A sulfur isotope study of pyrite genesis: The Mid-Proterozoic Newland Formation, Belt Supergroup, Montana

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Abstract-Different generations *of* sedimentary pyrite from the Mid-Proterozoic Newland Formation, USA, have been analysed for their sulfur isotopic compositions. The results indicate bacterial sulfate reduction as the pyrite forming process. The V'S values for early diagenetic pyrite, around *-14%o,* are in contrast to dominantly more positive values for many other Middle Proterozoic units. A progressive reduction *of* sulfate availability during diagenesis can be recognized by an increase in 34S content (Rayleigh Distillation) as well as through detailed petrographic observations. Contemporaneous seawater had a sulfur isotopic ratio between *+14* and *+18%o* as measured from sedimentary barite within the unit.

INTRODUCTION

THE MID-PROTEROZOIC Newland Formation (Belt Supergroup) contains horizons *of* pyritic shale. These and surrounding sediments have been investigated in detail by SCHIEBER *(1985)* and a continuous spectrum *of* pyrite types from early diagenetic fine crystalline to late diagenetic eudedral and concretionary pyrite has been distinguished.

In modern environments, sedimentary pyrite forms as a result *of* microbial sulfate reduction under specific environmental conditions (e.g., BERNER, *1970, 1984;* TRUDINGER et al., *1985)* and can be characterized by its sulfur isotopic composition (e.g., GOLDHABER and KAPLAN, *1974).* For ancient sedimentary sulfide accumulations recognition *of* microbially mediated sulfate reduction may provide clues to environmental conditions during deposition with regard to oceanic and atmospheric chemistry. Sulfur isotope ratios *of* sedimentary sulfides have been shown to yield valuable information regarding the paleoenvironmental conditions during their formation (e.g., SCHWARCZ and BURNIE, *1972;* CHAMBERS, *1982).* Determination *of* sulfur isotope ratios in ancient sulfate deposits has led to recognition *of* secular variations in 834S composition *of* ancient oceans (NIELSEN, *1965;* HOLSER and KAPLAN, *1966;* CLAYPOOL et al., *1980).* Such variations result from differences in net burial rates *of* sulfides and sulfates in sediments. Knowledge *of* secular variations *of* 8345 through geologic time is important for our understanding *of* atmospheric and oceanic evolution (HOLLAND, *1973, 1984).* However, whereas Phanerozoic sulfur isotope variations *of* seawater have been documented fairly well (NIELSEN, *1965;* HOLSER and KAPLAN, *1966;* VEIZER et al., *1980;* CLAYPOOL et al., *1980),* comparatively few data points are available for the Precambrian.

This study presents the results *of* a sulfur isotope investigation *of* pyrite and barite from the Newland Formation, and provides interpretations regarding the local paleoenvironment as well as the importance *of* these data in context *of* the Proterozoic sulfur cycle.

Geologic setting

The Newland Formation was deposited in the Helena embayment, an eastern extension of the Mid-Proterozoic Belt basin. The Belt Supergroup as a whole was deposited between 1450 and 850 Ma ago (HARRISON, 1972), and the Newland Formation accumulated early in basin history. OBRADOVICH and PETERMAN (1968) defined a 1325 Ma Rb-Sr isochron in Belt rocks (including the Newland Formation) of the Big Belt and Little Belt Mountains. Because the whole Lower Beltian sequence shows the 1325 Ma age, it is likely that this age represents the approximate time of diagenetic smectite-illite transformation of the sequence and represents a minimum age for the Newland Formation. The age of the Newland Formation itself should lie between 1400 and 1325 Ma (SCHIEBER, 1985).

Underlain by a transgressive orthoquartzite-shale sequence, the Neihart Quartzite (WEED, 1899) and Chamberlain Shale (WALCOTT, 1899), the Newland Formation comprises most of the outcropping Lower Beltian rocks in the Helena embayment. In the southern Little Belt Mountains and the Big 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-bearing unit (otherwise consisting of shales) is found in the transition between the upper and lower member and was informally named the Newland Transition Zone (NTZ) by SCHIEBER (1985). Basin evolution and stratigraphy of the Helena embayment are summarized in SCHIEBER (1986a). The upper portion of the NTZ in the southern Little Belt Mountains contains extensive occurrences of pyritic shales (Fig. 1) that were the subject of detailed studies by SCHIEBER (1985, 1986b, 1987a, 1989a).

Samples that were analysed for this study come mainly from the NTZ, but a few samples from the lower portion of the upper member of the Newland Formation were analysed as well (Fig. 2).

Pyrite types in the Newland Formation

Pyrite in the Newland Formation has been described in detail by SCHIEBER (1985). Most commonly observed is fine crystalline pyrite (1-10 microns), which may be irregularly scattered throughout the rock, form framboids (0.02-0.25 mm) or aggregate into thin lenticular-wavy laminae. The latter form laminated pyrite beds (may contain up to 50% pyrite by volume) which alternate with shale beds with little or no pyrite and produce a characteristic striped appearance (Fig. 3). Similar textural and sedimentary features from carbonaceous silty shale beds in the Newland Formation have been interpreted as probably resembling microbial mat deposits by SCHIEBER (1986b). Textural comparison suggests that the laminated pyrite beds could similarly be pyrite-mineralized microbial mats (SCHIEBER, 1989a). Accumulation of extensive deposits of pyritic striped shale in the upper portion of the NTZ has been related to riverine iron input along the basin margin

