Pyritic shales and microbial mats: Significant factors in the genesis of stratiform Pb-Zn deposits of the Proterozoic?

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Abstract. Extensive horizons of pyritic shale occur in Mid-Proterozoic sediments of the eastern Belt basin, Montana, U.S.A. These pyritic shales are of striped appearance. Laminated pyrite beds alternate with non-pyritic shale beds. Laminated pyrite beds have wavy-crinkly internal laminae and are interpreted as mineralized microbial mats. Pyrite is essentially the only sulfide mineral in these shales. Pyritic shale horizons occur along the basin margins, and it is feasible that colloidal iron was introduced by rivers into basin marginal lagoons and then incorporated into microbial mats and reduced to pyrite. The pyritic shales in the Newland Formation show great similarity to those that host the Pb-Zn deposits of Mt. Isa and McArthur River. It is suggested that pyritic shales of this kind are relatively common in Mid-Proterozoic shales, and that the processes that led to the occasional formation of Pb-Zn ore bodies in these shales are not related to those that formed the pyritic shales themselves.

Pyritic shale horizons described in this study 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), and pyritic shale horizons are known from two localities: 1) The Highland Mountains and 2) The southern Little Belt Mountains (Fig. 1). Gossans of these sulfide horizons contain anomalous amounts of Pb and Zn. Drilling by Anaconda Minerals Co. showed that these pyritic shales consist of thin beds of pyrite-rich shale that alternate with beds of normal shale. Thus, these pyritic shales are of striped appearance and bear great similarity to those that host the large Mid-Proterozoic Pb-Zn deposits of Mt. Isa (Queensland, Australia) and McArthur River (Northern Territory, Australia). However, the pyritic striped shales of the Belt basin were disappointingly unmineralized with regard to Pb and Zn. Individual pyritic shale horizons represent a rock volume on the order of 0.5-1 kin3, and to explain the paucity of Pb and Zn in such vast volumes of pyritic shale that elsewhere host major Pb-Zn deposits was the starting point for the author's Ph.D. research (Schieber 1985). A brief description of stratigraphy, sedimentary setting and evolution of the Helena embayment is given in Schieber (1986 a).

Belt sedimentation commenced with deposition of the Neihart Quartzite (Weed 1899), which is in turn overlain by the Chamberlain Shale (Walcott 1899; Schieber 1989) and the Newland Formation (Fig. 1). The Newland Formation of the southern Little Belt Mountains can be subdivided (Nelson 1963) into a lower (dolomitic shales) and an upper member (alternating shale and carbonate packages). In the transition between lower and upper member a sandstone bearing unit occurs, informally named the "Newland Transition Zone" (or NTZ; Schieber 1985). Deposition of the NTZ marks a major regression, and the Helena embayment changed from a smooth depression to an east-west trending half-graben with active faults along the southern margin (Fig. 1). The pyritic shale horizons of the Southern Little Belt Mountains occur in the upper portion of the NTZ (Fig. 1).

The purpose of this paper is to discuss the possible origin of pyritic shale horizons in the Newland Formation of the Little Belt Mountains and to evaluate their significance for Proterozoic stratiform base mental deposits that are associated with texturally very similar pyritic shales.

Pyrite mineralized microbial mats in the Newland Formation

Pyrite in the Newland Formation has been described in detail by Schieber (1985). It occurs as tiny spherical grains or euhedral crystals (0.001-0.01 mm in size) that are scattered irregularly, are clustered in framboids (0.02-0.25 mm), or form fine wavy-crinkly laminae (0.01-0.2 mm thick). Bundles of such laminae form laminated pyrite beds (Fig. 2). Scattered and framboidal pyrite occurs throughout the Newland Formation in low abundances

