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DIAGENESIS OF A PYRITIZED CONTACT OF THE MIDDLE TO LATE DEVONIAN TRANSITION FROM CARBONATE TO BLACK SHALE

HOLIDAY R. O'BRYAN, Macalester College
Project Advisors: Kelly R. MacGregor and Jeff T. Thole

INTRODUCTION

The geologic history of the Michigan Basin spans nearly the entire Paleozoic Era. Devonian outcrop and rock has been sampled extensively in cores across the state of Michigan as well as from the outcrop belts in the northern and southeastern Lower Peninsula. The mineralized contact between the "Squaw Bay Formation" and Traverse Group merits a greater degree of attention in order to differentiate early versus late diagenesis which has implications for the depositional environment and basin history, respectively. In every sample of this contact, where limestone of the Traverse Group is overlain by calcareous shale, pyrite occurs as nodules, framboids, and cubes. Petrographic and scanning electron microscopy (SEM) and x-ray fluorescence scanning (µXRF) were used to identify the mineralogies and define the microfacies present in these formations and at their contact. This work results in the reconstruction of a paragenetic sequence for the contact and both formations.

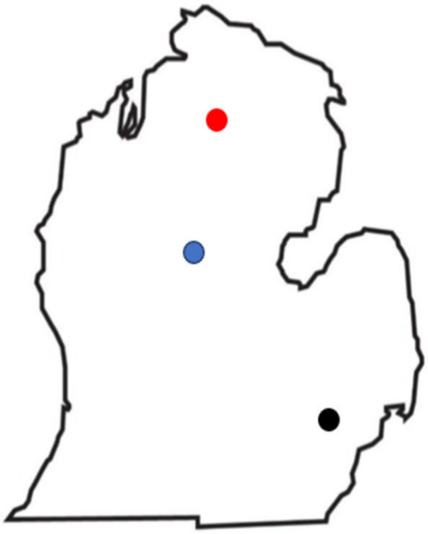
Paleogeographic Setting

The Michigan Basin represents 280 million years of geologic time, with around 4800 meters of preserved rock spanning nearly the entire Paleozoic (Milstein, 1987, Gutschick and Sandberg, 1991). During the Devonian, the Michigan Basin was a warm and tropical sea situated near or at the equator (Gutschick and Sandberg, 1991). Subsidence of the Traverse Group occurred conjointly with the Taghanic Onlap during the Middle-Late transition, and the "Squaw Bay Formation" is thought to have recorded the transition from carbonate platform to deep-water lime- and argillaceous mudstones (Gutschick and Sandberg, 1991).

The transition from the Middle to Late Devonian in the basin is marked by substantial development of a pycnocline and evidence of dys- to anoxic conditions on the seafloor (Gutschick and Sandberg, 1991). During the Late Devonian, the Acadian Orogeny influenced sediment supply and tectonic activity in the basin significantly. Erosion of the mountains led to an increase in fine sediment supply to the basin (Wylie and Huntoon, 2003). The Traverse Group was marked by basin centered subsidence, while the Antrim Shale (the shale unit overlying the "Squaw Bay Formation") was marked by eastern-tilted subsidence (Howell and van der Pluijm, 1999). In addition to basin subsidence, dys- to anoxic conditions have been identified, especially in Devonian carbonates and shales. Formolo et al. (2014) suggested that iron limitation led to increased sulfide accumulation and recycling and that the chemocline was subsequently pushed upwards in the water column.

METHODS

At the Michigan Geological Repository for Research and Education (MGRRE), drill cores from the Michigan Basin are housed, including cores through Upper Devonian strata. Both formations and the pyrite contact were identified from wire-line and gamma-ray log data as well as driller notes and measured sections of lithologies and contacts archived at MGRRE. Three cores were selected for sampling, each of which contained the pyritized contact. These were the State Chester Welch No. 18 core, the Krocker 1-17 core, and the BH-301 core (Fig. 1). Ten spots in the three



Core Name	Core Information			
Krocker 1-17 Well	***PN***	***API***	***Location***	***Included Formations***
	60134	21-035-60134-00-00	Clare County, MI	Ellsworth through "Squaw Bay" and Traverse Contact
	Lower Footage	***Upper Footage***	***Sampled Footages***	
	3497	3211	3463.8, 3494.3, 3497.5	
State Chester Welch No. 18	***PN***	***API***	***Location***	***Included Formations***
	33875	21-137-33875-00-00	Otsego County, MI	Norwood through Traverse
	Lower Footage	***Upper Footage***	***Sampled Footages***	
	1684	1435	1667.8, 1673.2, 1674.85, 1675.25	
BH-301	***PN***	***API***	***Location***	***Included Formations***
	None	None	Wayne County, MI	Norwood through Traverse
	Lower Footage	***Upper Footage***	***Sampled Footages***	
	120.5	60.5	110.1, 111.5, 117.5	

