Journal of
Sedimentary
Research

Journal of Sedimentary Research, 2005, v. 75, 907–920
DOI: 10.2110/jsr.2005.070

PYRITE AND MARCASITE COATED GRAINS IN THE ORDOVICIAN WINNIPEG FORMATION, CANADA: AN INTERTWINED RECORD OF SURFACE CONDITIONS, STRATIGRAPHIC CONDENSATION, GEOCHEMICAL "REWORKING," AND MICROBIAL ACTIVITY

JÜRGEN SCHIEBER[1] AND LEE RICIPUTI[2]
[1]*Department of Geological Sciences, Indiana University, Bloomington, Indiana 47405, U.S.A.*
[2]*Chemical and Analytical Services Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6365, U.S.A.*

ABSTRACT: **Sulfide-coated grains are enigmatic sedimentary particles that occur in sediments ranging in age from Archean to Jurassic. Although their oolitic and pisoidal texture suggests energetic and agitated conditions, their mineralogy seems to require a reducing and stagnant environment. Because of this conflict, they have long been considered diagenetic replacements of precursor iron oxide, chamosite, or carbonate ooids.**

Coated iron sulfide (CIS) grains from the Ordovician Winnipeg Formation of Saskatchewan, Canada, formed as primary diagenetic precipitates under shallow burial conditions, involving intermittent episodes of tractional reworking, grain abrasion, reburial, and precipitation of further concentric laminae. These iron sulfide grains are found in shallow marine sandstones with indications of episodic wave reworking, and indicate sufficient organic-matter burial to promote reducing pore waters and iron sulfide formation. Horizons with strong enrichment of iron sulfide grains (up to 40%) indicate negative net sedimentation to facilitate geochemical "reworking" of iron. CIS grains formed during intervals of maximum sediment starvation, when organic matter was enriched in surface sediments, and rare storm waves intermittently reworked the surface sediment.

Alternating laminae of pyrite and marcasite within these grains point to substantial fluctuations in pore-water pH, driven by intermittent oxidation of previously formed iron sulfides. Filamentous and coccoid structures within cortical laminae suggest microbial involvement in lamina formation through providing a growth medium for sulfate-reducing bacteria and potentially a template for mineral growth.

Coated iron sulfide grains of the Winnipeg Formation preserve a combined record of condensation, seafloor reworking, fluctuating chemical conditions in the surface sediment, and high surface productivity. This information-rich record is made even more valuable by the fact that the host sediment consists largely of heavily bioturbated monotonous sandstones that could not provide these insights on their own merit.

INTRODUCTION

This paper is the second in a series that reports findings from a broader study of coated iron sulfide (CIS) grains. Occurrences ranging in age from Proterozoic through Devonian (e.g., Hayes 1915; Kalliokoski 1966; Schieber and Riciputi 2004) were compared through detailed petrographic and geochemical study. Finding CIS grains in sedimentary rocks from a variety of lithologies, ranging from distal black shales to proximal sandstones, provided the initial impetus for the overall study. CIS grains from the Ordovician Winnipeg Formation of Saskatchewan (Figs. 1, 2), first reported by Paterson (1971), were of particular interest because they appeared to be of primary origin, in contrast to an earlier studied Devonian occurrence (Schieber and Riciputi 2004) that proved to be of replacement origin.

The early focus of the investigation was on the question whether such grains might be primary vs. secondary (via replacement) in origin, because of textural similarities to chamosite and goethite ooids in sedimentary ironstones. Diagenetic replacement of precursor goethite or chamosite grains has been demonstrated in other studies on the basis of petrographic observations and geochemical data (Kalliokoski 1966; Ranger 1979; Schieber and Riciputi 2004), but there have also been suggestions that CIS grains may be of primary origin (Carozzi 1972), such as via diagenetic accretion (Binda and Simpson 1989).

The methodology employed is the same as in an earlier study of pyrite ooids from the Devonian Chattanooga Shale (Schieber and Riciputi 2004). There a clear case could be made for an origin via replacement of chamosite ooids. CIS grains from the Winnipeg Formation, in contrast, appear to have formed as primary diagenetic precipitates. It was that finding that shifted the focus of the study away from the primary vs. secondary question towards the many intriguing implications of a primary origin.

Of particular importance in this study are the many conclusions about the prevailing depositional conditions and processes that we can extract from careful examination of CIS grains. For example, sedimentary features such as abraded cortices and cortex unconformities show that these grains resided in the surface layer for their entire growth history. Considerations of the frequency of the required high-energy events (most likely unusually strong storms) suggests that the time spans recorded by individual grains range from several thousand to more than ten thousand years. The grains also show corrosion pits on iron sulfide cortices that attest to intermittent oxidation and destruction of iron sulfides. Microbial remains within iron sulfide cortices suggest active microbial involvement in cortex formation, and cortex-to-cortex fluctuations of δ^{34}S values reflect bacterially mediated sulfate reduction and cortex accretion under various degrees of open-system vs. closed-system conditions.

What makes these grains so valuable for interpreting the rock record are the implications of the above attributes, such as bottom-current reworking, sediment-starved conditions, high productivity, and a need for stratiform iron enrichment through "geochemical reworking." Elsewhere such conditions might have produced beds of chamositic iron ooids (Maynard 1983), and the different mode of iron enrichment in Winnipeg CIS grains points to subtle yet significant differences in starting conditions and environmental controls. Unraveling the enigmatic origins of such grains thus provides new insights into the conditions that prevailed while their host rocks formed. In that sense, understanding the origin of CIS grains opens up yet another window for understanding processes operative in the geologic past.

The strata examined for this study belong to the Black Island Member (Fig. 2) of the Ordovician Winnipeg Formation in Saskatchewan, Canada (Paterson 1971), and are the 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 is composed of quartzose sandstone with minor shale and is overlain by the shale-dominated Icebox

FIG. 1.—Location map showing the occurrence of the Winnipeg Formation in Saskatchewan (shaded) and adjacent areas.

Member. The CIS grains occur in the upper portion of the Black Island Member, an interval dominated by bioturbated quartzose sandstone (Fig. 3) with as much as 15 to 25 percent clay matrix (Paterson 1971). The sand fraction contains abundant well rounded quartz grains that most likely were recycled from the underlying Deadwood Formation (Binda 1991).

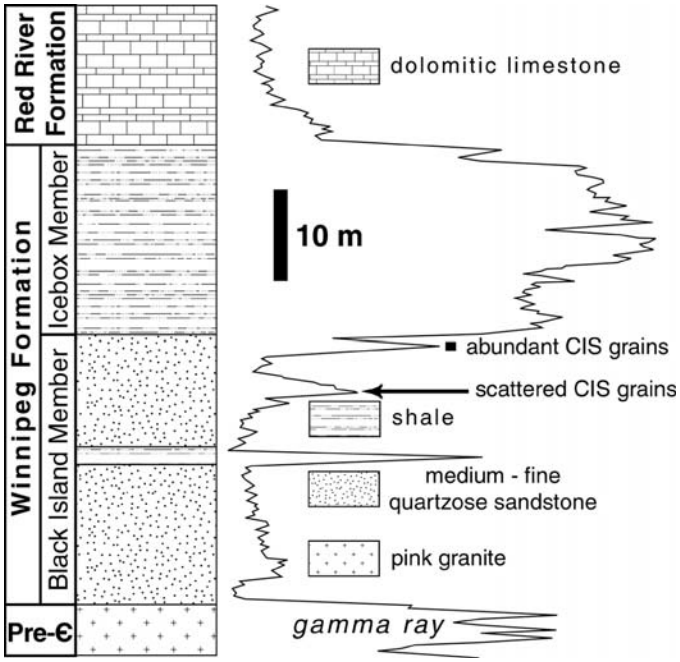

FIG. 2.—Stratigraphic overview of the Winnipeg Formation from a representative core intercept with accompanying gamma-ray log (Tidewater Wapella Crown No. 12-34-T, Saskatchewan coordinates: 12-34-14-1W2). The Winnipeg Formation is of Middle Ordovician age (Gerhard and Anderson 1988). Minor oscillations on the gamma-ray log reflect meter-scale variations in clay content.

METHODS

Approximately 200 samples were collected from a set of seven Winnipeg drill cores available at the Saskatchewan Mineral Resources Laboratories. Cores are discontinuous, and no single core covers the entire Black Island Member. Available core intervals were described and sampled for occurrences of CIS grains, and all samples were studied with a binocular microscope. A subset of 30 polished thin sections was studied by reflected-light microscopy and scanning electron microscopy (FEI Quanta 400 FEG, located at Indiana University, Department of Geological Sciences).

SEM study included energy-dispersive X-ray microanalysis (EDS) and phase identification via electron backscatter diffraction. In electron backscatter diffraction (EBSD) a stationary electron beam strikes a tilted mineral surface and the diffracted electrons form line patterns (Kikuchi patterns) on a fluorescent screen. These patterns are characteristic of the crystal structure of a given mineral (Prior et al. 1999; Schwartz et al. 2000), and allow phase identification for mineral grains of submicron size, as well as measurement of crystallographic orientation. The EBSD detector used was the Nordlys detector by HKL Technology, and data analysis was conducted with the Channel 5 software package by HKL Technology.

Quantitative microanalysis was performed with an electron microprobe (JEOL JXA-733 Superprobe, located at Southern Methodist University, Dallas), and an ion microprobe (Cameca 4f, located at Oak Ridge National Laboratories, for δ^{34}S measurements). Reproducibility of ion probe δ^{34}S measurements is 0.5‰ (Riciputi et al. 1998).

