The Role of an Organic Slime Matrix in the Formation of Pyritized Burrow Trails and Pyrite Concretions

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Sandstones from the Black Island member of the Winnipeg Formation (Ordovician) contain a variety of early diagenetic iron sulfide morphologies, including elongate concretions of variable length. Examination of sandstone samples with X-radiography reveals that these concretions, now consisting of pyrite, are associated with burrows.

Detailed textural examination of the pyrite shows an anomalously loose packing of sand grains within these concretions, and also suggests that iron sulfide nucleation commenced at multiple sites in what must have been a stiff matrix. Compositional data acquired by electron microprobe indicate that the iron sulfides did not replace fecal matter left behind by the burrower. Sulfur isotope data point to bacterial sulfate reduction as a sulfide source, corroborated by fossilized bacterial remains within the concretionary pyrite.

Mucus and slime trails of marine benthos were probably important for early diagenetic pyrite production in these sediments; they can be considered a favorable "culture" medium for sulfate reducing bacteria. Because the mucus seems to mineralize very early in burial history, it also provides for enhanced preservation of bacterial remains.

INTRODUCTION AND GEOLOGIC SETTING

The rocks examined for this study come from the Black Island Member of the Ordovician Winnipeg Formation in Saskatchewan (Paterson, 1971), and are earliest deposits of the Tippecanoe Sequence in the Williston Basin (Gerhard and Anderson, 1988). The stratigraphic context of the Winnipeg cores examined for this study has been described by Paterson (1971). The Black Island Member predominantly is composed of quartzose sandstone with minor shale. The upper portion of the Black Island Formation is dominated by bioturbated quartz wacke with 15–25 percent clay matrix (Paterson, 1971). The sand fraction largely is composed of very well rounded quartz grains that most likely were recycled from the underlying Deadwood Formation (Binda, 1991). The Black Island Member has been described as a shallow marine-basin-margin sandstone facies by Vigrass (1971) and Paterson (1971).

Judging from the examination of numerous specimens over the years, pyrite concretions in sandstones typically show poikilitic fabric, with the pyrite filling the pore space remaining between the sand grains. In most cases, such concretions may measure from 5mm to several cm across, and are spherical to somewhat oblate in shape. The pyrite concretions examined in this study, however, differ in that they are elongate and may be inclined rather steeply relative to bedding. They also show an unusually loose sand-grain fabric, with the sand grains "floating" in a pyrite matrix, instead of exhibiting the grain supported fabric of typical pyrite concretions in sandstones. This difference was explored further because it points to the hitherto unrecognized importance of benthos-produced mucus in the early diagenetic history of sediments.

METHODS

A total of seven drill cores were examined and sampled for this study at the Subsurface Geological Laboratory in Regina (Saskatchewan Energy and Mines). The cores are the same that were examined by Binda and Simpson (1989) in an earlier study of pyrite diagenesis in the Winnipeg Formation, and their paper also contains a map with core locations and coordinates. Core samples were slabbed and polished for visual inspection by binocular microscopy. Polished thin sections were prepared from selected samples for detailed petrographic study (reflected light microscopy). X-radiographs were prepared for samples that showed abundant elongate pyrite concretions. Powdered pyrite nodules were analysed by XRD for mineral components. Polished sections of pyrite nodules were examined by electron microprobe to detect chemical components other than iron and sulfur, and fragments of pyrite nodules were examined by SEM for small scale textural features. A few SEM samples were etched with HNO_3 prior to examination. A total of 13 sulfur isotope analyses were performed at the Biogeochemical Laboratories of Indiana University (Bloomington) on material from crushed and powdered pyrite nodules. The sulfur isotope ratios were determined using a high temperature furnace coupled to a Finnigan MAT 252 isotope ratio mass spectrometer in continuous flow mode. Results are expressed in the usual per mil notation relative to the Canyon Diablo Troilite (CDT). Accuracy and precision of $\delta^{34}S$ determinations were generally better than ± 0.5‰ as determined from duplicate measurements of samples and standards.