Figure 1. Locations and identification numbers of each core. The Krocker-17 Well is noted in blue, the State Chester Welch in red, and the BH301 in black. Abbreviations: PN = Permit Number, API = American Petroleum Institute Permit Number, MI = Michigan.

cores were sampled for thin sectioning, three of which were at the pyritized contact in each core. See Figure 1 for the locations of each well, footages selected from each core, and general information about the cores themselves. These billets were then sent to Wagner Petrographic of Lindon, Utah, and standard thickness (30µm) sections were prepared. The three samples which contained the pyritized contact were surface polished for microanalysis.

At Macalester College, a standard petrographic microscope with an attached CanonT5i DSLR camera was used to take pictures of all the thin sections at varying levels of magnification. Photographs were taken of not only the various minerals identified, but also of fossil structures and pyrite morphologies in the samples. High-resolution elemental abundance maps were collected on thin sections using the Bruker M-4 Tornado equipped with an Rh X-ray tube and thin-window silicon drift detector. Spatially-resolved X-ray maps display relative abundances of major elements including Mg, Al, Si, S, K, Ca, Fe, and Zn. Color intensities at each location represent semi-quantitative relative individual element abundance. Thin sections of the contact were analyzed with a JEOL JSM 6610LV scanning electron microscope equipped with a tungsten filament that was set to 15kV and operated under high vacuum. Select locations were imaged using backscattered electrons (BSE). The diameter of framboids in samples were measured using the SEM backscattered electron images and an average diameter for all framboids both in individual samples and all samples was calculated. This analysis was undertaken on the three thin sections of the contact. Using these findings, measures of framboid diameters are used to interpret the degree of oxygenation of the seawater these grains precipitated from based on work done by Chang et al. (2022).

RESULTS

Carbonates

Calcium is the most abundant element in all samples. In the "Squaw Bay Formation," lime mud is mixed with argillaceous muds in addition to other trace minerals. It is dispersed through the matrix of both formations and overlaps significantly with magnesium.

In the "Squaw Bay," calcite is mostly associated with fossil fragments and the clay matrix, but its altered form as dolomite is especially striking in the Traverse Limestone and within the pyritized contact. Dolomite crystals are abundant below the contact, and make up the entire matrix of the rock, showing significant overgrowth and deformation. Some twinning is present, especially in the lower (deeper) samples. Below the contact, crystals range from 0.5-3 microns in width and are relatively uniform in shape across this size range. Additionally, the dolomite crystals have preserved original crystal structures as well as fossil debris, especially when in close proximity to the contact. In SEM photomicrographs, a visible difference in the saturation of the crystals themselves is present. There is a differentiation between low- and high-Mg calcite within crystals, and some show reaction rims (Figure 2).

Silicates

Silicon is the second most abundant element in all samples, with a much greater degree of incidence in the "Squaw Bay Formation" as identified by XRF scans (O'Bryan, 2024). Silica makes up a large part of the clay and silt matrix in the "Squaw Bay Formation," and mostly appears as chalcedony throughout the Traverse Limestone. Silica in the "Squaw Bay Formation" appears in three forms. It appears as part of the cement and mud in the matrix, as detrital quartz grains, and as biogenic silica. In the Traverse Limestone, silica is much less abundant, and significantly more concentrated in the areas it does appear. Chalcedony is the major mineral hosting silicon and appears associated with fossil debris or filling vug space.

Sulfides and Sulfates

Pyrite is often associated with fossils in these samples. Pyrite encrusted both fossil debris and other crystals,