OBSERVATIONS

Core Description and Subsurface Data

The Black Island Member has been described as a shallow marine basin-margin sandstone facies by Vigrass (1971) and Paterson (1971), on

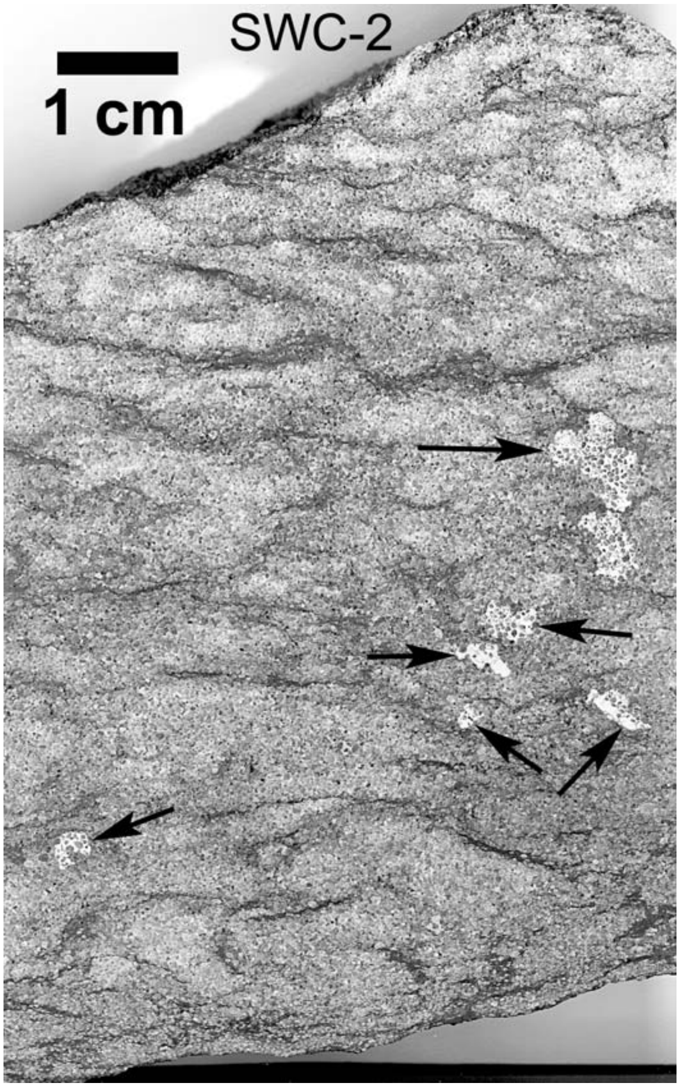

FIG. 3.—Photograph of typical core specimen from the Black Island Member. Burrow mottled fabric is dominant; primary sedimentary structures have been destroyed. Lighter areas pointed out by black arrows are patches of pyrite cement associated with pyritized and marcasitic burrow trails (Schieber 2002a). Exhumation, fragmentation, and reworking of these burrow trails yields the cores of many CIS grains in the Winnipeg Formation.

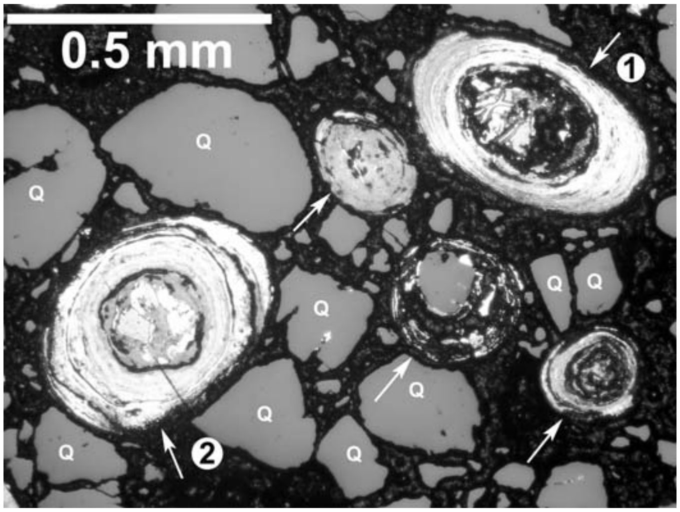

FIG. 4.—Reflected-light photomicrograph of quartz sandstone with CIS grains. White arrows point out CIS grains, Q = quartz sand grains. The CIS grains marked with arrow (1) and (2) both contain cores that consist of clusters of radiating pyrite crystals and/or coarse pyrite aggregates (after marcasite) that are reworked fragments of pyritized and marcasitic burrow trails (Schieber 2002a). These cores are overgrown by laminated cortices of pyrite and marcasite.

the basis of paleogeographic reconstructions, offshore increase of the clay/sand ratio, and intense bioturbation. It also shows a clear pattern of coastal onlap and oscillating shorelines (Vigrass 1971). Superimposed on the overall deepening trend that is recorded by the Black Island to Icebox succession (Fig. 2) are high frequency oscillations of the sandstone/shale ratio that range in thickness from 1.5 to 3 meters (Paterson 1971). Owing to pervasive bioturbation, the latter are very difficult to recognize in core. On wireline logs, however, they are clearly visible because increases in clay content coincide with gamma-ray spikes (Fig. 2). Detailed core descriptions (unpublished data) show that high abundances of CIS grains coincide with relatively high clay contents and (in places) shale interbeds.

Whereas the Black Island Member overall shows a bioturbated-mottled texture as seen in Figure 3, intervals that contain CIS grains may in places also show preserved flaser bedding, scours, and ripple cross-lamination attributable to wave action. The sand fill of scour depressions is enriched with CIS grains, and beds of reworked sandstone have abundant CIS grains in the basal portion. Sharp-based lag deposits (5 to 15 cm thick) with about 30 to 40% CIS grains and rounded bone fragments occur locally.

Petrography

Reflected-light petrography of polished thin sections (Figs. 4, 6) shows that CIS grains range in size from 0.2 to 10 mm and contain a variety of cores. The latter include rounded ilmenite grains, quartz grains, rare phosphatic fossil fragments, fragments of CIS grains, clusters of radiating pyrite crystals, and coarse pyrite aggregates with rounded quartz grains (Fig. 5A). The latter two are the most common core types, and their crystal habit is actually suggestive of marcasite. The latter supposition is supported by a previous petrographic study of these iron sulfide morphologies (Schieber 2002a) that suggested that they may represent marcasite (FeS_2) that had inverted to pyrite during burial (Murowchick 1992). Subsequent examination of CIS grains with electron backscatter diffraction (EBSD) under the SEM showed that a substantial proportion of the suspected marcasite in cores is still in its original state and did not invert to pyrite (Fig. 6).

Aside from differences in the core composition we observe two basic grain types that usually occur side by side in the same bed: (1) those with dominant cores and thin cortices (Fig. 5A), and (2) those with thick cortices and a small core (Fig. 5D). Typically, type 2 grains are well rounded and smaller than 2 mm, whereas many type 1 grains are larger (up to 10 mm) and have irregular outlines. Cortical laminae vary in thickness (a few µm to 40 µm) and are in many instances of irregular-wavy appearance (Fig. 5D). They may also show interlayering of fine crystalline pyrite and coarse crystalline marcasite laminae with outward-radiating crystals (Fig. 5B), a textural relationship that is confirmed by electron backscatter diffraction (EBSD) phase mapping of CIS grains (Fig. 6). Thick cortical laminae may also contain inclusions of quartz sand grains (Fig. 5C). Both grain types can show cortex unconformities where a given lamina (or set of laminae) displays an angular unconformity with successive laminae (Fig. 7). High-resolution SEM studies of CIS grains also show

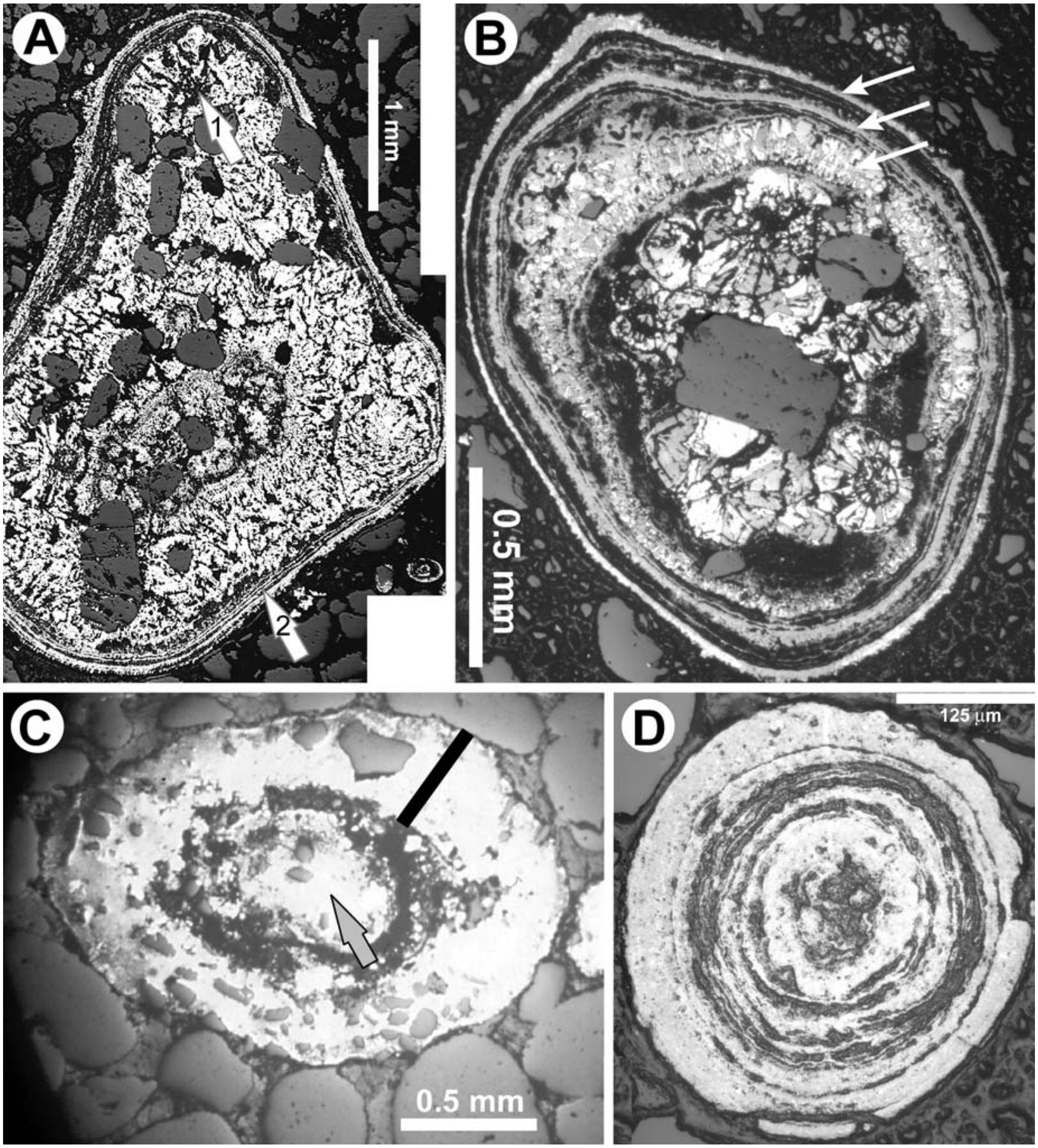

FIG. 5.—Four morphological variations of CIS grains. **Grain A)** large grain with dominant core of radial-bladed and blocky pyrite (originally marcasite) and inclusions of "floating" quartz grains (gray). Typically, radiating clusters of marcasite show sharply outward-projecting crystals and have an irregular-serrated outer margin. Marcasite cluster visible at the top of the core (arrow 1) is largely smoothed off at the margin, suggesting abrasion due to reworking. The abraded core is overgrown by a thin laminated cortex (arrow 2). **Grain B)** smaller grain with same type of core as in grain A. The core is surrounded by multiple laminae of pyrite and marcasite (marked by arrows). Identification of marcasite and pyrite by EBSD (see Fig. 6). **Grain C)** grain with a core (arrow) that is overgrown by a single thick overgrowth lamina (marked by black bar). This lamina contains inclusions of silt- to sand-size quartz grains that indicate that overgrowth occurred while the grain was buried. Note the large difference in grain size and rounding between quartz included in lamina and quartz in surrounding sandstone matrix. This contrast indicates that grain C was reworked from a finer grained sandy sediment. **Grain D)** small spherical grain with irregular-wavy overgrowth laminae of highly variable thickness.

corrosion pits in iron sulfide cortices that are infilled by pyrite or marcasite (Fig. 8).

