Pyrite mineralization in microbial mats from the mid-Proterozoic Newland Formation, Belt Supergroup, Montana, U.S.A.

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Abstract


The mid-Proterozoic Newland Formation, a shale-dominated unit of the Belt Supergroup, was deposited in an eastern extension of the Belt basin, the Helena embayment. A variety of different shale facies types can be distinguished. Of particular interest for this study is a shale facies that has been interpreted to be the result of microbial mat growth (resulting in carbonaceous shale beds) interrupted by storm deposition (causing deposition of graded silt/mud couplets). Alteration of carbonaceous beds with silt/mud couplets gives these shales a characteristic striped appearance. Along the basin margins a pyrite-rich sub-facies of these striped shales is found locally, consisting of laminated pyrite beds that alternate with non-pyritic silt/mud couplets. Laminated pyrite beds in pyritic striped shales are interpreted as mineralized microbial mats because of wavy-crinkly internal laminae and because of the direct association with unmineralized striped shales that contain microbial mat deposits. Excess iron in pyritic shale horizons was probably supplied by terrestrial run off in collodial form. Fine hydroxides, introduced by rivers into basin marginal lagoons, fossilized, and were then incorporated into microbial mats and reduced to pyrite upon burial.

Introduction

Within the Newland Formation shales of a characteristic striped appearance are common. These striped shales contain deposits of benthic microbial mats and were described earlier by Schieber (1986a). A pyrite-rich variant of these striped shales is described here. These pyritic shales occur along the margins of the Helena embayment, an eastern extension of the mid-Proterozoic Belt basin. The sediment fill of the Helena embayment consists predominantly of rocks of the Lower Belt Supergroup (Harrison, 1972). Pyritic shales from the southern Little Belt Mountains (Fig. 1) were investigated in detail. A brief description of stratigraphy, sedimentary setting and basin evolution is given in Schieber (1986b). Pyritic shales that are similar to those of the Newland Formation have been described from Proterozoic shale sequences in Australia, and are in places found in association with stratiform base-metal mineralization (Bennet, 1965; Cotton, 1965; Mathias et al., 1973; Loudon et al., 1975).

A scheme of the stratigraphy of the Helena embayment is shown in Fig. 2. Belt sedimentation commenced with deposition of the basal Nehart Quartzite (Weed, 1899). The Nehart Quartzite grades upward into the Chamberlain Shale (Walcott, 1899) and is in turn overlain by the Newland Formation. In the southern Little Belt Mountains the Newland Formation can be subdivided (Nelson, 1963) into a lower member (dolomitic shales) and an upper member (alternating shale and carbonate packages). A sandstone-
graben with active faults along the southern margin. Pyritic shales of the southern Little Belt Mountains occur mainly in the upper portion of the NTZ. Belt sediments in the Little Belt Mountains are unmetamorphosed.

Pyrite in the Newland shales

The occurrence of pyrite

Pyrite occurs throughout the shales of the Newland Formation (lower and upper members) as tiny sphenoid grains or as euhedral crystals (0.01–0.02 mm in size). Spherical and euhedral forms of pyrite occur together in any given sample. These pyrite crystals are either scattered irregularly throughout the rock, or are clustered together as frambois (0.02–0.25 mm in size), or may form fine wavy-bicrystal pyritic laminae (0.01–0.02 mm thick). Bundles of such laminae form laminated pyrite beds. Whereas scattered and frambooidal pyrite is a common minor constituent (up to 4%) of all the shales in the Newland Formation, laminated pyrite beds are only found in distinct horizons of pyritic shale.

Laminated pyrite

Laminated pyrite beds are some millimeters to several centimeters thick, and are separated by beds of dolomitic clayey shale (Fig. 3). These intervening unmineralized beds have in many places silt at the bottom (may show cross-lamination, parallel laminations, and graded ripples) that grades upwards into dolomitic clayey shale. Thus, many of the dolomitic clayey shale beds are actually silt/mud conglomerates. Boundaries between pyritic and non-pyritic beds are always sharp (Figs. 3). The intimate intercalation of beds of different lithology gives the pyritic shales a striped appearance (Fig. 3). When viewed in detail, the laminated pyrite beds have a wavy-anastomosing texture and individual laminae have a wavy-crinkly appearance (Figs. 3 and 4). Between the pyritic laminae lenses and discontinuous laminae occur, consisting of sediment with variable composition (mixtures of clay, quartz silt, and fine crystalline dolomite, see Fig. 5). Shales that are later equiv-
Formic acid is a weak acid that is used in various applications such as cleaning, personal hygiene, and food preservation. It is a colorless to light yellow liquid with a strong, pungent smell.

