IRON-SULFIDE CONCRETIONS OF THE OHIO SHALE: GLIMPSES OF DEEP SUBSEAFLOOR MICROBIAL ECOSYSTEMS OF THE LATE DEVONIAN

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Abstract

Recent interest in black Devonian shales for natural gas exploitation has brought shale research into new importance. At the same time, advances in the understanding of deep subseafloor microbial ecosystems have revealed that microbes play a more pivotal role in geologic processes than ever imagined. The convergence of these two areas provides an excellent opportunity to reexamine enigmatic concretions of the Ohio Shale. The Huron member of the Ohio Shale is distinguished by the presence of carbonate concretions (Hansen, 1994). These concretions vary considerably in size and differ in composition from the host rock (Clifton, 1957). Their origins have been questioned since they were first described in 1873 (Hansen, 1994). Current models attribute concretion formation to abiotic mineral replacement of organic substances. However, smaller, iron-sulfide concretions inhabit the same horizons and are less well studied (Criss, 1988). Iron-sulfide mineralization has been attributed to biotic processes and may be connected to the presence of the larger carbonate concretions.

Iron-sulfide concretions have been collected from three sites in Delaware and Franklin Counties in Ohio. These samples were investigated using reflected light microscopy, scanning electron microscopy, and energy dispersive x-ray spectroscopy. Based on morphology, composition and size, the iron-sulfide concretions have been categorized into four different stages of paragenesis. These stages correlate well with known microbial zonations of deep subseafloor environments.

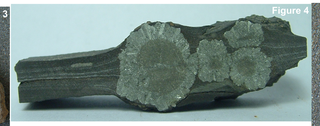
Understanding the microbiological processes at work in the creation of black Devonian shales may shed light on how to exploit modern microbial systems to develop sustainable sources for carbon fuels in the future..

Figure 1: A "swarm" of carbonate concretions at Bull Moose Run in Worthington, Ohio.

Figure 2: A pair of iron-sulfide concretions which were found in the same horizon as the above carbonate concretions.

Introduction

Modern microbial ecosystems have proven to be more versatile and more widely distributed than we could have possibly imagined. Even 800 meters below the ocean floor, microbes are still using minerals as terminal electron acceptors (D'Hondt, 2004), shaping the chemistry of pore waters and the geology of the surrounding sediments (Reith, 2011). Given that some of these microbes are known for producing methane (Parkes, 2011), understanding the conditions and processes at work in these ecosystems may provide us with insight into methods for locating natural gas reserves in shale or even for isolating organisms for the production of natural gas by modern microbes.



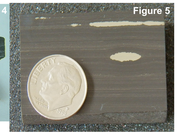


Figure 3: Two iron-sulfide concretions demonstrating the difference height:width ratios.
Figure 4: Several marcasite-rimmed iron-sulfide concretions. The bladed, more silver crystals around the rim is marcasite. The centers are pyrite crystals. The effect of the concretions on the bedding can be visible as a divergence of bedding planes.
Figure 5: Small iron sulfide concretions in the host shale. The displacement of shale bedding is clearly visible.

Background / Setting

The Ohio Shale lithified from deep-water, anoxic marine muds deposited during the late Devonian. These muds were laid down as the Acadian Orogeny caused the deepening of the Kaskaskian Sea. The evolution and proliferation of terrestrial plants may have contributed to eutrophication and acidification of the sea (Algeo, 1995). Depositional lags concentrated organic sediments and drove pH levels even lower (Scheiber, 2007). The result of these conditions are the organic-rich black shales which now exist the Eastern United States today.

The conditions at the late Devonian sea floor are of particular interest because of their potential effect on microbial ecosystems. Beneath the seafloor, microbes segregate into zones based on their terminal electron acceptors (TEA). TEA's with higher free energy are preferentially used before lower energy TEA's. These zones each produce unique products including calcium-carbonates, iron-sulfides and methane (Coleman, 1985). The purpose of this study is to document the composition and morphology of the iron-sulfide concretions in the Ohio Shale and to present a model for concretion growth within these microbial zones.

Methods

Samples of iron-sulfide concretions were collected from Bull Moose Run in Worthington, Ohio, Glen Echo Park in Columbus, Ohio, and Big Run in Delaware, Ohio. Samples were cut perpendicular to bedding with the intent to bisect the concretions where possible. Cut samples were polished with 0.25 micron diamond paste. Polished samples were examined with reflected light microscopy (RLM) and scanning electron microscopy (SEM) (Everhart Thornly detector (ET detector), electron diffraction X-ray spectrometer (EDS), and backscatter electron detector (BSE)).