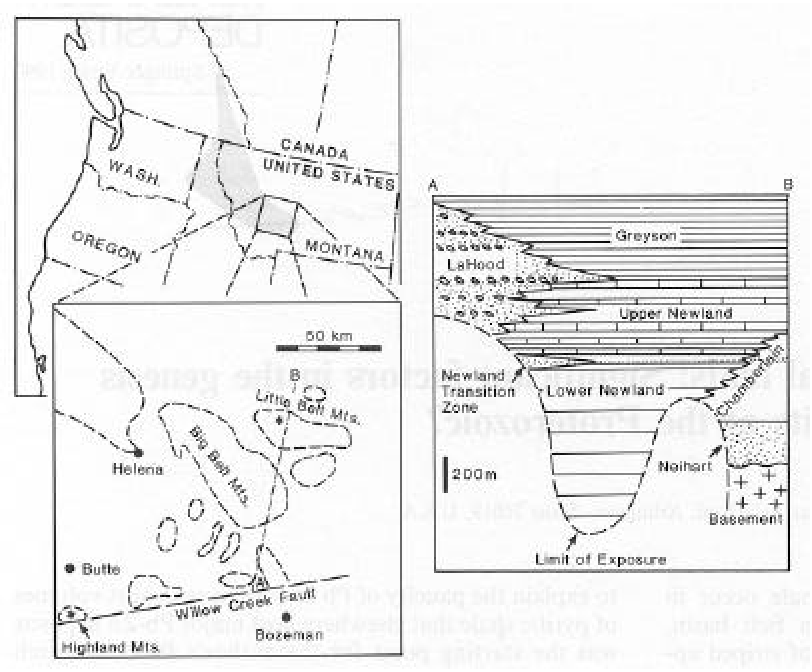


Fig. 1. Location map and stratigraphic overview. Present day outline of Belt basin indicated by stipple pattern. The Helena embayment portion of the Belt basin is essentially contained in the enlarged portion of the map. Star symbols point out the occurrences of pyritic shale horizons. The stratigraphic overview for the Helena embayment is based on data from McMannis (1963), Boyce (1975), and Schieber (1985). It represents a generalized restored cross-section along line AB in the enlarged map portion

(1-4%) and is identical in appearance to early diagenetic sedimentary pyrite observed elsewhere (Berner 1970; Love 1964; Sweeney and Kaplan 1973). In contrast, laminated pyrite beds are only found in distinct horizons of pyritic shale (Schieber 1985). Pyritic beds are some mm to several cm thick, contain up to 50% pyrite (Fig. 3), and are separated by be .. of dolomitic clayey shale (Fig. 2). The latter contain only small quantities of pyrite (1-4%, of the scattered and framboidal variety), have in many places silt at the bottom, and form graded silt/mud couplets (Fig. 4). The lower silty portion of these couplets may contain clasts, and may show cross-lamination, parallel lamination, and graded rhythmites (Fig. 2). Intercalation of laminated pyrite beds with silt/mud couplets gives these shales a distinct striped appearance (Fig. 2).

Striped shales of identical texture, but of much smaller pyrite content, have been described from the Newland Formation in an earlier publication (Schieber 1986b). Thin intervals (0.1-1 m thick) of these "normal" striped shales are found interbedded with pyritic striped shales in the pyritic shale horizons of the Newland Formation, and also constitute the lateral equivalents of pyritic striped shales. "Normal" striped shales consist of beds of carbonaceous silty shale that alternate with silt/ mud couplets (Schieber 1986 b; and Fig. 3). The latter are identical to silt/mud couplets in pyritic striped shales (Fig. 4). Upon close inspection (see Figs. 4 and 5) it also turns out that in both shale types the beds that are intercalated with silt/mud couplets (carbonaceous silty shale and laminated pyrite beds respectively), show identical textural features. Both show wavy-crinkly internal laminae (compare Figs. 4 and 5) and alternating dark carbonaceous silty laminae and light coloured sediment drapes consisting of clay, dolomite and silt. However, the carbonaceous laminae are strongly enriched with pyrite in the case of the pyritic striped shales (Figs. 3 and 4). The match of sedimentary structures and textures between the two shale types, as well as their interbedding and lateral equivalency, suggests that the conditions of sedimentation were the same in both cases.

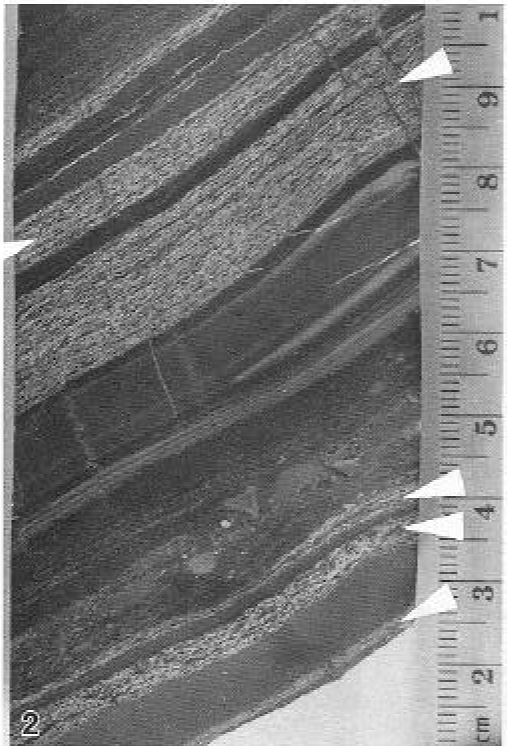
Carbonaceous silty shale beds in "normal" striped shales were examined in considerable detail by Schieber (1986b) and interpreted as fossil benthic microbial mats. The main reasons for that interpretation are listed below:

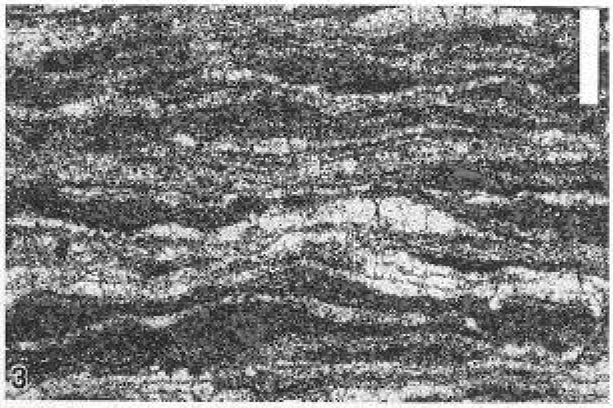
a) irregular wavy-crinkly laminae in carbonaceous silty shale beds (Fig. 5) resemble stromatolitic laminae. One would not expect to find such laminae in a compacted shale that was deposited from suspension in a stagnant environment. Shales deposited under the latter conditions typically are characterized by parallel laminae;

b) during soft sediment deformation and erosion the carbonaceous silty shale beds behaved like a tough leathery membrane, rather than like a soupy organic muck (see Schieber 1986b; his Fig. 11);

c) abundant filamentous microorganisms, probably remnants of filamentous bacteria and cyanobacteria, were observed by Horodyski (1980) in ripped up fragments of carbonaceous laminae.

The cumulative indirect evidence of microbial mat activity (Schieber 1986 b) justifies the interpretation of carbonaceous silty shale beds as microbial mat deposits. Because carbonaceous silty shale beds and laminated pyrite beds show the same textural features (compare Figs. 4 and 5), and because conditions of sedimentation were probably the same for "normal" and pyritic striped shales (see above), it is a reasonable extension of previous conclusions (Schieber 1986b) that laminated pyrite beds represent mineralized microbial mat deposits.





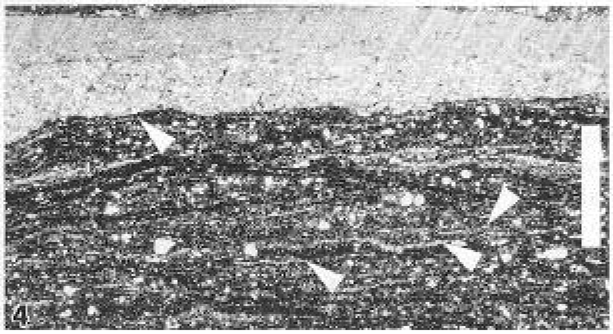


Fig. 2. Drillcore specimen of pyritic striped shale. Laminated pyrite beds indicated by arrows. Note wavy-crinkly internal laminations of laminated pyrite beds, and sharp boundaries to non-pyritic interbeds. Thick storm layer with pebbles at the base and parallel laminated silt and dolomitic shale towards the top is visible in the lower half of the specimen. Scale has mm subdivisions

Fig. 3. Photomicrograph (reflected light) of laminated pyrite bed. Note wavy-crinkly internal texture and wavy-lenticular sediment intercalations between pyrite laminae. Scale bar is 0.5 mm long

Fig. 4. Photomicrograph of pyritic striped shale (combined transmitted and reflected light). The figure shows a laminated pyrite bed (lower two thirds) with approximately 25% pyrite that is overlain by a graded silt/mud couplet. Pyrite grains appear as tiny white dots. Several pyritic laminae are pointed out with arrows. Note wavy-crinkly nature of laminae and compare to carbonaceous silty laminae in Fig. 5. Scale bar is 0.5 mm long