OBSERVATIONS

Concretion Morphology

Pyrite concretions in sandstones of the Black Island Member were observed on cut surfaces and range in size from 3–15 mm. They may be of irregular-subrounded outline, or may be elongated (Fig. 1A). In the latter case, several elongate concretions may show alignment within the rock and appear to have the same orientation (Fig. 1A). X-radiographs of concretion-bearing samples show that, in three dimensions, these elongate concretions are connected and typically follow a winding, curved, and meandering path (Fig. 1B).

Concretion Petrography

Ground powders from several concretions were examined by XRD. The only identifiable sulfide mineral is pyrite. Examining the concretions with reflected light microscopy reveals that the pyrite matrix contains well

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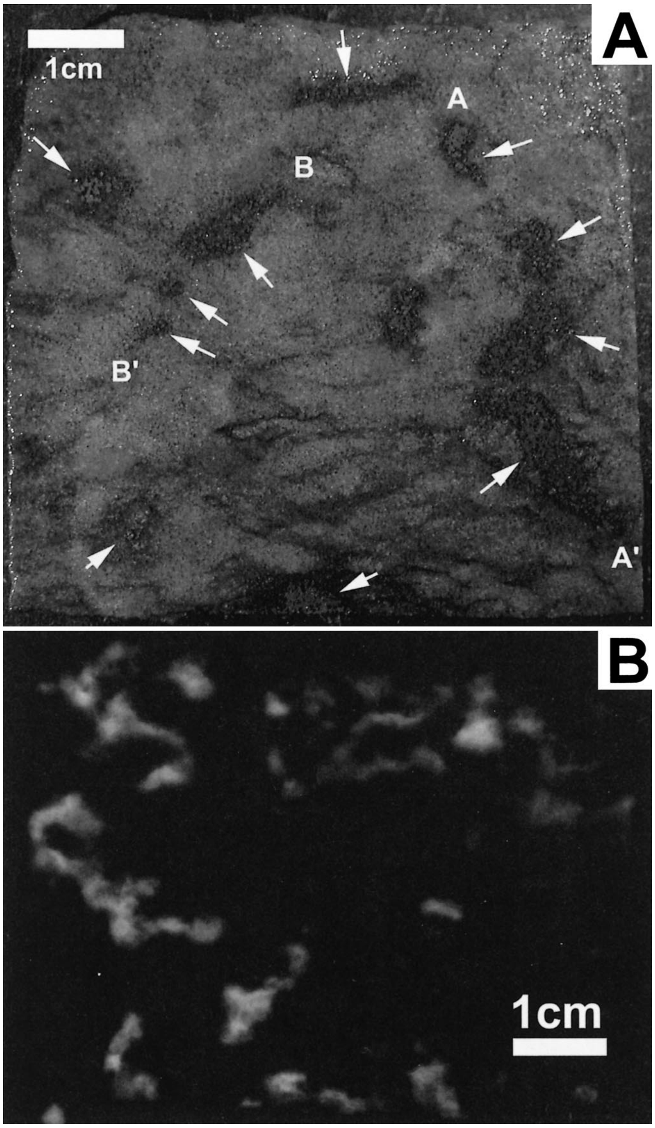

FIGURE 1—Pyrite-bearing sandstone from the Black Island Member of the Winnipeg Formation (A) Photo of slabbed sandstone core showing elongate pyrite concretions (arrows). Pyrite between A-A' probably belongs to a single burrow trail, likewise for pyrite between B-B'. The sandstone displays a mottled texture and shows no remaining primary sedimentary features. (B) X-radiograph of sandstone with pyrite concretions as show in Figure 1A. Light areas are occupied by concretionary pyrite. Their irregular winding and meandering path suggests emplacement by simple sediment feeders.

rounded grains of quartz sand (Fig. 2). These quartz grains are scattered randomly through the pyrite and are usually so far apart that they can not be considered part of a grain supported fabric. Examination under the SEM also shows that these quartz grains rarely touch each other and confirms that they usually are surrounded entirely by pyrite.