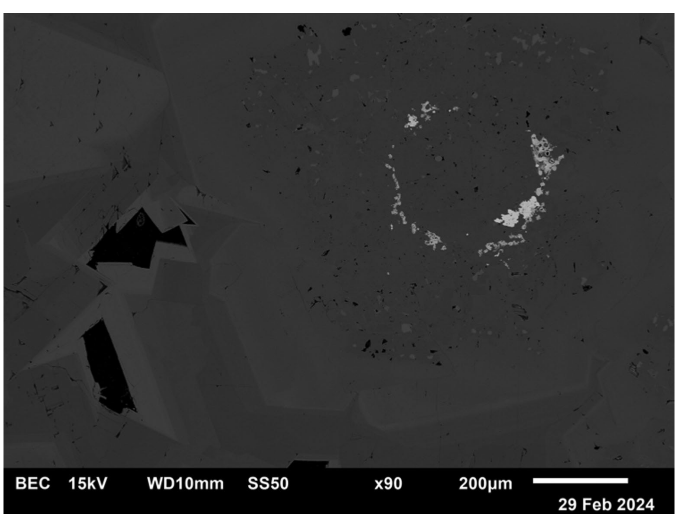


Figure 2. This is an SEM BSE image of calcite crystals found in the center of an echinoderm in the BH201-110 sample. High and low-Mg content differences are visible where lighter gray is lower-Mg calcite, darker gray is higher-Mg calcite, and white is pyrite. This zoning is indicative of multiple episodes of crystallization and dissolution.

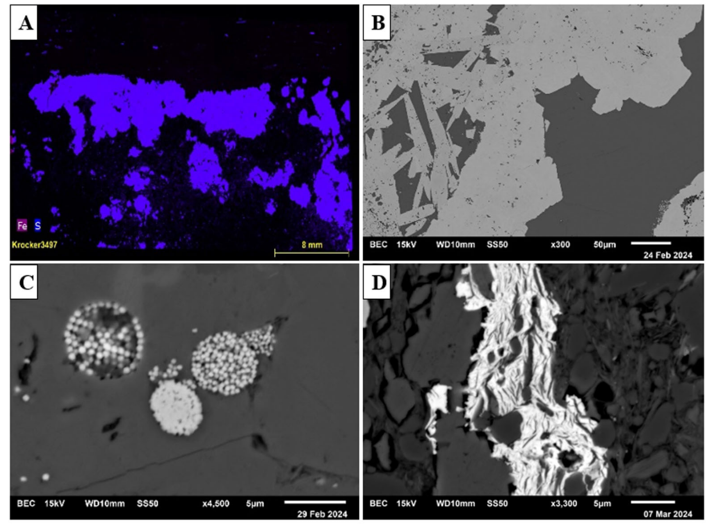


Figure 3. A) XRF Scan of the Krocker 3497 thin section showing abundance of pyrite (purple color created by the layering of Fe (violet) and S (royal blue). The upper limit of the pyrite is the contact between the "Squaw Bay Formation" and the Traverse Limestone. B) SEM BSE image of marcasite crystals (left center of image). Pyrite and marcasite are chemically indistinguishable from each other, but when viewed under reflected light, marcasite displays blue and green colors while pyrite is grayish gold. Here, marcasite is identified by its tabular crystal habit. C) SEM BSE image of framboids (light gray microaggregates) visible in the BH301-110 thin section. D) SEM BSE image of feathery barite (white) identified in the StChester 1674 thin section.

and original material was then dissolved and/or replaced while the pyrite remained. These pyritized fossil debris are especially helpful in determining the kind and abundance of marine life present in the samples and serve as an important indicator of the order of crystallization in some places.

In addition to being associated directly with organic content, pyrite exists in these samples as large masses or nodules, especially at the contact between the "Squaw Bay Formation" and the Traverse Limestone (Figure 3A). In the "Squaw Bay Formation," pyrite is more likely to occur as large nodules, and in the Traverse Limestone it is more likely to occur in association with fossils. Cubic pyrite is observed in all samples as well. Cubic crystals range from about 10 microns in length to about 2 millimeters.

The pyrite in these samples displays an additional uncommon morphology. Tabular crystals and rhombs of pyrite are visible at the margins of nodular masses and within the matrix of both the "Squaw Bay Formation" and the Traverse Limestone. Marcasite was identified, especially around the edges of the interior of the nodular masses. The elongate marcasite crystals are about 100 microns in length from tip to tip, but few are larger than that, and most smaller (Figure 3B). The rhombic pyrite and marcasite were commonly associated with each other.

Framboidal pyrite is observed at the contact in varying sizes and shapes. Figure 3C shows framboids present in the BH301-110 thin section. Framboids across all samples averaged 9.5 microns in length with a standard deviation of 5.7 microns. Though framboids are not associated with anything spatially, they do commonly appear in conjunction with other sulfide minerals (barite and sphalerite) and with fossil debris.

Barite and sphalerite were also identified. The sphalerite exhibits similar crystal morphologies to pyrite, but does not occur as framboids, needles, or cubes. Sphalerite is associated directly with pyrite. Barite is a barium sulfate which is only observed in the contact between the “Squaw Bay” and Traverse formations in the State Chester Welch sample. Barite is often elongate and prismatic, but in this thin section it showed a curved and feathery form, which wove in and out of the sediment matrix and around pyrite framboids (Figure 3D).