Approximately 20 CIS grains were separated from their rock matrix and gently crushed for examination of cortex surfaces by SEM (secondary and backscatter electron imaging). Grains were cleaned with acetone in a sonic bath, and a subset of grains was slightly etched with nitric acid to better reveal grain boundaries and textural details. Outermost cortex surfaces show in most instances a pavement of interlocking pyrite or marcasite crystals (Fig. 9B), whereas inner cortices show the same type of fine crystalline pyritic and coarser crystalline marcasite as seen in Figure 6. High-resolution imaging of cortices revealed masses of ovoid bodies a few microns in size (Fig. 9C). The latter are smooth-walled oval features that

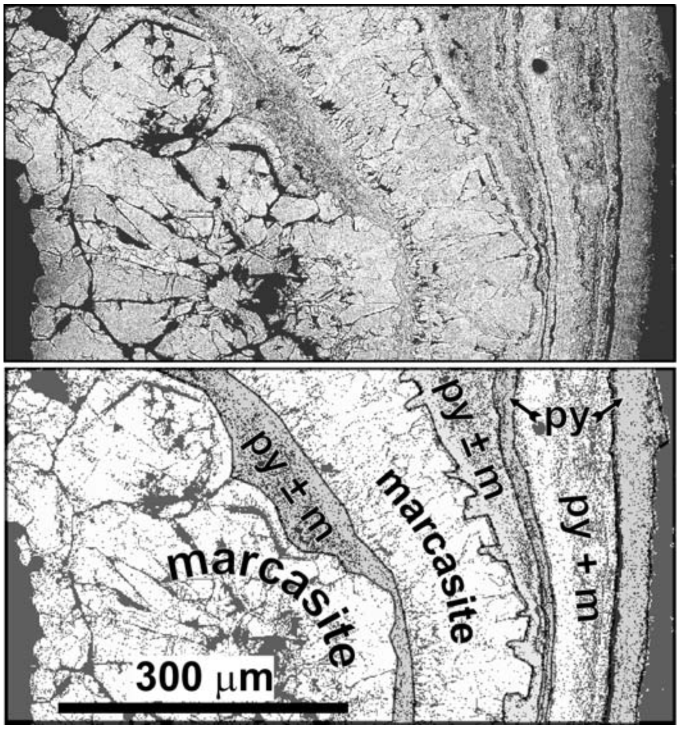

FIG. 6.—**A)** Detail view of grain shown in Figure 5B; showing a closeup of alternating marcasite and pyrite laminae. The radiating clusters of marcasite in the left third of the image belong to the core of the CIS grain, and the pyrite and marcasite laminae to the right belong to the cortex of the CIS grain. Different gray shades indicate variable crystal orientation of pyrite and marcasite grains. **B)** Same field of view as in A, showing distribution of pyrite and marcasite as mapped by EBSD.

consist of iron sulfide and are in turn encrusted with coarser iron sulfide grains (Fig. 9D). The smooth walls of these oval features show irregular perforations (Fig. 9E). In addition to these ovoid bodies, filamentous structures that consist of single or multiple filaments of about 0.5 µm width that may merge into sheet-like structures (Fig. 9A) are also found.

Electron Microprobe Analyses

Because concentrically zoned iron sulfide grains can for example form via replacement of chamosite ooids (Schieber and Riciputi 2004), we analyzed CIS grains by electron microprobe to see whether we could detect residual inclusions of chamosite. No chamosite was detected. EDS (spot analysis and element mapping), and microprobe analysis (Fig. 10A) conducted on dozens of grains rarely showed measurable amounts of SiO_2 and Al_2O_3. Pyrite cortices of Winnipeg CIS grains are typically free of visible inclusions except for scattered quartz grains in some instances (Fig. 5C).

Ion Microprobe Analyses

Five CIS grains from this study were analyzed for sulfur isotope ratios using an ion microprobe. Sulfur isotope data (in delta notation, relative to CDT [Cañon Diablo troilite]) average 6.7‰ for pyrite cores (5 measurements; range: −4.5‰ to 10.7‰) and 2.9‰ for cortex pyrite (17 measurements; range: −10.8‰ to 12.0‰). The number of measurements across cortices depended on cortex thickness and the diameter of ablation pits (approximately 50 µm). In most cases no more than three measurements were possible, but in one exceptionally large grain (Fig. 10B) seven measurements were possible. In all cases of multiple measurements of cortical pyrite in single grains, sulfur isotope values show considerable variability across the cortical thickness (Fig. 10B).

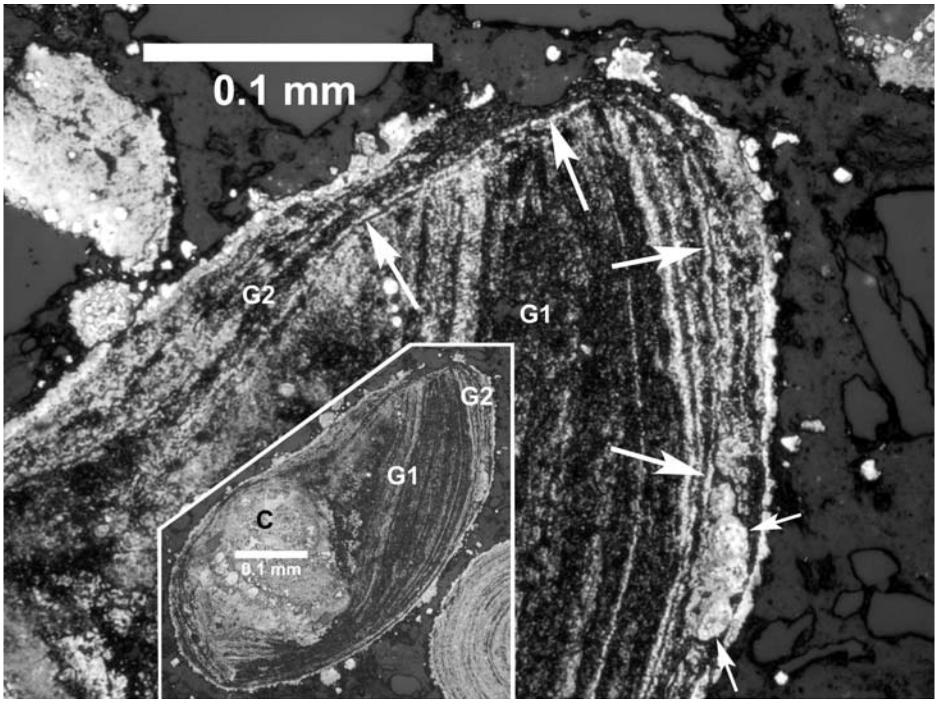

FIG. 7.—Example of cortex unconformity. Inset shows that grain started with accretion of a first generation of laminae (G1) around a pyrite core (C). The grain then broke up during reworking, and the resulting fragment was rounded and overgrown by a second generation (G2) of pyrite and marcasite laminae. Large arrows point out the cortex unconformity; small arrows point out pyrite framboids within laminae.

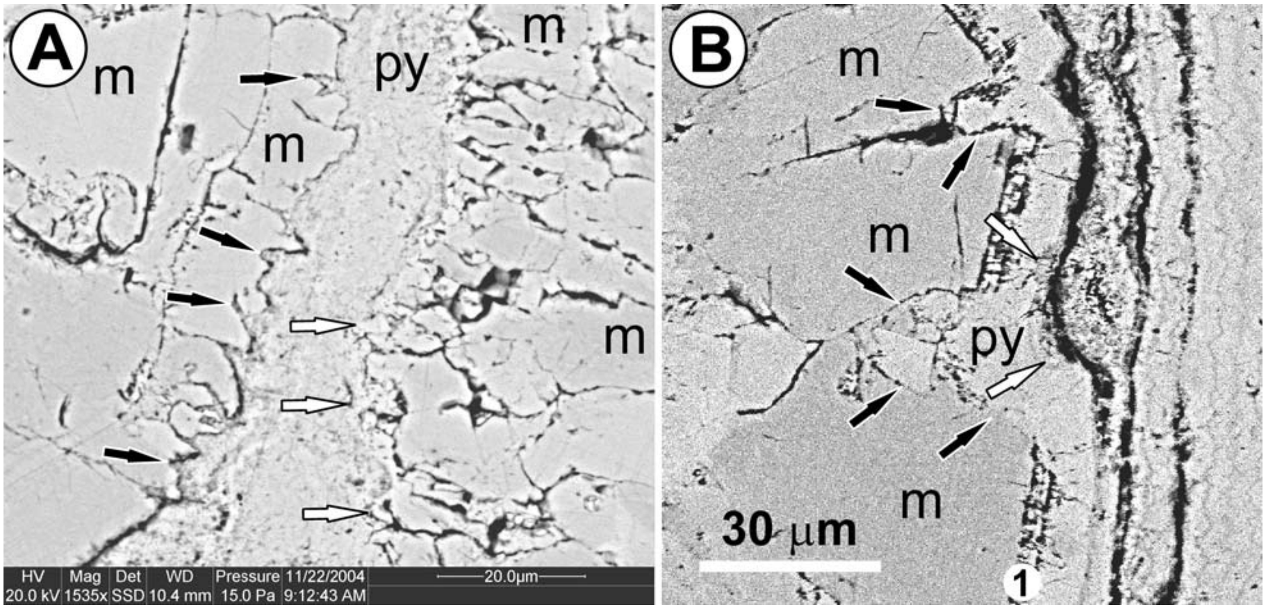

FIG. 8.—**A)** Irregularly corroded marcasite cortex from the grain shown in Figure 5B. The originally euhedral marcasite crystals show corrosive etching (black arrows). The corroded surface is overgrown with fine crystalline pyrite. This pyrite lamina as well shows corrosive etch pits (white arrows) that are filled in by marcasite of the succeeding lamina. Phase identification by EBSD. **B)** Corrosion pits into another cortex of euhedral marcasite crystals in the same grain. The overgrowing lamina consists of pyrite, and the etch pits (black arrows) are likewise filled with pyrite. This pyrite lamina has been etched in turn (white arrows), and the etch pits are infilled with pyrite of the succeeding lamina. Phase identification by EBSD.