Reflected light microscopy of polished blocks and thin sections provides further information about mineralogy and growth history of the iron sulfide matrix. Etching polished surfaces with HNO_3 reveals multiple growth generations of iron sulfides (Fig. 3). Initial iron sulfide precipitation led to rounded fine crystalline bodies (Fig. 3A) that subsequently were overgrown by successive rims of idiomorphic iron sulfide (Fig. 3B). At present, practically all of the iron sulfide is identified as pyrite via XRD and optical properties (bright yellow reflectance, isotropic character). Several observations, however, suggest that the pyrite that encloses and overgrows the initially formed rounded fine crystalline pyrite bodies formed by inversion of earlier precipitated marcasite. In every thin section one can find areas where the overgrowth pyrite (Fig. 3) shows anomalous optical anisotropy (Fig. 4A), cloudy distribution of micropores (Fig. 4B), gaps along grain boundaries (Fig. 4C), and alignment of larger pores along growth zones (Fig. 4B, C). These features were observed by Murowchick (1992) in experimentally inverted marcasite, and attributed to volume loss and strain due to the mismatch between the pyrite and marcasite structures.

Marcasite is a rarely observed mineral in modern sediments, and requires low pH for its formation (Canfield and Raiswell, 1991). What caused the acidic conditions during early diagenesis is not known, but it has been suggested that it might indicate the oxidation of earlier formed iron sulfides (Canfield and Raiswell, 1991), possibly due to aeration of the sediment by other burrowers, or due to intermittent reworking and erosion. Evidence of the latter, in the form of erosion surfaces and lag deposits, is common in the Black Island Member.

Geochemistry

Pyrite concretions that grow in a sediment matrix typically contain inclusions of silicate minerals, such as the quartz grains seen in Figure 2B. Because no additional inclusions were seen even under SEM, several concretions were examined by electron microprobe to detect submicroscopic inclusions of silicate minerals. For comparative purposes, occurrences of clear interstitial pyrite cement also were probed. In both situations, Al and Si were at or below the detection threshold of the instrument (0.01wt% or less).

A total of 13 sulfur isotope measurements were made on the studied pyrite concretions. The measured $\delta^{34}S$ values range from 0 to $-25‰$ with an overall average of $-12‰$.

SEM

To learn more about their origin, several of these concretions were crushed gently and the fragments examined by SEM. Low magnifications (500–100X) revealed the same textural features as observed with reflected light microscopy. Etching of samples with HNO_3 enhanced crystal boundaries and growth zones. At substantially higher magnifications (5000–9000X), however, curious and unexpected features at the micron scale became visible. These features are essentially smooth, round to oval shaped bodies of pyrite that range in size from 0.3 μm to several microns in size. They were observed most abundantly in the areas that are identified as pyrite nucleation sites in Figures 3A and B, showing a rounded outline and consisting of fine crystalline early pyrite.

INTERPRETATION AND DISCUSSION

The absence of primary sedimentary features in the sandstones that contain the pyrite concretions in question,