**Formic acid properties**

- **Chemical formula**: HCOOH
- **Molecular weight**: 46.04 g/mol
- **Density**: 1.090 g/cm³ at 20°C
- **Boiling point**: 120.7°C
- **Melting point**: -49.5°C
- **Color**: Colorless to pale yellow
- **Odor**: Strong, pungent

**Uses**

- **Cleaning**: Formic acid is used in cleaning products due to its ability to dissolve grease and grime.
- **Personal hygiene**: It is used in personal hygiene products for its antibacterial properties.
- **Food preservation**: Formic acid is used as a preservative in food products.

**Health and safety**

Formic acid can irritate the skin, eyes, and respiratory tract. It should be handled with care and worn protective gear when handling.

**References**


**Images**

- **Image 1**: A glass bottle containing formic acid with a dropper.
- **Image 2**: A chemical reaction between formic acid and sodium hydroxide, producing sodium formate and water.

**Additional Information**

Formic acid is produced naturally by many insects and is also found in certain foods such as cheese and meats. It is also a byproduct of the decomposition of organic matter.
Pyrite formation occurred in a completely unconsolidated sediment (Figs. 6 and 7), further burial led to "pyrite cementation" and hardening of strongly pyritic laminae in an otherwise unconsolidated sediment (Fig. 8) because of continued diagenetic pyrite growth. These fragile laminae were then broken up and telescoped in the event of soft-sediment deformation. Reworked fragments of hardened pyritic laminae and of laminated pyrite beds that are found in sandstone and conglomerate beds (Fig. 9) allow an estimate of the depth at which hardening of pyritic laminae occurred. Above sandstones and conglomerates are found as fills of erosional channels in the

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Fig. 4. Photomicrograph (reflected light) of a laminated pyrite bed. Note wavy-irregular internal texture and wavy-irregular sediment intercalations between pyritic laminae. The scale bar is 0.5 mm long.

Fig. 5. Photomicrograph (reflected light) of a laminated pyrite bed. It shows that individual pyritic laminae are composed of pyrite crystals (white). The wavy-irregular shale drapes between pyritic laminae consist of quartz, silt, clay, and dolomite. The scale bar is 0.1 mm long.
pyritic shale facies, and because these channels are up to 50 cm deep, pyritization and hardening of pyritic laminae must have occurred within the uppermost 50 cm of the sediment. Thus, textural evidence as well as comparison with modern sediments suggests that pyrite in pyritic striped shales of the Newland Formation formed very early in burial history.

Could the laminated pyrite beds be mineralized microbial mats?

"Normut" striped shale

A substantial portion of the Newland Formation is made up of striped shales that consist of interbedded dolomitic clayey shales and carbonaceous silty shales (Fig. 10), and these shales are the key to understand the origin of the pyritic shales described above. A detailed study of the sedimentary features of striped shales in the Newland Formation has already been published (Schieber, 1986a). From that study it appears that the carbonaceous silty shale beds in these striped shales are the result of the growth of benthi microbial mats. The main evidence for a microbial mat interpretation is summarized in the following paragraph.

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Fig. 6: Convolute bedding caused by soft-sediment deformation in a sample of pyritic striped shale. Pyritic beds are light colored. Scale bar is 10 mm long.

Fig. 7: Photomicrograph (reflected light) of a laminated pyritic bed that is overlain by graded silt/mud couplet. Note the load casts of silt into underlying pyritic bed. The scale bar is 0.5 mm long.
Irregular wavy-crinkly laminae in carbonaceous silty shale beds (Fig. 11) resemble stromatolitic laminae as described by B partly (1976), Bertrand-Sarfati (1976), Horodyski et al. (1977), and Krumbein and Cohen (1974), and are quite unlike the typically parallel laminae found in carbona-
aceous shales that accumulated in stagnant basins. The observation that carbonaceous silty shale beds behaved like a tough leathery membrane during soft-sediment deformation (Schieber, 1986a), rather than like a soupy organic suck, further supports a microbial mat interpretation of these carbonaceous beds. Rolling-up and folding over of zipped-up fragments of carbonaceous silty shale beds reveals considerable cohesive strength during transport and deposition and is further indication of a microbial mat origin (Schieber, 1986a). Remnants of filamentous bacteria and cyanobacteria that were identified in these fragments (Horodyski, 1980) further support a microbial mat interpretation.