Paragenetic Sequence

Based on all the above results, what follows is a paragenetic sequence for the contact. Additional paragenetic sequences for the Traverse Limestone and the “Squaw Bay Formation” can be found in O’Bryan (2024). The sequence presented here is based on extensive analysis of these samples but suffers from two major caveats. First, no absolute ages of any of the samples were determined, so all diagenetic processes described here are relative to each other. Second, thin sections were not stained nor subject to a pore analysis. While the lack of this information does not preclude the possibility of making conclusions about the sequence of diagenetic events, having it would certainly clarify spatial and temporal relationships.

Figure 4 shows the paragenetic sequence for the contact. At the contact between Traverse Limestone and “Squaw Bay Formation,” there is extensive evidence for multiple episodes of pyritization, precipitation of minerals, and dissolution. Following the deposition of the Traverse Limestone, framboidal pyrite likely formed first in a bacterially-mediated setting, rich in organics and low in oxygen and this conclusion is supported by Chang et al. (2022) and He et al. (2022). These framboids, once formed and settled, gradually recrystallized into the nodular massive pyrite that dominates the samples. Secondary precipitation of framboids is supported by the measure of framboid diameters using the methods outlined in Chang et al. (2022); the framboids visible in the samples formed in dysoxic conditions, and precipitation occurred during early diagenesis. This was followed by the dolomitization of the Traverse Limestone. At some point between the initial precipitation of pyrite and the full dolomitization of the Traverse, the pyrite nodules underwent some stress and void space formed in cracks. Within these vugs grew large, well-formed dolomite rhombs as well as the elongate marcasite crystals. The marcasite formation and the formation of dolomite were likely closely related.

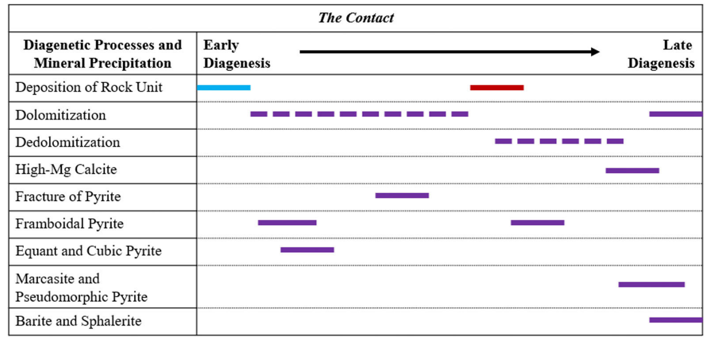


Figure 4. Paragenetic sequence of the contact between the “Squaw Bay Formation” and the Traverse Limestone. The deposition of the Traverse is blue, and the deposition of the “Squaw Bay” is red. Dashed lines represent uncertainty or otherwise continuous processes.

During the subsequent dedolomitization of the Traverse Limestone, which likely occurred sometime around when the “Squaw Bay Formation” was being deposited, pyrite replaced some of the dolomite rhombs, leading to the preservation of the initial crystal form with pyrite rather than dolomite. The second generation of framboidal pyrite also likely occurred around this time. The dedolomitization occurred before a precipitation of high-Mg calcite, filling the void space with clean, equant crystals. This final precipitation of high-Mg calcite preserved the pyrite rhombs. The precipitation of sphalerite and barite at the contact were the last minerals to have precipitated and were additionally accompanied by a final dolomitization process. These were the latest diagenetic processes to take place and are likely related to the migration of deep basinal fluids into the subsurface.

DISCUSSION AND FUTURE WORK

Paragenetic Sequence

Two generations of pyrite and one generation of marcasite are noted in the paragenetic sequence of the contact. The first pyrite generation formed the massive, nodular pyrite that makes up the bulk of the pyrite present in these samples, followed by marcasite precipitation associated with the initial dolomitization of the Traverse. The second generation of pyrite produced the framboidal and replacement forms of pyrite that are especially visible at the bottom of the "Squaw Bay Formation" and at the edges of the original pyrite masses. This sequence is supported by theories of massive pyrite formation, bolstered by the work of Jorgensen et al. (2004), Sawlowicz (1993), and Chang et al. (2022). This first generation likely occurred before the "Squaw Bay Formation" was deposited and was likely initially mediated by bacteria.