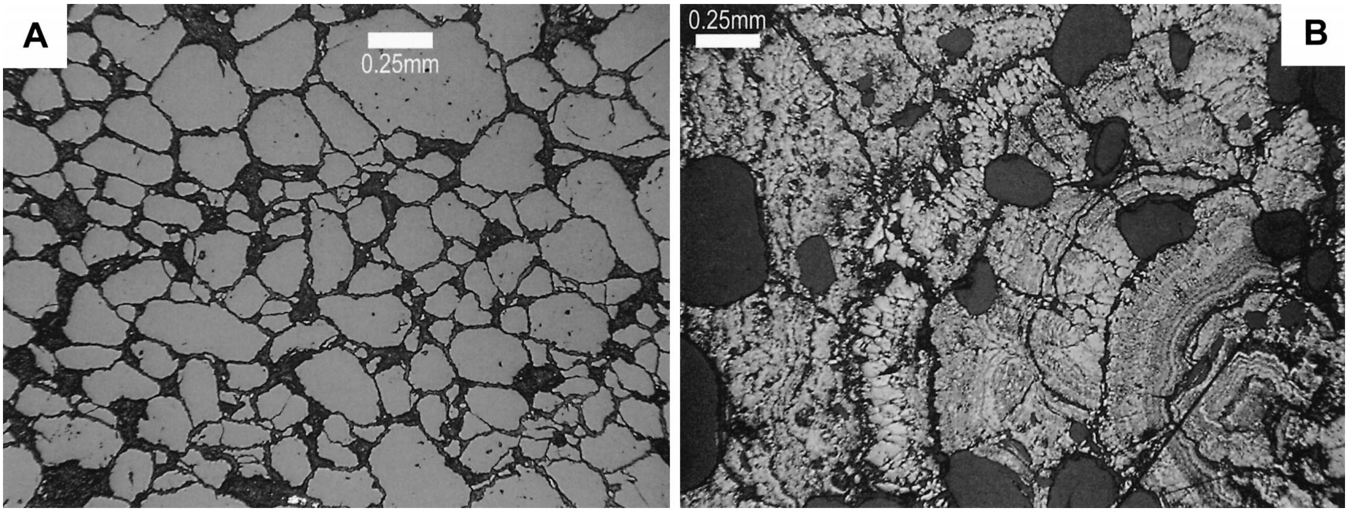

FIGURE 2—Photomicrographs (reflected light) of sand grain fabric in the sandstone matrix (A), and of sand grain distribution within concretionary pyrite (B). Note tightly packed grain fabric in (A) and widely spaced quartz grains within concretionary pyrite (B). Quartz grains in (B) are very well rounded, whereas those in (A) are less well rounded and show straight and concave contacts. This suggests that quartz grains within concretionary pyrite were protected from pressure solution during burial diagenesis.

as well as their overall mottled appearance (Fig. 1A), indicate that infaunal reworking kept pace with sedimentation (Howard, 1978), something to be expected in a shallow marine-basin-margin sandstone (Vigrass, 1971). Due to the bedding parallel orientation of the redox interface, pyrite concretions in sediments typically are aligned parallel to bedding (Canfield and Raiswell, 1991). The fact that the concretions discussed here can be oriented steeply subvertical (Fig. 1A) suggests other controlling factors. In the context of a thoroughly bioturbated sediment, the irregular winding and meandering path of these concretions strongly suggests that their origin is linked to bioturbation. These traces were emplaced in a loose sandy substrate, yet they lack visible wall structures needed to prevent collapse. Thus, it is unlikely that they were occupied for any length of time as open structures (Bromley, 1996). The irregular and winding nature of the trace further suggests that it was produced by an organism that exploited the substrate for food (Bromley, 1996).

Thomsen and Vorren (1984) described pyritized burrows from Pleistocene shelf sediments off Norway and interpreted them as the early diagenetic replacement of muco-polysaccharides of polychaete tubes. These tubes were permanent structures (domichnia) with uniform diameter and smooth exteriors that reflect long term emplacement of worm constructed mucus tubes. This strongly contrasts with the sandgrain-studded pyritized traces of variable diameter (Fig. 1A) described here. In conjunction with the irregular and winding nature of these traces (Fig. 1B), the pyritic traces seen in Figure 1 more likely reflect transient passage of organisms in search of food, rather than a permanently occupied structure.

The widely spaced quartz grains within concretionary pyrite (Fig. 2B) suggest that a material that was stiff enough to prevent settling of quartz grains took up the space between grains and hindered the formation of a grain supported fabric. Iron sulfide nucleation (pyrite and/or marcasite) occurred at multiple sites within this material (Fig. 3B), and over time the sites coalesced to form the observed concretions.

Ordovician seawater sulfate has $\delta^{34}S$ values of around 25–30‰ (Claypool et al., 1980). The strongly negative sulfur isotope values of the concretionary pyrite indicate, therefore, a high degree of fractionation via microbial sulfate reduction (Canfield and Raiswell, 1999). Localized iron sulfide growth in sediments requires that the sediment is anoxic but also non-sulfidic (Brett and Allison, 1998), and that there is localized production of hydrogen sulfide. As observed in other studies of pyrite-bearing sediments, decaying organism remains can lead to localized iron sulfide deposition because they provide food for sulfate reducing bacteria (Brett and Allison, 1998). In the rock record this may be manifested in the form of steinkerns (Brett and Allison, 1998). Model calculations suggest that in these cases high dissolved iron concentrations in the pore waters are required to restrict iron sulfide precipitation to the decay site (Raiswell et al, 1993).

The rounded-to-oval shaped bodies observed within the pyrite concretions (Fig. 5) actually could be direct evidence for localized sulfate reduction, because they resemble extant examples of sulfate reducing bacteria in size and shape (Stanier et al., 1986). The fact that they are found in a portion of the rock where there must have been abundant sulfide production during early diagenesis strongly suggests that they could be the mineralized remains of sulfate reducing bacteria.