IMPLICATIONS OF TEXTURAL AND COMPOSITIONAL DATA

Primary Origin of CIS Grains

CIS grains from the Black Island Member of the Winnipeg Formation lack any textural evidence that would suggest replacement of concentrically laminated precursor grains (chamosite, goethite, limonite, carbonate). No residual material of such precursor grains has been observed. Nonetheless, because replacement of comparable grains was demonstrated in other studies (Kalliokoski 1966; Schieber and Riciputi 2004), we evaluated the potential for replacement. Compared with concentrically laminated pyrite grains that owe their origin to replacement of chamosite ooids (Schieber and Riciputi 2004), the high purity of pyrite cortices as indicated by electron microprobe analysis (Fig. 10A) provides an argument against replacement. In addition, while it is very difficult to envision how any conceivable replacement process could have produced alternating concentric laminae of pyrite and marcasite (Figs. 6B, 7), this feature is readily explained through successive diagenetic accretion of iron sulfides. Diagenetic iron sulfide accretion on preexisting grains also is consistent with thick irregular-wavy laminae that contain inclusions of quartz sand grains.

Cores from Reworked Mineralized Burrows

Cores of CIS grains that consist of ilmenite, quartz, fossil fragments, and CIS grain fragments are readily explained as utilization of material available in the environment. The origin of the most common cores, consisting of clusters of radiating pyrite and/or marcasite crystals and coarse pyrite and/or marcasite aggregates (Fig. 5A), was determined in an earlier study of sulfide diagenesis in the Black Island Member (Schieber 2002a). Throughout the Black Island Member we find irregular iron sulfide concretions that follow burrow trails. They consist of a mixture of pyrite and marcasite in clusters and coarse aggregates with rounded quartz grains "floating" in the sulfide matrix. Textural considerations, e.g., "floating" quartz grains, strongly suggest that they represent mineralized mucus trails of infaunal organisms (Schieber 2002a). To find fragments of these mineralized burrows as the rounded cores of CIS grains (Fig. 5) implies that the original burrows were exhumed and reworked after early diagenetic mineralization and prior to cementation and consolidation of the host sediment.

Reworking Processes and Time Scales

Cortex unconformities (Fig. 7) provide evidence for intermittent mechanical reworking of CIS grains, quite possibly owing to the same events that produced marcasitic cores through exhumation and reworking of mineralized burrow trails. The observation that not all grains show cortex unconformities suggests that there is no direct linkage between accretion of successive cortical laminae and reworking. Co-occurrence in the same bed of irregular large grains with dominant cores and well rounded small grains with small cores and thick cortices suggests reworking events that span a broad range of current velocities.

CIS grains with diameters up to 10 mm require highly energetic events to accomplish transport and abrasion. Using Stokes' Law one can calculate for example that the hydraulic equivalent of a 10 mm pyrite grain would be a 16 mm quartz grain, and that of a 1 mm pyrite grain a 1.6 mm quartz grain. Measurements in natural environments (e.g., Sundborg 1956) indicate that 16 mm quartz grains would require flow velocities on the order of 120 to 300 cm/s for transport, whereas 1.6 mm quartz grains should require flow velocities between 30 to 40 cm/s. In modern shelf seas, processes that can produce velocities at the low end (30 to 40 cm/s) include tidal currents and winter storms (Duke 1990), but for the high-end velocities (120 to 300 cm/s) exceptionally strong but rare storms, such as hurricanes, are required (e.g., Murray 1976; Morton 1981). Rare, in this context, means a recurrence frequency on the order of 500 to 1000 years (Liu and Fearn 1993).

The co-occurrence of large and small pyrite grains implies that reworking was not caused by normal day-to-day currents. Considering that an epicontinental basin like the Williston Basin had smaller wave

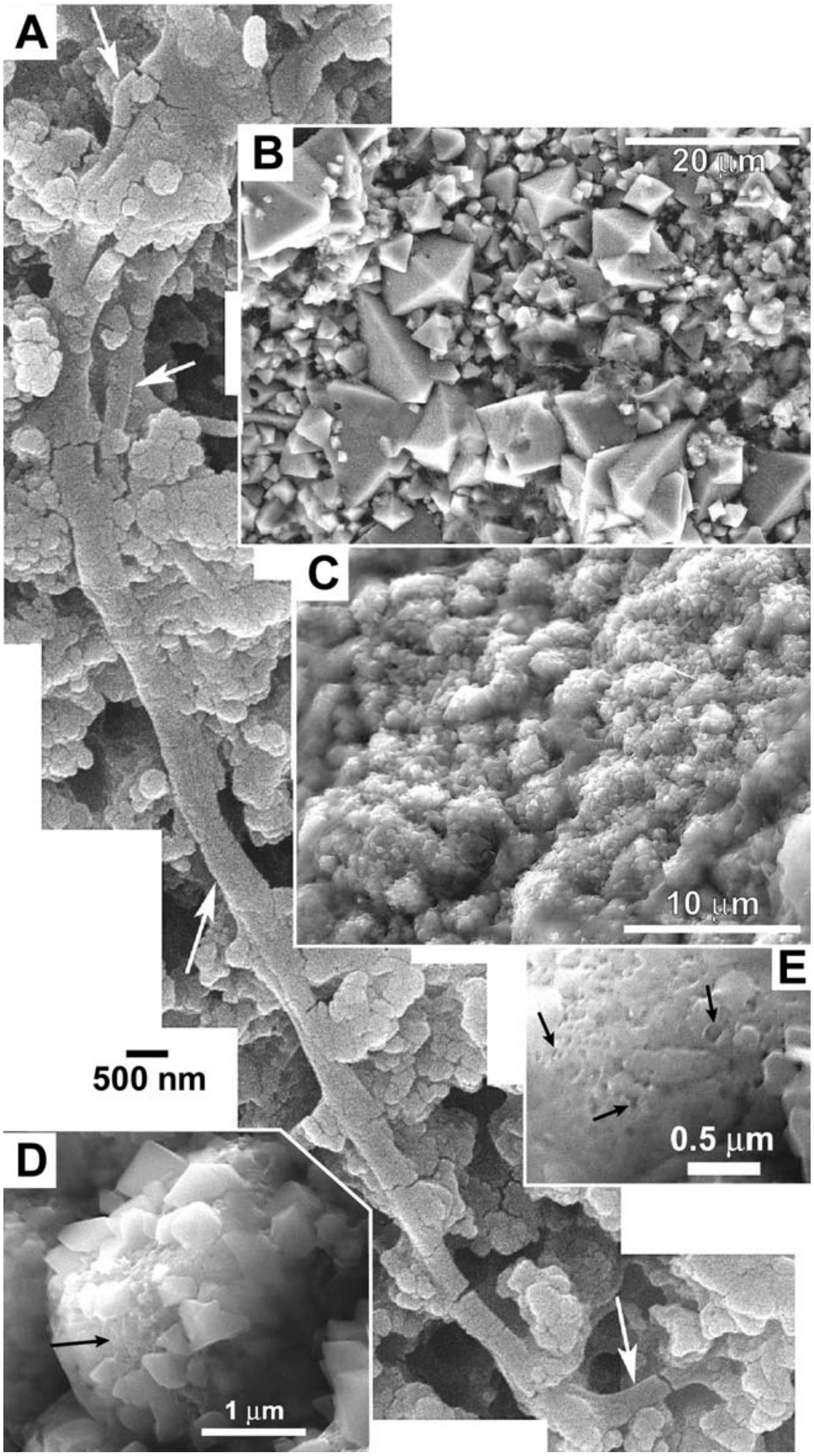

FIG. 9.—SEM images of microbial features in iron sulfide cortices. **A)** Filamentous structure (white arrows) in slightly etched iron sulfide cortex. Note multiple filaments in upper part of picture. In uppermost part of picture the filaments merge into a sheet-like structure, potentially remnant of a biofilm. **B)** Typical recrystallized appearance of an outermost cortex surface (unetched). Most crystals are pyrite octahedra. **C)** Between these crystal pavements one finds remnant patches of an earlier surface (unetched). The latter has a lumpy appearance and consists of tightly packed clusters (a few microns in size) of iron sulfide grains. **D)** Closeups of these clusters (unetched) show that they actually consist of an ovoid smooth walled structure (black arrow) that is overgrown by iron sulfide grains. **E)** (Unetched) shows that the smooth surfaces of these ovoids are typically perforated by irregular shaped openings (black arrows).

fetch than the large ocean basins adjacent to most modern shelf seas, it is likely that storms capable of moving large grains occurred less frequently than along modern coastlines (Liu and Fearn 1993). Thus, it is probably safe to assume that something like the proverbial 1000 year storm was required to accomplish significant reworking of pyrite grains. Transport and rounding of the largest pyrite grains probably took place only during the comparatively short time span of peak storm intensity, whereas small pyrite grains were transported for much of such a storm's duration and thus experienced better rounding.