Concretions were measured perpendicular to bedding at their greatest point (height) and parallel to bedding at their greatest point (width), represented in Table 1. SEM images were taken of interesting features within the concretions and their host shale. Elemental composition data of interesting features, host shale, and concretions were also collected.

Results

Three structures of iron-sulfide crystals are present in the concretions: pyrite, marcasite, and paramorphic marcasite-inverted-pyrite (MIP). These were distinguished based on crystal habit and anisotropism. The abundances are represented on the ternary diagram (Table 2). In general, concretions are composed of pyrite, pyrite / marcasite, or pyrite / MIP. Only three of fifty-five samples are composed of all three crystal structures.

The concretions contained some phosphatic fossil components as well as shale inclusions, calcite-filled cracks and crushed (and folded) *Tasmanites*. Uncrushed pyrite-infilled *Tasmanite* cysts are also present within the concretions.

The host shale has large quantities of pyrite framboids and in crushed *Tasmanite* fossils. *Tasmanites* comprise up to 30% of the shale matrix in some samples,. Calcite and quartz are also common in the host shale both as individual grains and as beds. The host shale is finely bedded; some cross-bedded samples were also found. *Callixylon* fossils occur in the same horizons as the concretions.

Table 1: Height vs Width of Iron-sulfide Concretions

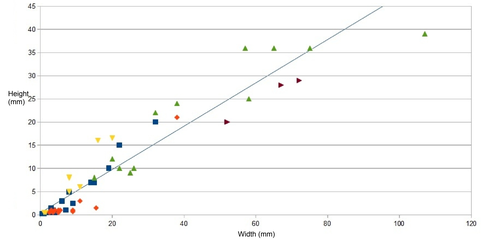
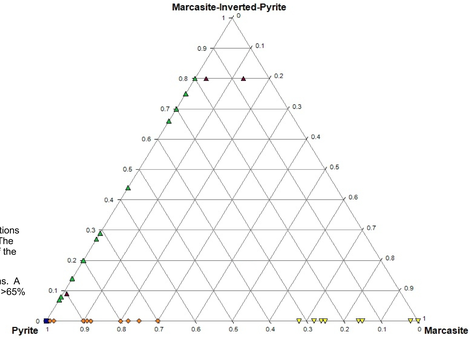


Table 1: Height & widths of iron-sulfide concretions are segregated by composition (see Table 2). The blue trendline represents the overall average of the concretions.

Table 2: Composition of iron-sulfide concretions. A natural segregation occurs between <30% and >65% marcasite composition.

Table 2: Composition of Iron-sulfide Concretions



Discussion

We are proposing four stages of concretion growth using the composition, size and shape of the concretions, internal features of the concentrations, their relationship with the host shale, and existing models for subseafloor microbial ecosystems. Each of these stages is based on the natural segregation of concretion samples on the iron-sulfide ternary plot. Comparison between the composition of the concretions and their relative height:width ratios confirms these segregations.

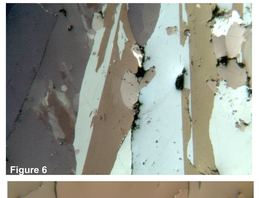
Iron-sulfide concretions begin forming under anoxic conditions in the sulfur reducing zone after compression of the mud layers has begun. This is indicated by both the presence of crushed *Tasmanites* inside the concretions and the behavior of the host shale at the concretion / shale interface. This is in conflict with estimated depths of >10m below the seafloor (Coleman, 1985) due to the required overburden.

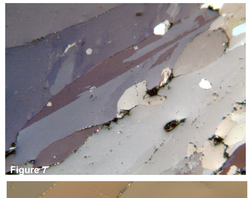
The sediments surrounding the concretion were deposited in an environment of low deposition or possibly even negative deposition based on the presence of cross-bedded shales, pyrite-filled cysts (Figure 12) and concentration of algal cysts (Figures 10 & 13) and framboids (Figures 10 & 11). Initial growth was entirely pyrite crystals at slightly higher rate than compression as indicated by the lower than average height:width ratio.

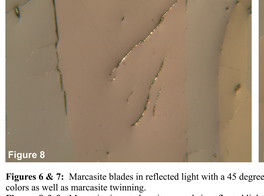
At some point during concretion formation, the pH levels dropped even further, facilitating the formation of marcasite. During this stage, the marcasite rims develop on the pyrite concretions with minimal, if any, reworking of the initial concretions. The results of this stage are concretions with lower than average height:width and concretions with 1-30% marcasite crystals / 70-99% pyrite crystals.