What remains to be discussed is the nature of the material that kept quartz grains separated and suspended, and also fostered localized sulfide production and iron sulfide precipitation. Assuming that these traces reflect the passage of an organism through the sediment in search of food, it might be assumed that this organism left behind fecal pellets, which could have separated the quartz grains and acted as a food source for sulfate reducing bacteria. A mechanism of this type has been invoked for other exam-

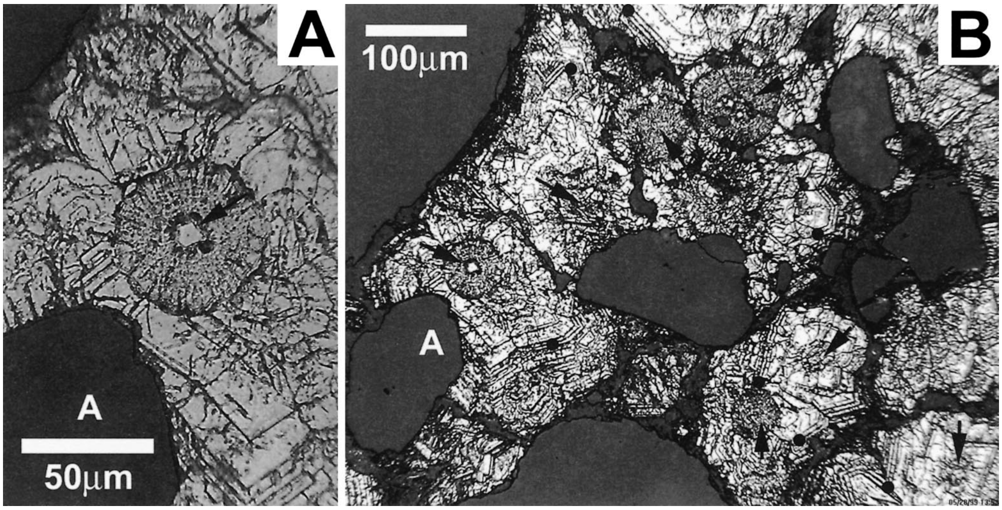

FIGURE 3—Iron sulfide nucleation and iron sulfide generations in concretionary pyrite. (A) Closeup photomicrograph (reflected light) of iron sulfide nucleation site (center marked with black arrow), showing the fine crystalline nature, rounded outline of early iron sulfide accumulation, and details of the later euhedral overgrowth. Under reflected light these early iron sulfide accumulations show none of the features indicative of a marcasite precursor (Fig. 4). This may indicate that initial iron sulfide formation favored pyrite. Quartz grain marked 'A' is the same as that marked in Figure 3B. Examination of the growth zones shows that the quartz grain is engulfed by an expanding iron sulfide (originally marcasite). (B) Photomicrograph (reflected light, etched thin section) of multiple iron sulfide generations in concretionary pyrite. Black arrows indicate multiple sites of iron sulfide nucleation early in nodule history. The iron sulfides in these areas usually form rounded, fine crystalline bodies (Fig. 3A) and, in turn, are overgrown by euhedral iron sulfide (probably original marcasite) with growth zonation. The geometric relations between growth zonation in iron sulfides and quartz grains (e.g., area marked A) show that quartz grains were simply enclosed by the expanding areas of iron sulfides. Some sets of growth bands are so characteristic (e.g., those marked with black dot) that they allow ''cement stratigraphy'' and make possible an understanding of the spread of iron sulfide over time.

ples of pyritized burrows (Baird and Brett, 1991; Thomsen and Vorren, 1984; Brett and Allison, 1998).

In the case of the pyritic traces examined here, however, the absence of visible mineral inclusions and geochemical signatures of silicate minerals are inconsistent with the pyritization of a fecal pellet matrix. Fecal pellets of infaunal organisms typically consist of a mixture of mineral grains, mucus, and other organic matter (O'Brien and Slatt, 1990), and their replacement by pyrite should leave abundant residual mineral inclusions. The latter should have been visible either under the SEM on etched surfaces, or should have been detected by electron microprobe analysis for silicate mineral components (Si, Al, etc.).