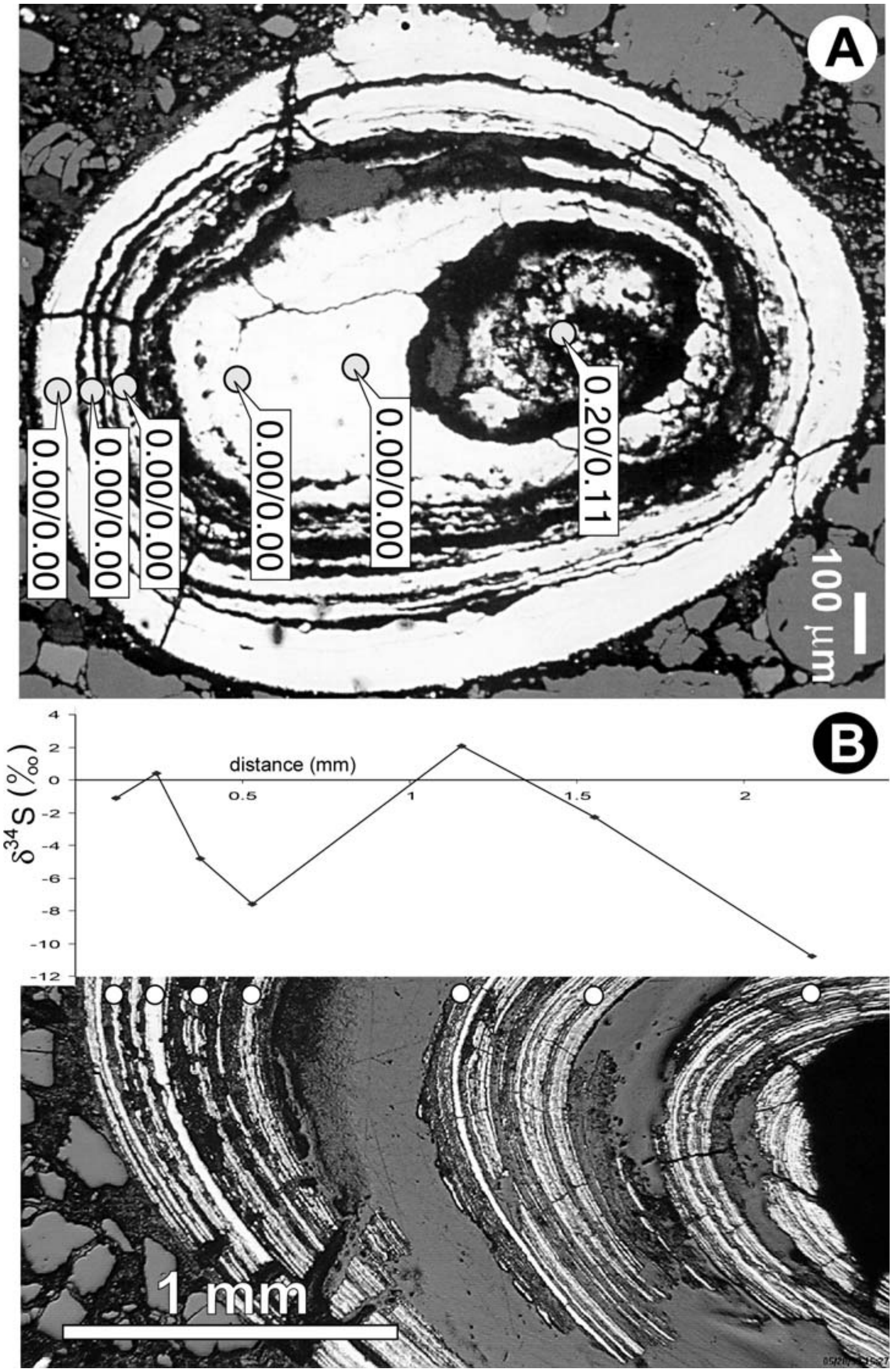

FIG. 10.—**A)** Electron microprobe data from a CIS grain (BSE image). Probe spots are marked with white circle; numbers in boxes are values for SiO_2 (first) and Al_2O_3 (second). Note that only the core contains minor amounts of SiO_2 and Al_2O_3, and that the cortex laminae are free of measurable quantities of SiO_2 and Al_2O_3. **B)** Ion microprobe data for large CIS grain (partial view). Some portions of grain broke out during sample polishing and are now filled with epoxy, but probe spots (white circles) are located in pyrite areas. Diagram on top shows $\delta^{34}S$ values for the marked spots, and shows variability across the cortex that is suggestive of pyrite accretion over time. The *x* coordinate of data points is the horizontal distance of the analysis spot from the left margin of the grain.

Grain Dissolution

Modification of CIS grains, however, was not only mechanical. Corrosion pits like those shown in Figure 8 indicate that iron sulfide grains experienced intermittent etching and dissolution, followed by more iron sulfide accretion. In the context of the sediment reworking and winnowing envisioned for these grains, partial destruction of iron sulfide cortices during oxidation of pyrite and marcasite seems a likely process that led to the features observed in Figure 8. The fact that these dissolution features are interspersed with further accretionary laminae implies that for the grains in question the pore waters repeatedly oscillated between reducing and oxidizing conditions. In the context of storm abrasion with a recurrence period on the order of 1000 years, the observation of multiple pyrite and marcasite laminae (e.g., Fig. 5B) implies that iron sulfide accretion on typical CIS grains should record time spans ranging from a few thousand years to more than ten thousand years.

Implications of $\delta^{34}S$ Measurements

The highly variable δ^{34}S measurements across the cortical envelope of CIS grains (Fig. 10B) provide further support for viewing these grains as the result of successive accretion of pyrite and marcasite laminae over time, rather than as replacements of concentrically coated precursor grains (Schieber and Riciputi 2004). If accretion was for example driven by vertical oscillations of the redox interface through an organics-rich surface sediment in concert with episodic reworking (Pufahl and Grimm 2003), δ^{34}S variability between cortex laminae should be expected. With each reworking cycle the subsequent burial depth of a given grain should be different from before, and that should affect the degree to which the pore waters are insulated from the overlying seawater at any given time, and in turn should result in variable δ^{34}S values across the cortex.

The 2.9‰ average δ^{34}S values for cortical pyrite and marcasite are distinctly lower than those of contemporary Ordovician marine sulfates ($\delta^{34}S = +25‰$ to +30‰; Claypool et al. 1980). The overall fractionation indicates early diagenetic microbial sulfide reduction, and the variability suggests that open-system conditions (most negative values) were interspersed with closed-system (or partially closed) conditions (most positive values, deeper burial). Because bioturbation and mixing of clays with the CIS host sandstones should occur within years or decades of a given reworking event, iron sulfide accretion under open-system conditions would probably require very shallow burial (centimeters to perhaps a decimenter) to allow diffusive communication with the overlying seawater sulfate reservoir. Applying the same reasoning, closed-system or partially closed-system conditions would probably require deeper burial (several decimeters?).

Another factor that could have influenced δ^{34}S values of newly formed iron sulfides was the preceding oxidation of iron sulfides that had been reworked into the surface layer during storms. The "light" sulfate that is released during oxidation of these grains should lower the overall δ^{34}S values of the pore waters. Sulfate-reducing microbes will utilize this sulfate to produce the H_2S that will be incorporated into newly precipitated iron sulfide laminae. Thus, there is the potential to see laminae with δ^{34}S values that show a larger fractionation than what we would expect via "one step" fractionation from seawater sulfate.

BASIC CONSIDERATIONS FOR THE ORIGIN OF CIS GRAINS

Cyclic Diagenetic Accretion

On the basis of the above observations a primary origin of CIS grains by successive diagenetic accretion of pyrite and marcasite cortex laminae is indicated. This could for example have happened as a result of vertical oscillations of the redox interface through an organics-rich surface sediment combined with episodic reworking, similar to a "redox-pumping" model proposed by Pufahl and Grimm (2003) for coated phosphate grains in condensed intervals. With each reworking cycle the subsequent burial depth of CIS grains would change, the degree to which pore waters would be insulated from overlying seawater would differ each time, and as a result produce the observed δ^{34}S variability between cortex laminae (Fig. 10B).

Reworking and Concentration of Iron

Average terrigenous clastic sediments can contain up to a few percent reactive iron in the form of iron oxyhydroxide coatings on terrigenous grains (Carroll 1958; Berner 1969). Therefore, the high iron concentrations in lag deposits with up to 40% CIS grains require a mechanism for iron enrichment. Because sea water contains very little iron in solution (~ 2 ppb; Drever 1982), sequestration of iron from sea water is not an option for growing new iron sulfide cortices on the initial pyrite and/or marcasite cores. Generation of new iron sulfide cortices demands that underlying strata with sedimentary pyrite grains be eroded in order to add more iron. Such a scenario is consistent with rounded and broken CIS grains. Repeated reworking of original sediments provides a simple mechanism for removal of clays and quartz grains and a growing concentration of iron sulfide grains in the residuum. It also implies that CIS grains must have formed at times of stratigraphic condensation when net sedimentation rates were negative.

Intervals rich in CIS grains coincide with increased clay contents of the associated sediments, as well as with sedimentary features suggestive of reworking by waves and bottom currents. Increase in clay is considered a consequence of sea-level rise (e.g., Vigrass 1971) suggesting that CIS grains formed on transgressive surfaces, when the sediment-trapping capability of the transgressive shoreline promoted sediment starvation and offshore winnowing and reworking (Swift et al. 1987; Nummedal and Swift 1987). Thus, the broader sedimentologic and stratigraphic context likewise suggests that CIS grains are associated with condensed intervals within a sandstone-dominated basin-margin succession (Vigrass 1971).

Redistribution of Iron

After mechanical enrichment, however, a portion of the sulfide iron has to be remobilized to form new cortices. This requirement necessitates that a portion of the preexisting sulfide grains be destroyed, either wholly or partially, in order to supply dissolved (Fe^{2+}) or readily soluble (e.g., $Fe(OH)_3$) iron for the growth of new sulfide coatings. Corrosion features, such as shown in Figure 8, attest to intermittent grain dissolution, most likely by iron sulfide oxidation:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

The reaction in Equation 1 produces acidity and dissolved ferrous iron. Further oxidation of ferrous to ferric iron leads to formation of iron hydroxide and production of further acidity:

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+ \qquad (2)$$

Thus, oxidation of iron sulfides causes formation of iron hydroxides and substantial lowering of pH. The newly formed iron hydroxides would form coatings on surface sediment grains (Berner 1969) and would not diminish the overall iron enrichment of the surficial sediment layer. A sufficiently large drop of pore water pH would promote large pore-water concentrations of dissolved ferrous iron (Fe^{2+}) (Maynard 1983, p. 43), a condition that is likely to favor reprecipitation of marcasite.

Formation of Marcasite

In order to form within sediments, both pyrite and marcasite require reducing pore waters, H_2S production, and a source of iron. Experiments suggest that the two minerals differ substantially with regard to the pH value of the fluids they precipitate from. Research by Murowchick and Barnes (1986), Schoonen and Barnes (1991a, 1991b), and Benning et al. (2000) consistently indicates that marcasite formation is strongly favored over pyrite at low pH values (approximately 4 to 5). These experiments also suggest that low-pH marcasite growth is substantially faster than pyrite growth at higher pH, resulting in coarse crystalline marcasite vs. fine crystalline pyrite (Schoonen and Barnes 1991b). Observation of generally coarse crystalline marcasite cortices and fine crystalline pyrite (Figs. 6, 9) in CIS grains of the Winnipeg Formation suggests that these experimental results may have general applicability to natural systems.