The beds of dolomitic clayey shale were interpreted as storm deposits. Silt layers that are commonly found at the base of these shale beds show a variety of sedimentary structures, such as cross-lamination, normal grading, and graded rhythms (in the transition to the overlying shale). These silt/mud couplets show great similarity to modern storm deposits described from the North Sea (Gardew and Reineck, 1969) and other modern shelf seas (Allen, 1965; Reineck and Singh, 1972).

The occurrence of hummocky cross-stratified sandstone beds within striped shales also suggests that storms played a role in the deposition of these shales. Recurring deposition of storm layers on benthic microbial mats was responsible for the intimate interlayering of carbonaceous silty shales and dolomitic clayey shales and for the striped appearance (Fig. 10) of this type of shale facies (Schieber, 1986a).

Pyritic striped shale

Specimens of pyritic striped shale and “normal” striped shale are strikingly similar (Figs. 3, 10; cf. Schieber, 1986a, p. 522), suggesting that they are of related origin. Additional observations that indicate a common origin are:

1. Beds of dolomitic clayey shale with silt at the bottom (silt/mud couplets) occur in “normal” as well as in pyritic striped shales (Figs. 7, 11, and 12, and Schieber, 1986a, p. 526), and have the same sedimentary structures in the silt portion (cross-lamination, parallel lamination, graded rhythms). Sedimentary structures were observed in polished slabs and in thin section.

2. Laminated pyrite beds (in pyritic striped shale) and carbonaceous silty shale beds (in “normal” striped shale) have the same wavy-anastomosing internal texture and the same wavy-crinkly appearance of individual laminae (Figs. 4, 11, 12 and 13).

3. Sediment between individual pyritic laminae consists of lenses and discontinuous laminae of a mixture of clay, dolomite, and quartz silt (Fig. 5), and is in every respect identical to shale drapes and silt-rich laminae that occur between carbonaceous silty laminae in carbonaceous silty shale beds (Fig. 13) of “normal” striped shale.

4. “Normal” striped shales are the lateral equivalents of pyritic striped shales, and are also interbedded with pyritic striped shales.
(5) A smooth transition in pyrite content can be observed, from "normal" carbonaceous silt shale beds with 1-4 vol% pyrite (Fig. 14), over beds with intermediate amounts of pyrite (Fig. 12), to highly pyritic laminated pyrite beds with as much as 50 vol% pyrite (Fig. 4).

Two conclusions can be drawn from these observations and textural comparisons: (1) carbona-
ceous silty laminae in carbonaceous silty shale beds (in "normal" striped shale) are the direct equivalents of pyritic laminae in laminated pyrite beds (pyritic striped shale); (2) pyritic striped shales are simply a pyrite-rich variety of the striped shales that are so common in the Newland Formation. The first conclusion is also supported by the observation that in "normal" striped shales most of the pyrite is found in the carbonaceous silty laminae of carbonaceous silty shale beds (Fig. 14). Finally, under the assumption that carbonaceous silty shale beds in "normal" striped shales are fossil microbial mats (Schieber, 1986a), the textural equivalency between pyritic and "normal" striped shales leads to the conclusion that laminated pyrite beds in pyritic striped shales are pyrite-mineralized benthic microbial mats.

Origin of pyritic shale horizons

Pyritic shale horizons in the southern Little Belt Mountains extend laterally for as much as 8 km, may reach up to 60 m in thickness, can contain the order of 10^6 tons of iron in pyrite (Schieber, 1987a), and grade laterally into "normal" striped shales. Even though laminated pyrite beds contain up to 50% pyrite by volume, averaging over the whole thickness of a pyritic shale horizon results in an average iron content of about 10% (calculated as metallic iron). Of this iron, 70% are contained in pyrite and the remaining 20% in the terrigenous clastic component. Thus, even though the amount of iron in individual pyritic shale horizons is of the same magnitude as found in Phanerozoic iron-oxide deposits (Schieber, 1987a), the pyritic shales have no economic significance.