An alternative explanation is that the mystery matter represents slime trails left behind by passing worms. Scolecodonts, the jaws of polychaete worms, are a common fossil in the Winnipeg Formation (Binda, 1991) and polychaetes are known for abundant mucus production. Freely burrowing forms that pass through unconsolidated sediment produce mucus to ease their passage and leave behind a slime trail (Bromley, 1996). These slime trails can persist for extended periods of time in the sediment (Davies and Hawkins, 1998), and can serve as a ready food source for microbes, including sulfate reducers. The mucus that constitutes these slime trails is comparable in many respects to agar, a widely used culture medium in microbiology (Stanier et al., 1986). Thus, the mucus may have served both as a food source and as a "culture" medium for the sulfate reducers. Within the mucus matrix, numerous scattered bacterial colonies could promote local-

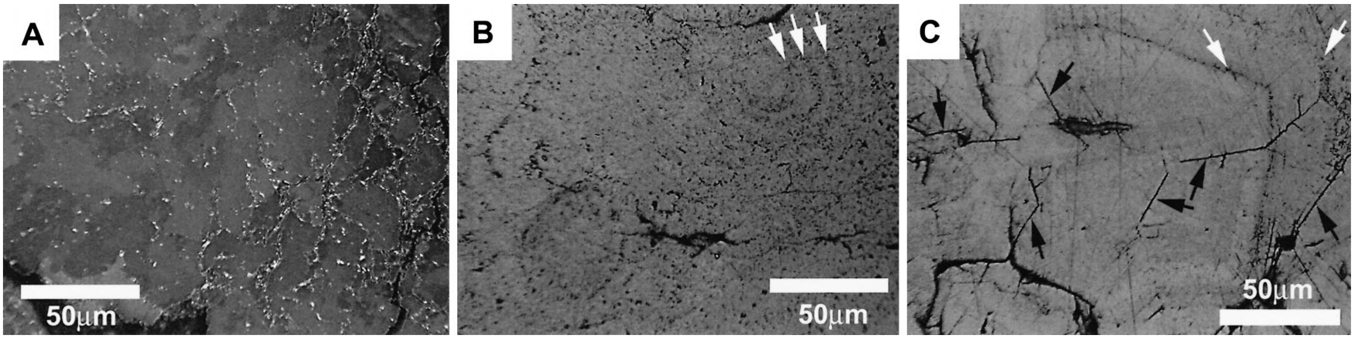

FIGURE 4—All images are photomicrographs of concretionary pyrite taken under reflected light. (A) The anomalous anisotropy inherited from marcasite is visible as dark vs light gray domains that impart a speckled appearance (crossed polarizers). (B) Image shows micropores due to volume loss from maracasite to pyrite. Micropores either occur as clouds of irregularly distributed small pores or may be concentrated/ aligned along growth zones (white arrows). (C) Well developed gaps along grain boundaries (black arrows) and concentration of large micropores along growth zones (white arrows). Both features reflect volume loss during maracsite-to- pyrite inversion.