Whereas sulfide oxidation furnishes soluble iron for new cortex growth, as well as low-pH conditions for marcasite formation, the winnowed lags are unlikely to contain much organic matter to support reducing conditions and H_2S production, the other requirements for cortex formation. These latter conditions could for example be produced by

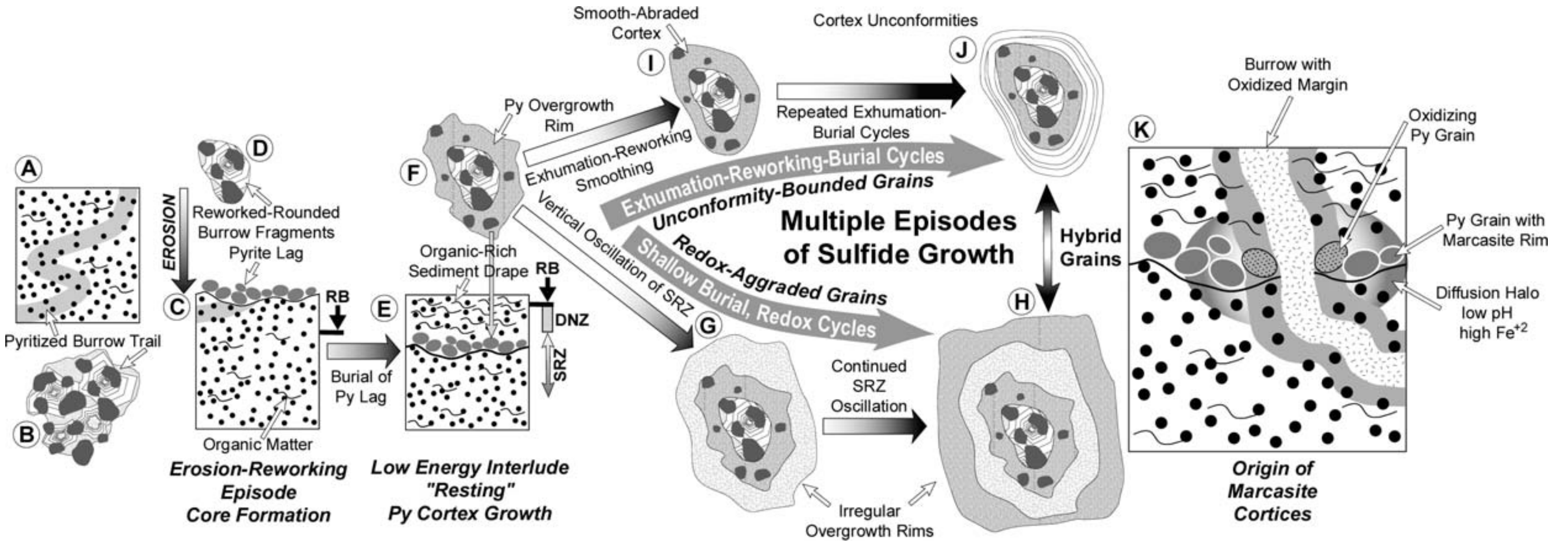

FIG. 11.— Model for formation of CIS grains. **A)** Starting material for pyrite–marcasite cores forms via mineralization of slime-rich burrow trails (Schieber 2002a). **B)** The latter consist of pyrite and marcasite concretions with included "floating" sand grains. **C)** During erosion-reworking episodes mineralized slime trails are broken up, rounded, and form a lag on top of an erosion surface **(D)**. RB = redox boundary, DNZ = denitrification zone, SRZ = sulfate reduction zone. **E)** During low-energy interludes (resting stage) the lag is buried beneath an organics-rich sediment blanket, the redox boundary moves upwards above the lag, and a rim of pyrite (or marcasite) accretes on the initial core (F). Grains like the one shown as **(F)**, with irregular outer rim, do occur within CIS deposits but are not pictured in this report. Once grains of type F have formed, there are two possible pathways for further grain development: (1) **redox-aggraded grains**, where through vertical oscillation of the SRZ **(G)** the grains go through repeated cycles (H) of overgrowth formation; and (2) **unconformity bounded grains**, where over repeated exhumation-reworking and resting cycles successive overgrowth rims are smoothed and abraded **(I)**. Abrasion results in characteristic cortex unconformities **(J)**. Hybrid grains result when grains switch between these modes. **K)** Subroutine for producing marcasite cortices. Burrows that cut across layers with CIS grains cause oxidation of iron sulfides along their margins. This lowers the pH in the vicinity and raises the levels of dissolved iron. As a result, marcasite precipitates on adjacent CIS grains and forms marcasite cortices.

upward diffusion of H_2S and dissolved organic matter from underlying iron-poor sediments. In this way pore-water oxygen could be eliminated by aerobic bacteria, iron hydroxides would buffer H_2S, and iron could be mobile in an anoxic and nonsulfidic environment (Berner 1969, 1981). Alternatively, we could envision that organics-rich sediments blanketed these sulfidic lags during intervening low-energy intervals, caused an upward shift of the redox boundary, moved the lags into the sulfate reduction zone, and allowed formation of iron sulfide cortices. Whether pH values necessary for marcasite formation were reached may have depended on the overall iron sulfide concentration in the lag. High-sulfide lags were probably more likely to produce sufficiently low pH values than lags with low amounts of iron sulfide grains.

A COMPREHENSIVE MODEL

A model that incorporates the envisioned sedimentary setting and explains the observed range of textural and chemical features is shown in Figure 11. Parallel to gradual iron enrichment in the top stratum during repeated reworking and winnowing cycles, successive iron sulfide coatings are deposited on preexisting cores and CIS grains that remain in the surficial lag because of their size and density. Early in the history of a CIS lag, pyrite and/or marcasite burrow trails are broken up, rounded, and concentrated during erosion-reworking events such as strong storms (Fig. 11A, B, C, D).

In the model we envision two basic pathways for producing CIS grains. In one pathway, grains remain in the surface layer but are not physically reworked (Fig. 11F, G, H). Vertical movements of the redox boundary (redox pumping) could be prompted by changes in surface productivity that result in variable organic-matter content and consequent fluctuations of biological oxygen demand in the surficial sediment layer. Moving grains above the redox boundary would promote partial dissolution and iron hydroxide formation, moving them below the redox boundary would lead to precipitation of new cortices. In the other pathway, grains are cycled between oxidizing and reducing environments by repeatedly undergoing physical reworking and reburial (Fig. 11F, I, J), resulting in CIS grains with smooth and thin cortices, as well as cortex unconformities.

Ubiquitous bioturbation in the Black Island Member (Fig. 3) provides a third potential pathway of sulfide grain dissolution and marcasite precipitation. Oxidation along burrows that penetrate CIS-bearing beds should promote localized oxidation and dissolution of CIS grains as well a lowering of pH (Fig. 11K). Analogous to above scenarios of simple downward oxidation, whether marcasite or pyrite precipitation results would depend on the amount of sulfide grains available for oxidation and the resulting degree of pH depression.

In the model introduced here, a broad spectrum of grain morphologies (Fig. 11) can be produced that imply a wide range of grain histories, controlled by the random interplay of reworking, reoxidation of sulfide grains, and the duration of lag evolution. For example, grains with large cores and thin cortices (e.g., Fig. 5A) would imply that the grain was involved in only a few reworking cycles, whereas a grain with a thick cortex and many cortex laminae would imply many reworking cycles prior to final burial. Smoothly rounded cortices with thin laminae would imply a dominance of mechanical reworking, whereas thick irregular cortices with quartz grain inclusions would suggest prevalence of diagenetic overgrowth episodes driven by vertical fluctuations of the redox boundary. Prevalence of marcasite cortices may indicate formation in a thick lag with abundant sulfide grains, whereas dominantly pyritic grains may indicate formation in thinner or less concentrated lags.

While for a given sample certain grain morphologies may dominate the CIS grain population, most thin sections nonetheless contained the entire range of CIS grain morphologies. This suggests that through continued condensation CIS grains of diverse evolutionary stages were mixed together, and that CIS beds record a multitude of reworking events and encompass a long depositional history.

DISCUSSION

The CIS grains described here show textural parallels to coated phosphate grains with cortical laminae of diverse composition (Pufahl and Grimm 2003). The latter authors interpreted variable mineralogy (chamosite, francolite, pyrite) of cortical laminae to reflect seasonal variations in the amount of sedimentary organic matter that arrived at the sediment–water interface. For example, a seasonal increase in the supply of organic matter would increase the biological oxygen demand at the sediment–water interface and cause the redox boundary to move upwards (Fig. 8). Once most of that organic matter was oxidized it allowed oxygen, nitrate, and sulfate to diffuse deeper into the sediment, depressing the redox boundary. Successive laminae accreted as the redox boundary continued to move up and down through the sediment, not unlike the redox-aggradation branch of the model shown in Figure 11. The coated phosphate grains investigated by Pufahl and Grimm (2003) were deposited under conditions of negligible net sedimentation (flooding surfaces, condensed intervals) and fluctuating surface productivity, and were interpreted as "granular equivalents of condensed beds." CIS grains from the Winnipeg Formation may represent an end-member situation within a broader spectrum of "granular condensed beds" (*sensu* Pufahl and Grimm 2003).

Unlike the phosphatic coated grains studied by Pufahl and Grimm (2003), however, no phosphatic or chamositic cortices were observed in Winnipeg CIS grains. One possible reason for this difference could for example be that these sediments experienced negligible rates of phosphate deposition. Alternatively, upwards movement of the sulfate-reduction zone and telescoping of the other redox zones (Mn, N, Fe) may have tilted the balance towards accretion of only iron sulfide laminae (Pufahl and Grimm 2003). The latter case would be favored by high deposition rates of sedimentary organic matter (Pufahl and Grimm 2003). In conjunction with the clay matrix of these sediments, this may have curtailed downward diffusion of oxygen and sulfate, thus allowing the redox boundary to be positioned very closely below the sediment–water interface. With the redox boundary very close to the sediment water interface, concentrations of dissolved phosphate probably stayed too low for francolite precipitation because of the ease of phosphate diffusion into the overlying water column.

The assumption of a fine-grained and organics-rich sediment blanket to cover reworked pyritic lags (Fig. 8) seems to be at odds with electron microprobe analyses that generally do not show appreciable amounts of SiO_2 and Al_2O_3 in the cortices of CIS grains. Why do the clay and silt grains that one should expect in such a sediment blanket not get abundantly incorporated into the pyrite cortices? A possible explanation could be the presence of organic mucus that once must have been abundant in these sediments (Schieber 2002a). This mucus can persist for extended periods of time in the sediment (Davies and Hawkins 1998), and it serves as a ready food source for microbes, including sulfate reducers. Because the mucus is comparable in many respects to agar, a widely used culture medium in microbiology (Stanier et al. 1986), it may have served both as a food source and as a "culture" medium for sulfate reducers. Accreted during reworking, mucus coatings on CIS grains could have hosted numerous bacterial colonies that promoted localized sulfide production and led to growing masses of iron sulfide that eventually coalesced and formed contiguous cortices. Mineralization of mucus coatings on CIS grains, rather than pyrite accretion on grains surrounded by a clay-rich matrix, could explain the negligible amounts of SiO_2 and Al_2O_3 observed in cortices of CIS grains.