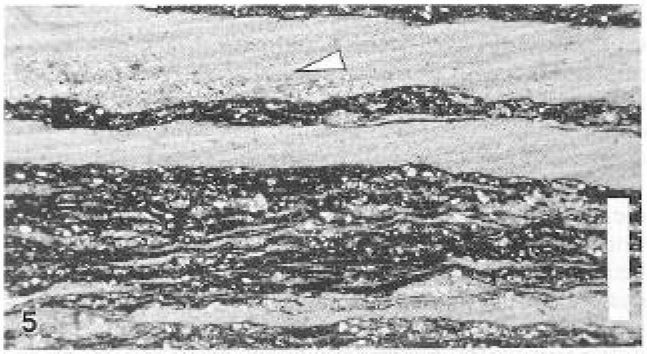


Fig. 5. Photomicrograph of "normal" striped shale. Carbonaceous silty shale beds are dark and show wavy-crinkly internal laminae. These beds were interpreted as microbial mat deposits by Schieber (1986b). A silt/mud couplet is pointed out by an arrow. Scale bar is 0.5 mm long

Erosional channels in striped shales can be as deep as 50 cm and are filled with sandstone and conglomerate. In the pyritic striped shale facies these channel fills contain ripped up fragments of laminated pyrite beds. Laminated pyrite beds also show load casts, caused by overlying silt, sand, and conglomerate beds. These observations indicate that the pyrite formed very early in diagenesis (Schieber 1985).

Source of iron

Pyritic shale horizons of the southern Little Belt Mountains can be traced laterally for as much as 8 km, are up to 60 m thick, cover an area of approximately 20 km', and grade laterally into unmineralized "normal" striped shales (Schieber 1986 b). From chemical analyses of pyritic striped shales one can calculate that pyritic shale horizons of the southern Little Belt Mountains contain on the order of several 108 tons of iron in pyrite (Schieber 1987 a). The potential source of this pyrite iron was discussed at length by Schieber (1987 a) and is only briefly summarized here. Because the pyrite was obviously present very early during sedimentation history, only syn-genetic and diagenetic mineralization models need to be considered. A variety of models were evaluated by Schieber (1985, 1987 a), and the conclusion was that the pyritic shale horizons can not be explained with a syngenetic exhalative or an early diagenetic model that requires the iron to be derived from within the basin (intra-basinal iron source). The reducing character of the sedimentary sequence below the pyritic shale horizons, the absence of iron enrichment in diagenetic dolomite, and pyrite formation throughout most of the diagenetic history of these sediments all indicate that iron was only redistributed locally, that pore waters were very low in iron, and that no significant quantities of iron could have been mobilized from within the basinal sediment pile at any time during burial history. An alternative model in which iron is brought into the basin by continental runoff is clearly feasible (Schieber 1985, 1987 a) and in accord with the sedimentary history of the basin. In that model, semiquantitative estimates of potential iron supply (Schieber 1985, 1987a) that took into account the constraints imposed by the sedimentary record and the chemical behaviour of iron in recent terrestrial waters, led to the conclusion that under assumption of granitoid source rocks (Schieber 1986 a), a thin cover of immature alluvium in the hinterland can supply many times more iron to continental runoff than needed for formation of the observed pyritic shale horizons. It was further concluded that iron probably entered the basin in colloidal form (as iron oxyhydroxides), and that only very small amounts of colloidal iron (< 1 ppm) were needed in the terrestrial runoff to account for the iron in the pyritic shale horizons.

It is envisioned that during deposition of the lower and upper member of the Newland Formation erosion was slow, and that the small amounts of mafic minerals that were present in the granitoid source rocks of the Newland Formation (Schieber 1986 a) were oxidized early in the weathering cycle. Erosion was more rapid when uplift occurred and the NTZ was deposited. A blanked of immature alluvium which contained mafic minerals was spread out in the hinterland and acted as an iron source to terrestrial waters until most of the mafic minerals were destroyed. Thus, for a relatively short time span after the regression, there was a comparatively large amount of iron available to be mobilized and carried to the basin (Schieber 1987 a). Such a scenario would explain occurrence of pyritic shale horizons directly above regressive deposits of the NTZ. Considering the oxidation state of the Mid-Proterozoic atmosphere (Schidlowski et al. 1975), iron was probably carried into the basin in the form of iron oxyhydroxides.