The possible source of the iron that accumulated in these pyritic shale horizons was discussed in detail by Schieber (1987a), and a summary of pertinent conclusions follows below. Because of the reducing character of the sediments below the pyritic shale horizons, it is considered quite unlikely that iron was mobilized from within the basin. An alternative model in which iron is brought into the basin by continental runoff is clearly feasible (Schieber, 1985, 1987a) and in accord with the sedimentary history of the basin. Only very small amounts of iron are needed in the terrestrial runoff to account for the iron in the pyritic shale horizons. Considering the oxidation state of the Mid-Proterozoic atmosphere (Schidlowski et al., 1973), iron was probably introduced into the basin in the form of iron oxhydroxides.

"Normal" striped shales in the Newland For-
sedimentary features in the interbedded sandstones of the Newland Formation. However, in the Proterozoic strongly reducing shales may have accumulated in shallow aerated environments in the presence of benthic microbial mats (Schieber, 1986a). Microbial mats act as an ecological membrane that causes several environmental parameters, such as Eh, H2S concentration, dissolved O2, and light intensity, to undergo abrupt changes at the interface (Bauird, 1981). Below such a mat strongly reducing conditions can exist despite surficial water above the mat (Bauird et al., 1980). Similar to their modern counterparts, benthic microbial mats in nearshore-lagoons of the Newland Formation were probably sticky and gelatinous (Golubic, 1976). Iron hydroxides that flocculated in nearshore areas would eventually become trapped on the mud surface, and would be transformed into pyrite after incorporation into the buried reducing layers.

Pyrite-rich shales are usually thought to accumulate in quiet water under anoxic conditions, but such a notion is contradicted by the high-energy sedimentation. These features indicate episodic strong currents, high-energy events (such as storms), and fairly shallow-water conditions during deposition of pyritic striped shales. Stratigraphic and sedimentologic investigations by Schieber (1985) led to the conclusion that pyritic striped shales accumulated in coastal embayments that were partially enclosed by offshore sandbars.

![Fig. 14. Photomicrograph (combined reflected and transmitted light) of carbonaceous silty shale bed in "normal" striped shale. Pyrite (tiny white specks) occurs mainly in the carbonaceous clay laminae. Arrows 1, 2, and 3 point out larger, spherical pyrite grains, the other arrows point out areas with abundant small pyrite grains. Scale bar is 0.5 mm long.](image)

![Fig. 15. Proposed formation of pyritic-stripped shales. Ferro-
diomite fossils are trapped by microbial mat filaments and converted to pyrite after burial because of large surface reduc-
tion rates below the mat surface. Enlarged pore space to the left. (a) is approximately 0.5 mm thick shows tripping of Fe-
hydrsulfide and alternation of Fe-rich (pyritic) mat layers with shale screens (consisting of clay, detritus, and quartz silt, see also Figs. 4 and 5). The latter may be related to pulses of sediment that were supplied to inner-bay areas during river floods (Schieber, 1986a). Deposition of ash/mud rafts by storms interrupted microbial mat growth enlarged porosity to the right, (b) approximately 5 cm high, and new mats were established on top of storm deposits (see also Figs. 5 and 8).](image)
of the mat. The envisioned scenario for formation of pyritic striped shale is summarized in Fig. 15.

Conclusion

The pyritic striped shales in the Newland Formation are a pyritic-rich variant of the "normal" striped shales described earlier (Scheber, 1966a). Pyritic-rich shale beds are mineralized benthic microbial mats that accumulated in marl-shelf lagoons. Intercalated storm deposits (silt/turbid couples) give this type of shale its characteristic stepped appearance. Iron was probably supplied to these shales by riverine collodial iron oxhydroxides that flocculated in nearshore areas and then was trapped on microbial mat surfaces. Upon burial, pyrite formation commenced in the reducing environment below the mat. Improved understanding of this pyrite of pyritic shales could be of economic importance because similar appearing Proterozoic shales elsewhere are associated with uranium-base metal deposits.

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References