One can argue that the processes of oxidation and precipitation of sulfide minerals that are at the heart of CIS grain formation are thermodynamically driven and thus do not ultimately require the involvement of microbes (e.g., Schoonen and Barnes 1991a, 1991b; Benning et al. 2000). Nonetheless, in natural environments oxidation of sulfide minerals is greatly accelerated by microbial activity (Nordstrom and Southam 1997). The ovoid bodies and filaments that have been observed by SEM in the cortices of CIS grains (Fig. 9) resemble microbial cocci and filaments that are commonly observed in biofilms. Figure 9A shows in the upper portion a bundle of fused filaments that may at one time have been part of a sheet-like contiguous biofilm. The smooth oval bodies (Fig. 9D) that form the cores of the iron sulfide encrusted ovoids in Figure 9C are of the right size and shape for mineralized coccoid bacteria, and their perforations resemble features observed in cell walls of experimentally pyritized microbes (Bubela and Cloud 1983). Thus, the mucus coatings alluded to above may actually have been biofilms that covered individual CIS grains and promoted precipitation of sulfide minerals into new cortices. In an indirect way, these biofilms could have promoted cortex formation by providing a substrate (culture medium) for sulfate-reducing bacteria that produced the H_2S necessary to precipitate iron sulfides on the surface. In a more direct manner, the extracellular polysaccharides of such biofilms could also have acted as growth templates for sulfide minerals. An analogous mechanism has been suggested some time ago for nucleation of diagenetic minerals in replaced fossils (Holdaway and Clayton 1982), and more recently the role of microbially produced polysaccharides as templates for mineral growth has been documented directly by Chan et al. (2004). Thus, microbial surface colonization and biofilm formation may have been an important factor to expedite chemical processes that led to the formation of CIS grains.

Alternatively, of course, the H_2S production from underlying iron-poor sediments could have been sufficient to render the pore spaces of at least the lower portion of a CIS lag anoxic. In such a scenario formation of iron sulfides would have been possible in the iron-hydroxide-rich CIS lag even without the benefit of a "protective" organics-rich sediment blanket (e.g., Berner 1969). Thus, the resulting iron sulfide cortices would have expanded into open pore spaces and would be free of inclusions. However, while such a scenario seems workable if the underlying sediments are organic-rich mudstones that produce abundant H_2S (e.g., Schieber and Riciputi 2004), it seems doubtful whether the H_2S flux from a marine sand would be sufficient. We assume therefore that a benthic fluff layer was nonetheless an important factor in the production of Winnipeg CIS beds. Without the protection afforded by this layer, iron sulfide grains would probably have been completely destroyed by oxidation during the long "resting" periods in the surface layer (Morse 1991). This would have erased all of the prior accretion history and effectively forestalled the formation of CIS grains.

The fine-grained and organics-rich sediment blanket postulated above would have formed following reworking events. Mucus, sedimentary organic matter, and fine-grained terrigenous matter would have settled out and formed a benthic flocculent (fluff) layer (Pilskaln and Pike 2001; Laima et al. 2002). Present-day examples of such fluff deposits are cohesive and gelatinous, and usually also contain mucus producing polychaete worms (Laima et al. 2002). Because of their organic content, the biological oxygen demand in these layers is so strong that soon after deposition the redox boundary moves up into the fluff layer (Laima et al. 2002), thus for example protecting underlying pyritic lags from prolonged oxidation. As a consequence, anoxic bottom waters are not a necessary requirement (Baird and Brett 1991) in order for pyritic lags to survive for extended periods of time on the seafloor.

In this context, oxidation of CIS beds and the attendant low-pH conditions that allowed marcasite formation should have been short-lived transient events. Low-temperature experimental marcasite crystals grow very rapidly under low-pH conditions, reaching a size of 5 microns within a week (Schoonen and Barnes 1991b). Thus, short-lived oxidation events and transient low-pH conditions probably were sufficient to generate the observed marcasite cortices.

Formation of iron sulfides in CIS intervals requires organic matter to fuel sulfate reduction. Using a variety of simple organic substances, such as lactate, ethanol, acetate, and formaldehyde, in conjunction with sulfate-reduction equations proposed by Canfield and Raiswell (1991), one can calculate that approximately 5 cm^3 of pure organic matter is required to precipitate 1 cm^3 of pyrite. In order to produce a 15-cm-thick CIS lag with 40 volume percent pyrite one would need at a minimum a 30-cm-thick layer of pure organics. One also needs to factor in that only a fraction of the organic matter will be utilized for sulfate reduction, and that the redox boundary needs to be kept close to the sediment water interface in spite of the sandy and bioturbated host sediments. In view of these constraints, it seems obvious that not only slow accumulation but also high surface productivity is a basic requirement for the formation of CIS grains.

SIGNIFICANCE

Coated iron sulfide (CIS) grains in the Ordovician Winnipeg Formation are primary diagenetic precipitates. They formed in condensed intervals, and are most likely related to marine flooding surfaces. However, rather than simply indicating reducing pore waters, they reveal a complexly intertwined history of reworking, intermittent oxidation, fluctuating pH, redox pumping, microbial activity, and iron sulfide precipitation. Although the grains in question consist of iron sulfide minerals and at first glance might be interpreted to simply indicate anoxic bottom waters (Baird and Brett 1991), a fundamental requirement for their formation is the oxidation of sulfide minerals in surface sediments. Thus, their presence does in fact attest to oxygenated bottom waters.

Because seawater has a slightly alkaline pH of approximately 8, it is commonly presumed that marcasite cannot form in marine sediments during early diagenesis (e.g. Rickard et al. 1995). In contrast, our textural and sedimentologic analysis of CIS grains in the Winnipeg Formation clearly shows that "sulfide reoxidation" is a plausible mechanism for formation of early diagenetic marcasite. Examination of other marcasite occurrences in the rock record may well establish that marcasite formation via sulfide reoxidation is a widely applicable mechanism.

Because CIS grains are a manifestation of geochemical "reworking" of iron from underlying sediments, the degree of iron enrichment in a given CIS bearing interval can be considered a measure of the intensity of stratigraphic condensation. For example, if we consider the amount of iron sulfide in core samples (approximately 1 volume percent, e.g., Fig. 3) as representative of the background sediments, then a well developed CIS bed with 40% CIS grains and 15 cm thickness would imply forty-fold iron enrichment and condensation of 6 meters of sediment into a 15 cm bed. On the basis of this relationship one can estimate that on the order of 20 to 30 meters of sediment may have been "lost" from the Black Island Formation (overall thickness approximately 40 m).

As outlined above, only very rare storms were likely to provide the flow velocities required for transport and rounding of larger CIS grains. Thus, complex CIS grains with large numbers of cortical laminae may well represent accretion histories that span several tens of thousands of years. By the same token, thick CIS beds that represent a multitude of reworking events and incorporate variably "evolved" CIS grains might represent sedimentation histories on the order of hundred thousand years or more. On the other end of the time scale, individual marcasite cortices in a CIS grain may record as little as a few months of accretion history.

CIS beds are granular condensed beds (*sensu* Pufahl and Grimm 2003), and individual grains may represent in excess of ten thousand years of near-surface mineral precipitation in a finely resolved record of cortical laminae. In the future it may be possible to utilize this record for paleoceanographic studies through the analysis of fluid inclusions, stable isotopes, and trace elements. Also, in a given occurrence it may be possible to identify laminae with unique geochemical or textural signatures that are common to a whole population of grains. These could be used to build up an extended lamina record for a given CIS bed, analogous to overlapping tree-ring records for the Holocene. Potentially one could reconstruct stretches of geologic history as long as several hundred thousand years that have no other physical record than that contained in CIS beds.

Essential parameters for production of CIS grains are (1) extreme condensation and negative net sedimentation, coupled with (2) intermittent reworking and (3) high surface-water productivity to make for a shallow position of the redox boundary within the sediment. High surface productivity is considered an essential ingredient for maintaining an organics-rich sediment blanket to cover and protect reworked pyritic lags by keeping the redox boundary very close to the sediment water interface. Organic mucus may have been an important component of this surficial sediment layer. The proposed model may represent a special case of a more general model for formation of condensed-zone coated grains proposed by Pufahl and Grimm (2003). Elsewhere in the rock record, condensation and reworking are considered necessary conditions for the formation of oolitic ironstones (Maynard 1983). The different mode of iron enrichment in the case of Winnipeg CIS grains could for example point to the importance of a more reducing surface sediment (due to higher productivity) or to a lack of reactive clays.

Because of the apparently intimate relationship between microbes and sulfide mineral growth, CIS grains and related grains in the "granular condensed bed" category (Pufahl and Grimm 2003) may also be good targets for finding mineralized microbes in the rock record (Schieber 2002b) and possibly on other planets where the surficial chemistry favored formation of iron sulfides in sediments (Schieber 2001). One might also ask in this context whether CIS grains as described here, as well as related coated grains (e.g., Pufahl and Grimm 2003), could in themselves constitute a biosignature. Basically, is a biological component necessary to make grains of this kind, or could they also be grown in a sterile environment? It is a problem analogous to the argument over the biological vs. abiological origin of pyrite framboids in sediments (e.g., Kalliokoski 1974), including the possibility that the products of the two pathways can be distinguished using textural criteria (Schieber 2002b). Because experiments indicate rapid growth of marcasite (Schoonen and Barnes 1991b), there is the prospect that the biogenic vs. abiogenic issue is amenable to experimentation under controlled laboratory conditions.

The sandstones in which the studied CIS intervals occur are bioturbated throughout and show only minor variability over tens of meters. Thus, detection of condensed intervals during standard core description proves rather difficult. In this situation CIS grains provide two pieces of otherwise unavailable information about the history of these sandstones: (1) there was intermittent stratigraphic condensation, probably associated with marine flooding surfaces; and (2) there was high surface productivity and organic-matter deposition, even though none of that organic matter is ultimately preserved.

Although there is currently no published record of other successions with pyrite grains of exactly this kind, the fact that they seem to form analogously to more commonly reported coated phosphate grains (Pufahl and Grimm 2003) suggests that they probably occur elsewhere as well. Because of their mineralogy they will easily escape detection in outcrops (because of iron sulfide weathering), or may be mistaken for simple pyrite concretions in core descriptions.