Iron supply by continental runoff poses a certain dilemma, because one has to explain the decoupling of terrigenous sedimentation from iron deposition. Climatic conditions during deposition of the Newland Formation were probably semi-arid (Schieber 1985, 1987 a), as indicated by a predominance of fine-crystalline dolomite (probably penecontemporaneous) in basin marginal carbonates, occurrences of nodules and rosettes of barite (probably replaced precursor gypsum), and a general abundance of carbonate. Under such (semi-arid) conditions major surface runoff is restricted to periods of strong rainfall and flooding. During those time periods relatively large amounts of water would leave the drainage basin within a matter of days, and pulses of sediment would be introduced along the basin margins. Most of the time however the rivers would be almost dry. In the lower reaches of the rivers groundwaters (ironbearing in our case) would have entered the rivers, and would have maintained slow discharge into the basin. Under those conditions only minor dilution of the iron input by terrigenous sediment would have occurred.

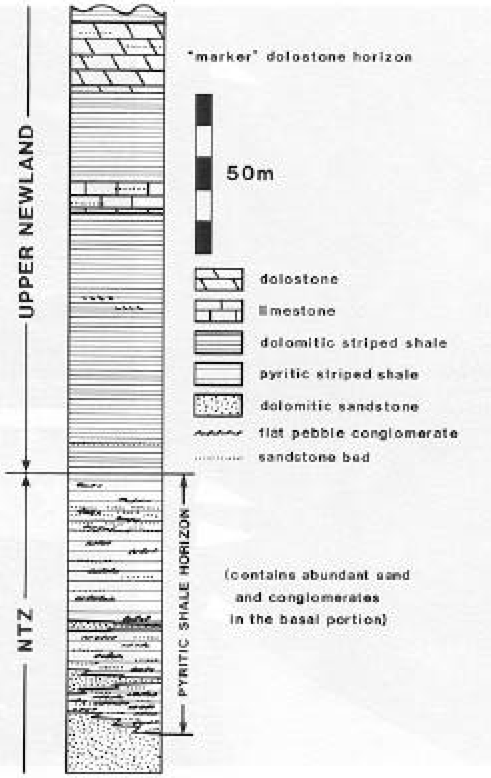


Fig. 6. Generalized lithologic log from the western portion of the pyritic shale occurrences in the southern Little Belt Mountains. The "marker" dolostone horizon can be found in most areas of the southern Little Belt Mountains, and is an important stratigraphic reference horizon

Depositional setting

Silt/mud couplets in "normal" striped shales of the Newland Formation were interpreted as storm deposits because of their great similarity to storm layers found in modern muddy shelf seas (Schieber 1986b). By analogy, silt/mud couplets in pyritic striped shales are also interpreted as storm deposits. Storm deposition is further suggested by beds of hummocky cross-stratified sandstone that are found interbedded with shales of the NTZ (Schieber 1987 b). Identical sandstones are also found interbedded with pyritic striped shales. Thus, the available evidence indicates that the pyritic striped shales were deposited between fair weather and storm wave base (Schieber 1986 b, 1987 b). In pyritic striped shales of the Little Belt Mountains the number of sandstone interbeds increases downsection, and the basal portion of the section consists entirely of sandstone (Fig. 6). Conglomerate beds that contain lithified carbonate clasts, soft deformed shale clasts, and sand are also interbedded with these shales (Fig. 6). The sandstones show erosion surfaces, erosive channels, hummocky cross-stratification, planar cross-bedding, and variable amounts of carbonate, sandstone, siltstone, and shale pebbles. These features indicate episodic strong currents, high energy events (such as storms), and shallow water

