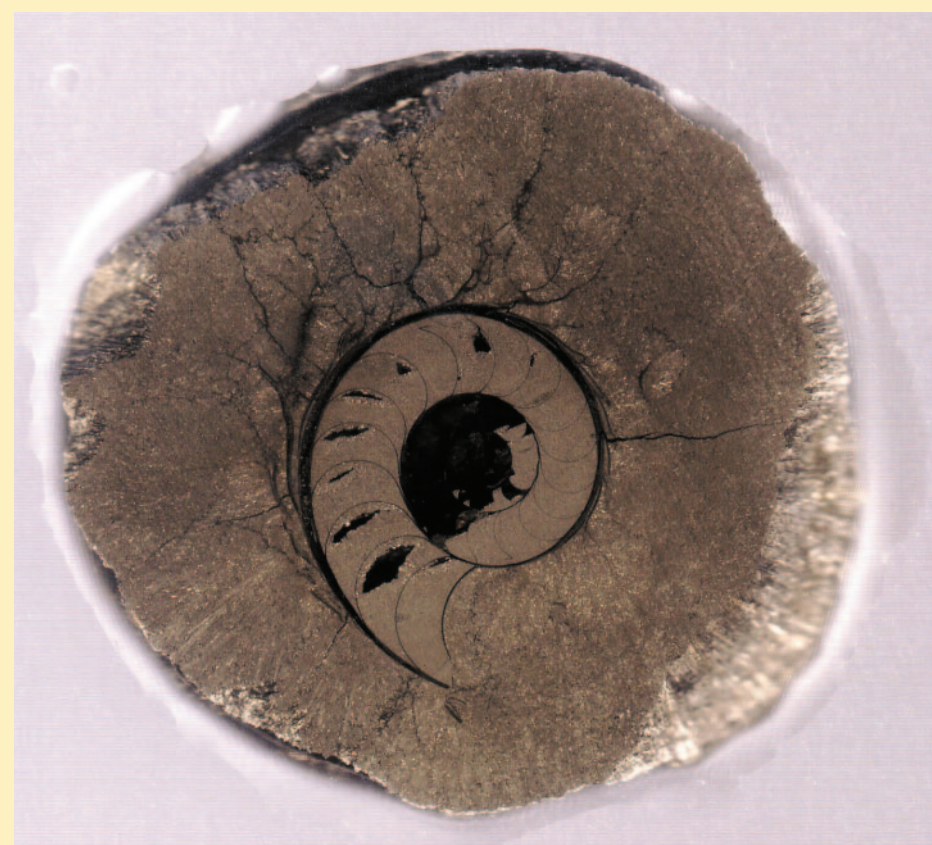


Figure 6: Cross-section of pyrite concretion formed around ammonoid shell; from the Alden Pyrite Bed (Ledyard Shale Member of Ludlowville Formation; Devonian) of western New York. Diameter of concretion approximately 2 cm.

Under anaerobic conditions, halos composed of sulfate-reducing bacteria attached to fungal mycelia (or possibly cyanobacterial strands) formed around decaying organic matter, and the bacteria released pockets of sulfide into slime. The pockets could extend into the surrounding matrix. Bacteria deficient in microbial networks would, in contrast, form mats along organic surfaces. Sulfide produced at sites of bacterial colonization in network-stabilized EPSs would promote the deposition of pyrite throughout the consortia; this explains the precipitation of pyrite in concretions. By contrast, the lack of network-supported consortia would restrict bacteria to positions close to decaying organisms, thus causing pyrite precipitation close to nuclei of decay. In such cases, pyritization of bacterial sheets would occur through microbe entombment (Schultze-Lam et al., 1996).

IMPLICATIONS

The implications of microbial consortia for influencing fossilization are far reaching. In addition to accounting for variation in the ways that pyritization of fossils occurs, the biofilm consortium hypothesis suggests a mechanism by which other types of concretions (e.g., carbonate and silica) may form. Preservation differences within beds containing sedimentary pyrite seem to record variability in the composition of microbial species involved in decay. It is conceivable that there was also some environmental variability in the composition of microbial communities, and that may help to explain some differences in style of pyritization among different sedimentary strata.

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The title of Dr. Van Wagoner's talk is "Energy Dissipation: Origin of Structure and Organization in Siliciclastic Sedimentary Systems."