ACKNOWLEDGEMENTS

Research on pyrite ooids in the Chattanooga Shale was supported by the National Science Foundation (grant EAR-9706178). An NSF instrumentation grant (EAR-0318769) provided funds for acquisition of an analytical ESEM with EBSD capabilities. D.F. Paterson provided access to cores stored at the Saskatchewan Mineral Resources Laboratories and to subsurface data on the Winnipeg Formation. JS would like to thank Pier Binda of the University of Regina in Saskatchewan for generously sharing his knowledge on sedimentary pyrite features in the Winnipeg Formation, and for his encouragement and hospitality during visits to Regina. Constructive reviews by Kurt Grimm, Robert Raiswell, and Joe Macquaker helped to focus the message of this manuscript.

REFERENCES

Baird, G.C., and Brett, C.E., 1991, Submarine erosion on the anoxic sea floor: Stratinomic, palaeoenvironmental, and temporal significance of reworked pyrite-bone deposits, *in* Tyson, R.V., and Pearson, T.H., eds., Modern and Ancient Continental Shelf Anoxia: Geological Society of London, Special Publication, 58, p. 233–257.

Benning, L.G., Wilkin, R.T., and Barnes, H.L., 2000, Reaction pathways in the Fe–S system below 100°C: Chemical Geology, v. 167, p. 25–51.

Berner, R.A., 1969, Migration of iron and sulfur within anaerobic sediments during early diagenesis: American Journal of Science, v. 267, p. 19–42.

Berner, R.A., 1981, A new geochemical classification of sedimentary environments: Journal of Sedimentary Petrology, v. 51, p. 359–365.

Binda, P., 1991, Anoxic sulphidic diagenesis in the Ordovician Winnipeg Formation of Saskatchewan, *in* Christopher, J.E., and Haidl, F.M., eds., Sixth International Williston Basin Symposium: Saskatchewan Geological Society, Regina, p. 257–264.

Binda, P., and Simpson, E.L., 1989, Petrography of sulfide-coated grains from the Ordovician Winnipeg Formation, Saskatchewan, Canada: European Journal of Mineralogy, v. 1, p. 439–453.

Bubela, B., and Cloud, P., 1983, Sulfide mineralization of microbial cells: Bureau of Mineral Resources, Journal of Australian Geology and Geophysics, v. 8, p. 355–357.

Canfield, D.E., and Raiswell, R., 1991, Pyrite formation and fossil preservation, *in* Allison, P.A., and Briggs, D.E., eds., Taphonomy; Releasing the Data Locked in the Fossil Record: New York, Plenum Press, p. 337–387.

Carozzi, A.V., 1972, Microscopic Sedimentary Petrography: Melbourne, Florida, Krieger Publishing Company, 485 p.

Carroll, D., 1958, Role of clay minerals in the transportation of iron: Geochimica et Cosmochimica Acta, v. 14, p. 1191–1206.

Chan, C.S., De Stasio, G., Welch, S.A., Girasole, M., Frazer, B.H., Nesterova, M.V., Fakra, S., and Banfield, J.F., 2004, Microbial polysaccharides template assemble nanocrystal fibers: Science, v. 303, p. 1656–1658.

Claypool, G.E., Holser, W.T., Kaplan, I., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, p. 199–260.

Davies, M.S., and Hawkins, S.J., 1998, Mucus from marine molluscs: Advances in Marine Biology, v. 34, p. 1–71.

Duke, W.L., 1990, Geostrophic circulation or shallow marine turbidity currents? The dilemma of paleoflow patterns in storm-influenced prograding shoreline systems: Journal of Sedimentary Petrology, v. 60, p. 870–883.

Drever, J.I., 1982, The Geochemistry of Natural Waters: Englewood Cliffs, N.J., Prentice Hall, 388 p.

Gerhard, L.C., and Anderson, S.B., 1988, Geology of the Williston Basin (United States portion), *in* Sloss, L.L., ed., Sedimentary Cover; North American Craton; U.S. Geological Society of America, The Geology of North America, v. D-2, p. 221–241.

Hayes, A.O., 1915, Wabana iron ore of Newfoundland: Geological Survey of Canada, Department of Mines, Memoir, v. 78, 162 p.

Holdaway, H.K., and Clayton, C.J., 1982, Preservation of shell microstructure in silicified brachiopods from the Upper Cretaceous Wilmington Sands of Devon: Geological Magazine, v. 119, p. 371–382.

Kalliokoski, J., 1966, Diagenetic pyritization in three sedimentary rocks: Economic Geology, v. 61, p. 872–885.

Kalliokoski, J., 1974, Pyrite framboids: animal, vegetable, or mineral?: Geology, v. 2, p. 26–27.

Laima, M., Maksymowska-Brossard, D., Sauriau, P.-G., Richard, P., Girard, M., Gouleau, D., and Joassard, L., 2002, Fluff deposition on intertidal sediments: effects on benthic biota, ammonium fluxes and nitrification rates: Biogeochemistry, v. 61, p. 115–133.

Liu, K.B., and Fearn, M.L., 1993, Lake sediment record of late Holocene hurricane activities from coastal Alabama: Geology, v. 21, p. 793–796.

Maynard, J.B., 1983, Geochemistry of Sedimentary Ore Deposits: New York, Springer-Verlag, 305 p.

Morse, J.W., 1991, Oxidation kinetics of sedimentary pyrite in seawater: Geochimica et Cosmochimica Acta, v. 55, p. 3665–3667.

Morton, R.A., 1981, Formation of storm deposits by wind-forced currents in the Gulf of Mexico and the North Sea, *in* Nio, S.D., Shuttenhelm, R.T.E., and van Weering, T.C.E., eds., Holocene Marine Sedimentation in the North Sea Basin: International Association of Sedimentologists, Special Publication 5, p. 385–396.

Murowchick, J.B., 1992, Marcasite inversion and the petrographic determination of pyrite ancestry: Economic Geology, v. 87, p. 1141–1152.

Murowchick, J.B., and Barnes, H., 1986, Marcasite precipitation from hydrothermal solutions: Geochimica et Cosmochimica Acta, v. 50, p. 2615–2629.

Murray, J.W., 1976, A method of determining proximity of marginal seas to an ocean: Marine Geology, v. 22, p. 103–119.

Nordstrom, D.K., and Southam, G., 1997, Geomicrobiology of sulfide mineral oxidation, *in* Banfield, J.F., and Nealson, K.H., eds., Geomicrobiology; Interactions between Microbes and Minerals: Reviews in Mineralogy, v. 35, p. 361–390.

Nummedal, D., and Swift, D.J.P., 1987, Transgressive stratigraphy at sequence-bounding unconformities: some principles from Holocene and Cretaceous Examples, *in* Nummedal, D., Pilkey, O.H., and Howard, J.D., eds., Sea-Level Fluctuation and Coastal Evolution: SEPM, Special Publication 41, p. 241–260.

Paterson, D.F., 1971, The stratigraphy of the Winnipeg Formation: Saskatchewan Department of Mineral Resources, Report, v. 140, 57 p.

Pilskaln, C.H., and Pike, J., 2001, Formation of sedimentary laminae in the Black Sea and the role of the benthic flocculent layer: Paleoceanography, v. 16, p. 1–19.

Prior, D.J., Boyle, A.P., Brenker, F., Cheadle, M.C., Day, A., Lopez, G., Peruzzo, L., Potts, G.J., Reddy, S.M., Spiess, R., Timms, N.E., Trimby, P.W., Wheeler, J., and Zetterstrom, L., 1999, The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks: American Mineralogist, v. 84, p. 1741–1759.

Pufahl, P.K., and Grimm, K.A., 2003, Coated phosphate grains: Proxy for physical, chemical, and ecological changes in seawater: Geology, v. 31, p. 801–804.

Ranger, M.J., 1979, The sedimentology of a Lower Paleozoic peritidal sequence associated iron formations, Bell Island, Conception Bay, Newfoundland [Unpublished M.Sc. thesis]: Memorial University of Newfoundland, 125 p.

Riciputi, L.R., Paterson, B.A., and Ripperdan, R.L., 1998, Measurement of light stable isotope ratios by SIMS: Matrix effects for oxygen, carbon, and sulfur isotopes in minerals: International Journal of Mass Spectrometry, v. 178, p. 81–112.

Rickard, D., Schoonen, M.A.A., and Luther, G.W., 1995, Chemistry of iron sulfides in sedimentary environments, *in* Vairavamurtry, M.A., and Schoonen, M.A.A., eds., Geochemical Transformations of Sedimentary Sulfur: Washington, D.C., American Chemical Society, Symposium Series, v. 612, p. 165–193.

Schieber, J., 2001, Finding life on Mars: A mudrock geologist's perspective: 32nd Lunar and Planetary Sciences Conference, Houston, Texas, March 12–16. 2001, Abstract Volume, CD-ROM.

Schieber, J., 2002a, The role of an organic slime matrix in the formation of pyritized burrow trails and pyrite concretions: Palaios, v. 17, p. 104–109.

Schieber, J., 2002b, Sedimentary pyrite: A window into the microbial past: Geology, v. 30, p. 531–534.

Schieber, J., and Riciputi, L., 2004, Pyrite ooids in Devonian black shales record intermittent sea level drop and shallow water conditions: Geology, v. 32, p. 305–308.

Schoonen, M.A.A., and Barnes, H.L., 1991a, Reactions forming pyrite and marcasite from solution. I. Nucleation of FeS_2 below 100°C: Geochimica et Cosmochimica Acta, v. 55, p. 1495–1504.

Schoonen, M.A.A., and Barnes, H.L., 1991b, Reactions forming pyrite and marcasite from solution. II. Via FeS precursor below 100°C: Geochimica et Cosmochimica Acta, v. 55, p. 1505–1514.

Schwartz, A.J., Kumar, M., and Adams, B.L., 2000, Electron Backscatter Diffraction in Materials Science: Berlin, Springer, 350 p.

Stanier, R.Y., Ingraham, J.L., Wheelis, M.L., and Painter, P.R., 1986, The Microbial World: Englewood Cliffs, New Jersey, Prentice Hall, 689 p.

Sundborg, A., 1956, The River Klaralven: A Study of Fluvial Processes: Geografiska Annaler, v. 38, p. 127–316.

Swift, D.J.P., Hudelson, P.M., Brenner, R.L., and Thompson, P., 1987, Shelf construction in a foreland basin: Storm beds, shelf sandbodies, and shelf slope depositional sequences in the Upper Cretaceous Mesaverde Group, Book Cliffs, Utah: Sedimentology, v. 34, p. 423–457.

Vigrass, L.W., 1971, Depositional framework of the Winnipeg Formation in Manitoba and eastern Saskatchewan: Geological Association of Canada, Special Paper, v. 9, p. 225–234.

Received 26 February 2004; accepted 11 February 2005.