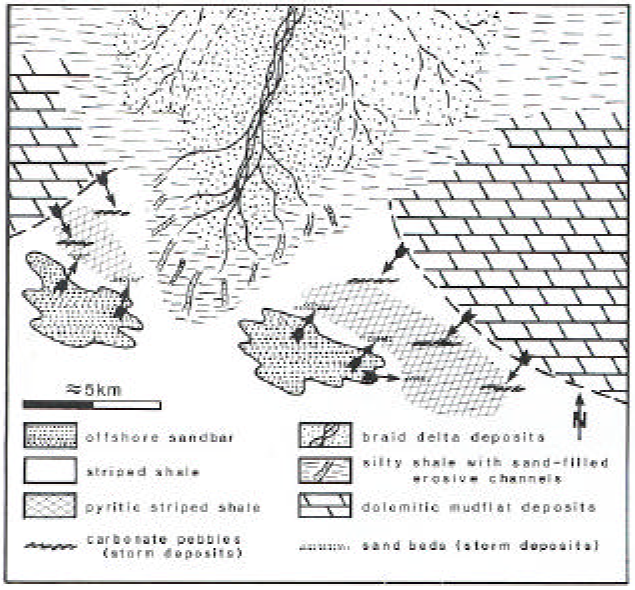


Fig. 7. Proposed depositional setting for accumulation of pyritic striped shales in the southern Little Belt Mountains. Pyritic striped shales accumulated in coastal embayments between carbonate mudflats and braid deltas (McPherson et al. 1987) that were partially enclosed by offshore sandbars. Southward directed lobe of deltaic silty shales led to formation of an eastern and western pyritic shale horizon. Arrows indicate storm-transport of carbonate pebbles (from dolomitic mudflats) and sand (from offshore sandbars) into nearshore lagoons. Silt/mud couplets in pyritic shale were probably caused by weaker storms (Schieber 1986 b, 1987 b)

conditions. The sandstones at the base of the section (Fig. 6) can be traced for about 2.5 km in east-west direction, and may extend for up to 5 km in intermittent exposures. In drill cores the boundary between pyritic shales and basal sandstones (Fig. 6) moves upwards in the stratigraphy (relative to overlying carbonate horizons) as one goes from north to south. Thus, pyritic shales were the northern lateral equivalents of the basal sandstones during deposition. The proposed depositional setting of pyritic shales in the Little Belt Mountains is shown in Figure 7, a synthesis of the author's investigations of stratigraphy and sedimentology of the NTZ in that area (Schieber 1985).

High energy conditions, as indicated by sedimentary structures in the interbedded sandstones, suggest that pyritic striped shales were deposited in shallow, agitated water. Under modern conditions it is unlikely that highly pyritic shales would form in a shallow, agitated, and aerated setting. However, the apparent incompatibility between an aerated water column and strongly reducing pyritic sediments is removed in the case of a sediment surface that is covered with microbial mats. Microbial mats act as an ecological membrane that causes environmental parameters, such as H_2S concentration and dissolved OZ, to undergo abrupt changes at the interface (Bauld 1981). Most living microbial mats consist of a cohesive surface layer (a few mm thick) of cyanobacterial filaments (blue-green algae), underlain by decaying older laminations (favor and Castenholz 1981; Bauld 1981, 1984). Above the mat the water is usually aerated, but directly below it the decomposition of organic matter leads to production of abundant H_2S (Bauld et al. 1980). Benthic microbial maps were probably widespread in shallow water Mid-Proterozoic environments because of the absence of grazing metazoans, and may have allowed the formation of highly pyritic shales in shallow, aerated environments.

Scenario for formation of pyritic striped shales

Modern microbial mats have gelatinous sticky surfaces that tend to trap particulate matter that is moved over the mat surface (Gebelein 1969; Golubic 1976; Bauld 1984). If the same is assumed for mats of the Newland Formation, fluvial iron oxyhydroxides, flocculated in nearshore areas, could have been trapped on mat surfaces, become incorporated into H_2S-rich sediment below the mat, and be converted to pyrite. Storm reworking of nearshore sediments would have caused deposition of silt/mud couplets on top of pyritic microbial mats. Repeated interruption of mat growth by storm sedimentation would then lead to formation of pyritic striped shales.

The above scenario can be supported with observations on recent sediments. The author himself observed freshwater springs along the shoreline of northern Taiwan and Oregon that were so rich in dissolved iron that iron oxyhydroxides formed on contact with air. In both cases iron oxyhydroxides were dispersed because of vigorous wave activity. Small freshwater springs with large amounts of dissolved iron were also observed along a water filled construction pit in Texas. Iron oxyhydroxides formed in the spring waters on contact with air. Thin microbial films covered the sediment surface and iron hydroxides were deposited on the microbial layer. Iron oxyhydroxide deposition did not hinder microbial mat growth, and sediment below the mat was black and smelled of H_2S By comparison with studies of recent microbial mats (Bauld 1984; Javor and Castenholz 1980; Gerdes et al. 1985), the black colour was probably due to finely disseminated iron sulfides. Thus, observations of recent environments allow us to speculate that given an environment where sedimentation rates are small enough to allow establishment of microbial mats, and where sufficient iron oxyhydroxide is supplied, microbial mats may well incorporate enough iron to form laminated pyrite beds upon lithification. A lagoonal setting was probably beneficial to the formation of pyritic striped shales because it counteracted scattering of iron oxyhydroxide flocculates by wave and current action.