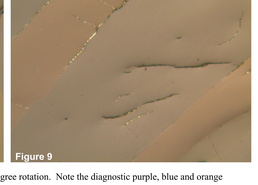
Increased marcasite formation marks the third stage of growth during which the rate of growth greatly outpaces compression of the sediment. This leads to round concretions with thick marcasite rims. These concretions have a higher than average height:width and are composed of 65-100% marcasite and 0-35% pyrite. This increase in growth rate is most likely due to the fact that marcasite crystals grow more readily than pyrite crystals (Scheiber, 2005).

The final stage of growth is marked by an inversion of the marcasite back to pyrite. These concretions apparently continue to grow as they tend to be larger than the previous stages. Their height:width tends to correlate with the average ratio of all concretions. This is due to crystal growth which is outpaced by compression of the sediments.









Figures 6 & 7: Marcasite blades in reflected light with a 45 degree rotation. Note the diagnostic purple, blue and orange colors as well as marcasite twinning.
Figures 8 & 9: Marcasite-inverted-pyrite crystals in reflected light with a 45 degree rotation. Note that the twinning is identical to marcasite but the anisotropism is indicative of pyrite crystals.

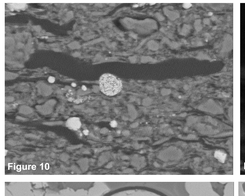
Conclusions

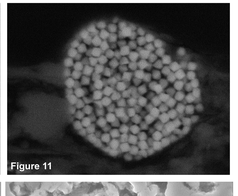
Several significant questions still remain.

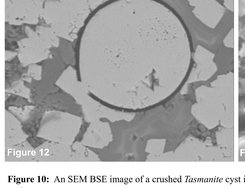
- What is the source of the iron in the concretions? It does not seem to be framboidal or from the cysts as both of those features are present either in or near the concretions.
- What are the controlling conditions which regulate the growth of concretions? What causes the variations in sizes or variations in the stages of growth?
- What is the cause of the marcasite inversion? The inversion could be temperature related, but if that is the case why are only some concretions effected?
- Are the iron-sulfide concretions related to the larger carbonate concretions? If so, in what way?

While this project raises more questions then it answers, it does lay the groundwork for understanding the pyrite concretions of the Ohio Shale. These concretions may be the precursors to the larger, better studied carbonate concretions or may be sister features which grow simultaneously with the carbonate concretions.

Most importantly, however, this study begins to explore ancient Devonian deep subseafloor microbial environments. These environments led to the natural gas component of the shale which is of economic importance today. Understanding the conditions under which the natural gas reserves were initially formed may help in identifying future reserves or similar modern environments in which methanogenic bacteria are producing natural gas.







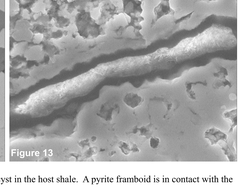
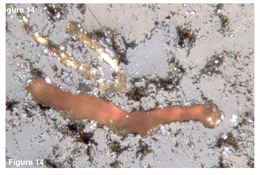
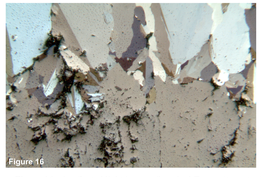


Figure 10: An SEM BSE image of a crushed *Tasmanite* cyst in the host shale. A pyrite framboid is in contact with the cyst.
Figure 11: A close-up SEM BSE image of the framboid from Figure 10.
Figure 12: An SEM BSE image of a pyrite-infilled *Tasmanite* cyst. These have been interpreted to have originated during depositional lags (Schieber, 2001).
Figure 13: An SEM image of a crushed *Tasmanite* in a pyrite concretion.





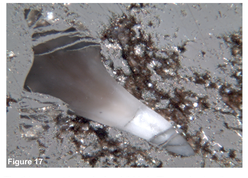


Figure 14: A reflected light image of crushed *Tasmanite* cysts. The thinner cyst is crushed and folded. The mechanism for folding is unknown but perhaps related to the growth of the concretion as folded cysts do not occur in the host shale.
Figure 15: A *Callixylon* sample recovered from a concretion rich horizon. These support the "Devonian plant hypothesis".
Figure 16: A reflected light image of the boundary between the pyrite core and the marcasite rim of a concretion which has undergone stage 3 growth.
Figure 17: A reflected light image of a phosphatic fossil entombed within a pyrite concretion.

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