Because it is assumed that the massive nodular pyrite was formed from the precipitation of framboids, the presence of well-formed framboids in the matrix of the "Squaw Bay Formation" is clear evidence of a second generation of pyrite. The exact chemistry of this relationship is unresolvable with the available data, but it is likely that pyrite formed both during a cessation of sediment supply to the basin (when the carbonate platform subsided) and when the "Squaw Bay Formation" began to be deposited and lithified. That said, the framboid diameter analysis results from Chang et al. (2022) suggest that the visible framboids in these samples were formed in early diagenetic processes, as precipitation of pyrite that occurred after burial of organics and was initially mediated by bacteria.

Rhombs are not a typical crystal form of pyrite. While it is not possible to determine exactly how these crystals formed, it is likely that pyrite forms as a pseudomorph of dolomite rhombs (Figure 5). The fluid that was responsible for the initial dolomitization of

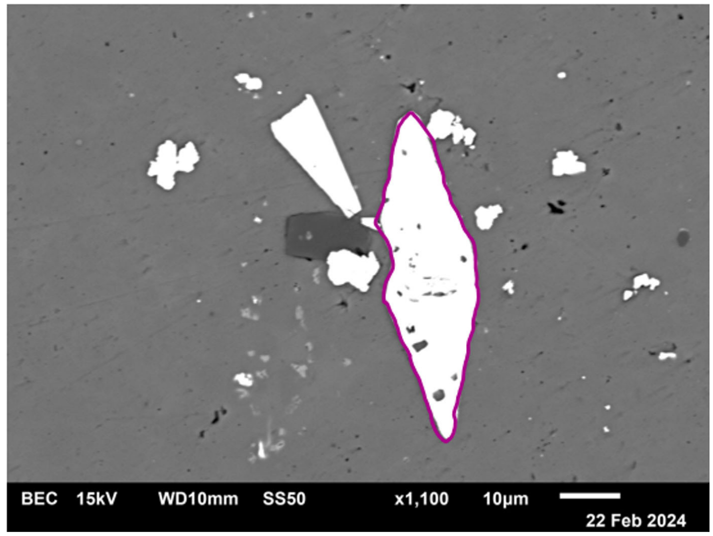


Figure 5. Pseudomorphic pyrite rhomb outlined in purple.

the Traverse allowed the growth of rhombic dolomite crystals in the available void space, which was created as a result of the initial dissolution in the Traverse Limestone. The process of dolomitization also resulted in the recrystallization or growth of marcasite on the initial pyrite nodules. What happened next is unclear. What we know is that dolomitization took place and that high-Mg calcite precipitated in void spaces, preserving both pyrite rhombs and elongate marcasite. The rhombs likely formed as a result of dolomite being leached out and pyrite filling in the pore left behind. The multiple dolomitization processes described above are supported by reaction rims of dolomite crystal, which grade between dolomite and high-Mg calcite.

Sphalerite, Barite, and MVT Mineralization

This study suggests the precipitation of sphalerite and barite along with a final dolomitization process were the latest diagenetic processes to occur. Both minerals are commonly associated with carbonate facies and other sulfide minerals (here pyrite) but how they came to appear in these samples is a larger question than simple alteration.

Mississippi Valley type deposits are concentrations of elements including zinc and barite, which manifest here as the minerals sphalerite and barite. Pyrite, dolomite, sphalerite, and barite specifically are all commonly associated with each other and with MVT deposits (Smith, 2021). MVT mineralization is hypothesized to occur as a result of tectonic activity which directs hydrothermal ore-bearing fluid to flow through already lithified rock units. Regional hydrothermal systems play a large part in the occurrence of these deposits, and tectonic activity and bedrock chemistry is also a key variable associated with the availability of elements in host rocks (Paradis et al., 2007).

The fluids associated with MVT mineralization must be warm and chemically rich. The Michigan Basin is underlain by the failed Mid-Continental rift in North America. Volcanic bedrock formed in the Precambrian which underlies the north-western portion of the Basin likely formed the supply for Mg- and trace element rich fluids which dolomitized and precipitated sphalerite in the Krocker and State Chester wells (Heinrich, 1976). The fracture of Precambrian rock beneath the entire basin and the migration of deep, warm fluid through these fractures would provide the right amount of fluid with the correct composition to the Devonian subsurface. Importantly, barite was only identified in the BH-301 well, which is in the southeastern part of the basin.

Future Work

Limitations of the study include the limited number of samples available for analysis, which may have skewed results. Additionally, the complexity of dolomite and pyrite formation presents challenges in interpretation due to their rarity in modern environments and the variability of their forms. Future work would involve testing interpretations presented herein with isotopic data, performing point counting and porosity tests on samples, and conducting further SEM analysis with standardized chemical spectra to quantify the extent of diagenetic processes more accurately.

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