Significance for other mineral deposits

Quite a number of Australian Mid-Proterozoic Pb-Zn deposits, such as Lady Loretta (Loudon 1975), Hilton (Mathias et al. 1973), Mt. Isa (Bennet 1965), and McArthur River (Lambert 1976), are hosted by extensive pyritic shale horizons. At Mt. Isa the Pb-Zn ore bodies are hosted by approximately 1,000 m of pyritic shales (Bennet 1965; Mathias and Clark 1975) that show the same alternation of pyritic and non-pyritic beds as observed in pyritic shales of the Newland Formation. At McArthur River the ore

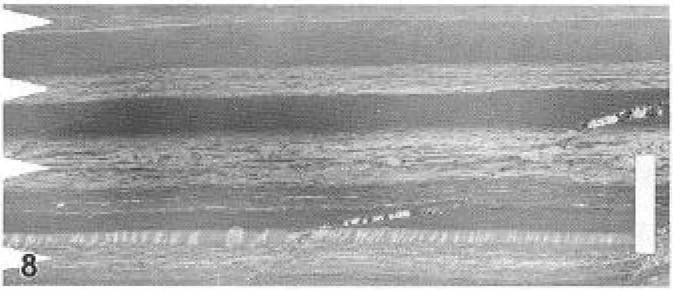


Fig. 8. Specimen of pyritic striped shale from Mt. Isa. Note sharp separation into pyritic (arrows) and non-pyritic beds. Note also the wavy-crinkly internal laminations of pyritic beds. The light coloured bed above the lowermost pyrite bed is a tuff layer, also described as cross-fracture beds in the Mt. Isa literature. Scale bar is 10 mm long

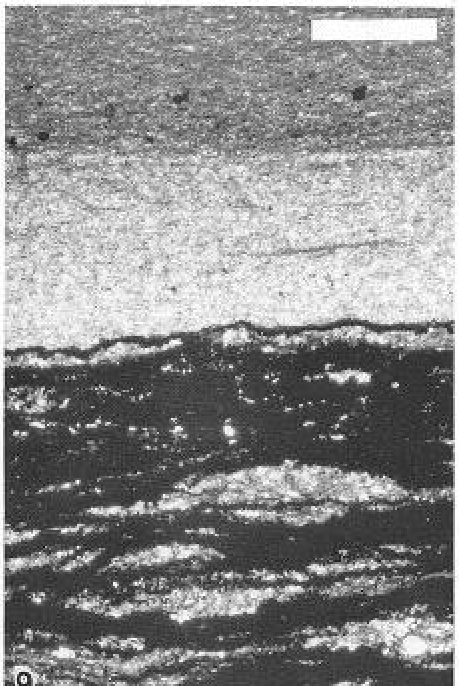


Fig. 9. Photomicrograph (transmitted light) of pyritic striped shale from Mt, Isa. Black laminae in lower half of photo are pyritic laminae, separated by wavy-lenticular beds of clay, quartz-silt and dolomite. Laminated pyrite bed is overlain by graded silt/mud couplet. Scale bar is 0.5 mm long

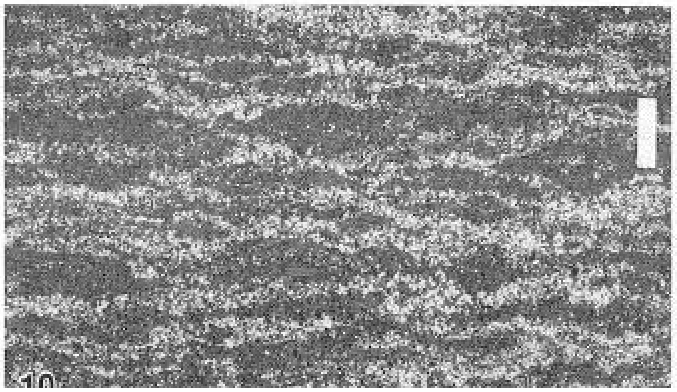


Fig. 10. Photomicrograph (reflected light) of laminated pyrite bed from Mt. Isa. Note wavy-crinkly pyrite laminae. Pyrite laminae are separated by wavy-lenticular laminae of clay, quartz-silt, and dolomite. Compare texture to Fig. 3 (Newland Formation). Scale bar is 0.2 mm long

bodies are hosted by the 500 m thick HYC pyritic shale unit, which is also characterized by alternating pyritic and non-pyritic beds (Cotton 1965; Murray 1975; Lambert 1976; Williams 1978 a, b). Figures 8, 9 and 10 illustrate the great similarity of pyritic shales from Mt. Isa with those from the Newland Formation. This textural likeness suggests that pyritic striped shales that host the above mentioned Australian Pb-Zn deposits might similarly be mineralized microbial mat deposits. Possible involvement of microbes in stratiform sulfide mineralization at Mt. Isa and McArthur River has also been indicated by studies of Love and Zimmerman (1961), Hamilton and Muir (1974), and Oehler and Logan (1977).