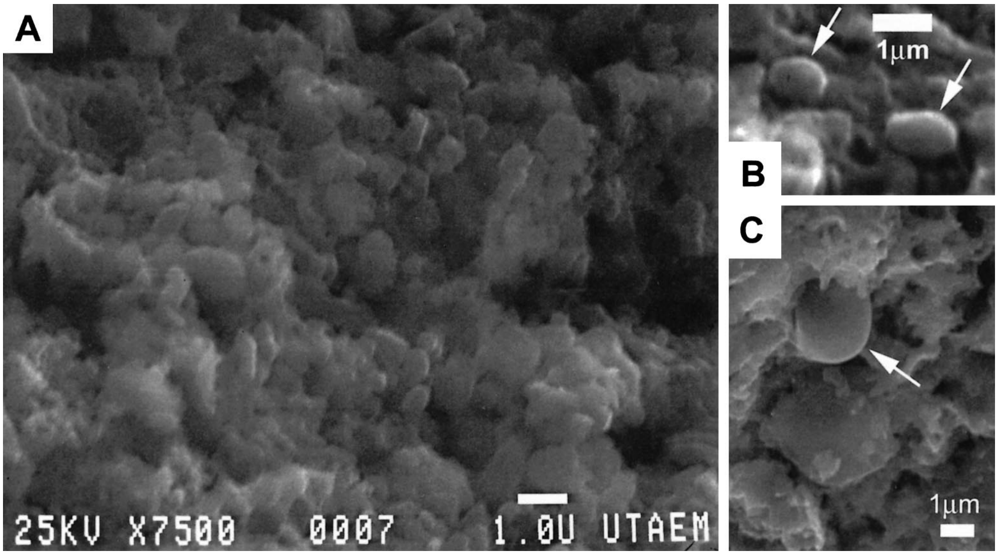

FIGURE 5—SEM photos of rounded-to-oval pyrite bodies (broken surfaces, briefly etched with HNO_3). (A) The etched pyrite in these fine crystalline nucleation areas typically shows a ragged-irregular morphology. In contrast, the rounded pyrite bodies have a distinct smooth exterior. (B) C lose up photo of oval pyrite bodies with smooth exterior. (C) A fairly large rounded pyrite body, partially enclosed by ragged pyrite (due to etching). These features are interpreted as the mineralized remains of sulfate reducing bacteria.

ized sulfide production and lead to growing masses of iron sulfide that would eventually coalesce and form massive concretions. The slime trail scenario explains the overall morphology of the burrows, their variable diameter, the abnormally loose packing of sand grains, and the lack of mineral inclusions. Sulfur isotope data, preserved microbial remains, and the presence of multiple nucleation sites within the "mystery" matrix all support the view that the latter was a food source for sulfate reducing microbes, and a site for localized sulfide production and iron sulfide precipitation.

Stochiometric considerations, however, suggest that metabolization of the organic matter of the slime trails can not account for all of the sulfur present in these mineralized burrows. For example, if the burrows initially had been filled with pure metabolizable organic matter, approximately 5 cm^3 of organic matter would need to be metabolized for each cubic centimeter of pyrite precipitated. This estimate was arrived at by using a variety of simple organic substances, such as lactate, ethanol, acetate, and formaldehyde. The latter is used, for example, in sulfate reduction equations proposed by Canfield and Raiswell (1991). Then, it must be considered that mucus trails do not represent pure organic matter, but rather consist of organic matter interspersed with a large proportion of water. Assuming a 10-to-1 ratio between water and organic matter, approximately 50 cm^3 of mucus would be needed to provide the "food" for the preciptiation of 1 cm^3 of pyrite. This clearly demonstrates that a large share of the organic matter metabolized by the sulfate reducers must have originated in the sediment surrounding the slime trails, probably due to the activity of fermenting bacteria. The organic matter of the mucus trails could have sustained sulfate reducing bacteria only during the initial stages of iron sulfide deposition, possibly during formation of the early spherical iron sulfide accumulations that are shown in Figure 3. Diffusion of ions through mucus is necessarily slower than through the surrounding pore waters; thus, the slime trails would have been the most likely site of reducing microenvironments very early in sediment history. Therefore, the main importance of the mucus trails seems to lie in the provision of a stable habitat for sulfate reducing bacteria.

CONCLUSIONS

The observations presented here illustrate the importance of mucus produced by infaunal benthos on the early diagenesis of sandstones. The importance of this infaunal mucus is that it serves simultaneously as an (initial) food source and culture medium for infaunal microbial communities. Because ions diffuse through mucus more slowly than through water, the slime trails probably serve as a more solidly anoxic "haven" for the anaerobes that try to colonize surface sediments. Iron sulfide precipitation at the actual site of microbial sulfate reduction also leads to very early encapsulation and preservation of microbial remains.

Observations that suggest pyrite growth in a mucus matrix include (1) an abnormally loose grain fabric with "floating" grains, (2) pyrite that is free of mineral inclusions, and (3) an association with burrow structures. Sedimentary pyrite nodules that, for textural reasons, suggest pyrite growth in a mucus matrix should be good prospects in the search for microbial remains in sediments of all ages. This could be of particular importance for those that search for traces of earliest life. To date only cherts and carbonate rocks have been examined in this quest (Schopf and Walter, 1983), and pyrite nodules, common in the more abundant terrigenous clastic rocks, are essentially virgin territory.

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