The absence of significant Pb-Zn mineralization in pyritic shales from the Newland Formation may indicate that the coincidence between pyritic shales and Pb-Zn orebodies in the Australian examples is fortuitous. According to observations by experienced exploration geologists (Ilmars Gemuts, pers. comm.), there are quite a number of pyritic shale horizons in the Australian Proterozoic that were drilled in search of Pb-Zn orebodies, but were found barren. Unfortunately, in contrast to the mineralized examples, descriptions of barren pyritic shale horizons rarely make it into the published geologic literature. However, unpublished observations indicate that Pb-Zn mineralized pyritic shale horizons are the exception rather than the norm.

The McArthur River deposit has been studied in considerable detail, and several studies have indicated that pyrite and Pb-Zn mineralization were brought about by different processes. Sulfur isotope studies led Smith and Croxford (1973) to the conclusion that Fe (in pyrite) was introduced separately from Pb and Zn. Their notion was seconded by Gulson (1975), who on the basis of Pb-isotope studies stated that distinct Fe and Pb-Zn solutions must have been derived from different sources and must have migrated separately to the site of mineralization. More recent studies of the McArthur River deposit by Williams (1978 a, b) also indicate that laminated pyrite that formed early in diagenesis is not genetically related to Pb-Zn mineralization.

Of course, if pyritic shales and Pb-Zn mineralization are not related, than there should also exist Pb-Zn deposits that are not connected to occurrences of pyritic shales. The Dugald River deposit in the Proterozoic of Queensland, Australia (Whitcher 1975) could be one such example, because there the Zn-Pb mineralization is not hosted by pyritic shales.

Several authors (Lambert 1976, 1983; Williams 1978 a. b) have argued that in the case of the Australian deposits the pyritic shales formed adjacent to basin marginal growth faults, which were the channel ways for iron rich exhalative fluids. As an alternative, in the model proposed here, iron is brought in by rivers and deposited in nearshore lagoons. In general, emmanation of iron rich fluids from basin marginal faults can not be excluded as an iron source for pyritic shale horizons in Proterozoic basins. However, as pointed out earlier, an intrabasinal iron source is unlikely in the case of the Newland Formation. Thus, even though basin marginal faults can in principle supply iron-rich fluids to form pyritic shale horizons, they probably did not do so in the case of the Newland Formation.

With regard to the general case of pyritic shale horizons, one will have to consider that in both scenarios of iron input, riverine as well as by basin marginal fault, resulting pyritic shales are deposited along the basin margins. Thus, there is a good chance that in a number of cases basin marginal faults and pyritic shales do coincide even though there may be no causal relationship between fault and mineralization. Unless metal supply through the supposed feeder fault can be demonstrated, be it by direct evidence of mineralization or by geochemical fingerprinting, riverine iron supply to basin marginal pyritic shale horizons must be considered a viable alternative.

Conclusion

Pyritic striped shales in the Newland Formation accumulated in nearshore lagoons and are mineralized microbial mat deposits with intercalated storm deposits. Colloidal iron was supplied to these lagoons by rivers. The best potential for pyritic shale formation via riverine iron input appears to be immediately after regressions, because then the best conditions for iron mobilization in the hinterland exist. Pyritic shales that host several major Pb-Zn deposits in Australia appear very similar to those of the Newland Formation, a suggestion that they might be of comparable origin. Pyritic striped shales of the Newland Formation contain no conspicuous Pb-Zn mineralization. The existence of quite a number of similarly barren pyritic shales in the Proterozoic of Australia suggests that occurrences of barren pyritic shales are far more abundant than those that contain Pb-Zn ore bodies. That consideration in turn suggests that there is no genetic linkage between the formation of Proterozoic pyritic shales and the Pb-Zn deposits that they contain in some instances. The latter conclusion is supported by the results of several studies of the McArthur River deposit (Smith and Croxford 1973; Gulson 1975; Williams 1978 a, b).

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