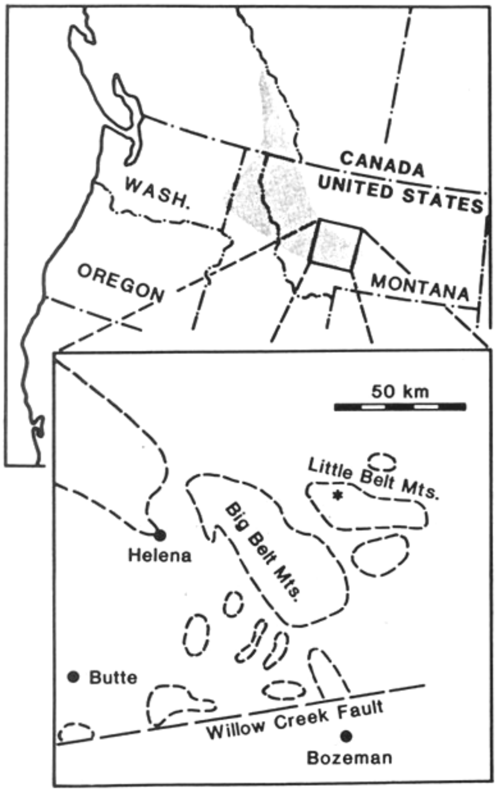

FIG. 1. Location of study area. Stipple pattern indicates present day outline of Belt Supergroup exposures. The enlarged portion of the map shows the Helena embayment, dashed outlines indicate outcrop areas of Belt rocks. Asterisk in Little Belt Mountains indicates occurrence of pyritic shales that were investigated for this study.

basin margin (SCHIEBER, 1987a). Textural features such as soft sediment deformation of pyrite laminae and framboids and rip-up clasts of laminated pyrite suggest that the fine crystalline pyrite in the striped shales formed postdepositionally during early diagenesis (SCHIEBER, 1985).

Etching of polished thin sections with HN03 shows that fine crystalline pyrite as described above may be overgrown to various degrees by sometimes several later diagenetic pyrite generations. Pyrite that formed during a second stage of diagenesis has a massive to fibrous appearance and is found as overgrowths and encrustations on early diagenetic pyrite (Fig. 4). In places these encrustations can attain considerable thickness (up to 5 mm), and lead to the formation of pyrite concretions (Fig. 5). Differential compaction around pyrite concretions indicates growth before compaction of the shales was completed. Pyrite that formed during late stages of diagenesis occurs as euhedral cubic crystals (0.1-2 mm), overgrowing earlier pyrite generations (Fig. 4), or forming single crystals along bedding planes. These pyrite crystals are essentially post-compactional because they cut across shale laminae and no differential compaction of the surrounding shale is observed.

In this study pyrite from laminated pyrite beds of pyritic striped shale, pyrite from carbonaceous striped shale, and concretionary pyrite was analysed for sulfur isotopes.

Barite in pyritic shales of the Newland Formation

In places, the pyritic shale horizons of the NTZ contain variable amounts of barite. It is found within laminated pyrite beds as well as in the non-pyritic interlayers of pyritic striped shales. The barite occurs as scattered crystals (some mm long and up to 1 mm wide), as clusters of radiating crystals (5-15 mm across), as accumulations of small nodules, and as a framework of unorientated barite crystals within sediment layers. Singular barite crystals are mainly bladed shaped, and in a number of cases serrated crystal terminations were observed.

The radiating clusters of barite strongly resemble gypsum rosettes (or gypsum daisies) that are found in recent intertidal sediments (MASSON, 1955). Crystals with serrated terminations and the small barite nodules resemble anhydrite as described from other evaporite sequences (SHEARMAN arid FILLER, 1969). In a few cases where a crystal was cut perpendicular to its long axis, measurement of interfacial angles indicates that the barite replaced preexisting gypsum.

Thus textural observations indicate that the barite replaced preexisting calcium sulfates. Sediment layers and laminations that are displaced by barite nodules, as well as barite crystals that cut across sediment layers and laminations, suggest that these precursor sulfates formed after deposition of the host sediments. Differential compaction around barite crystals and nodules indicates that the precursor sulfates formed while the sediment was still soft.

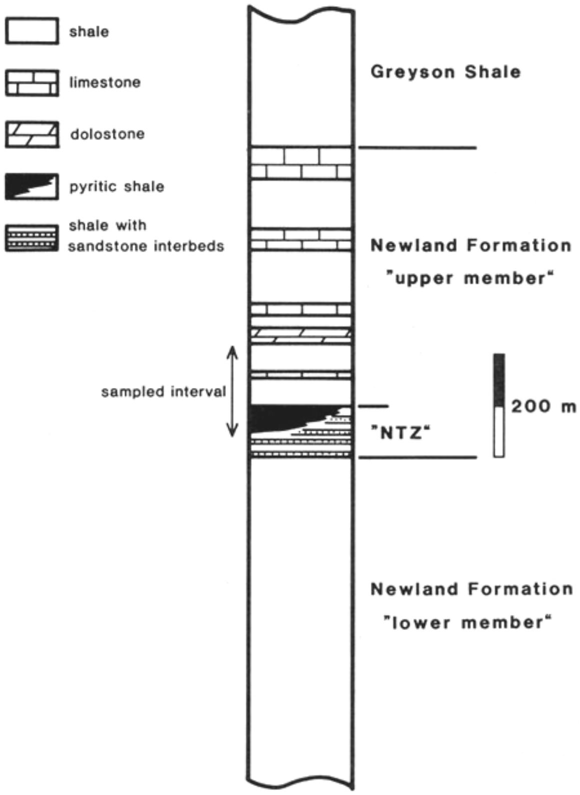

FIG. 2. Stratigraphic column of the Newland Formation showing the sampled interval.

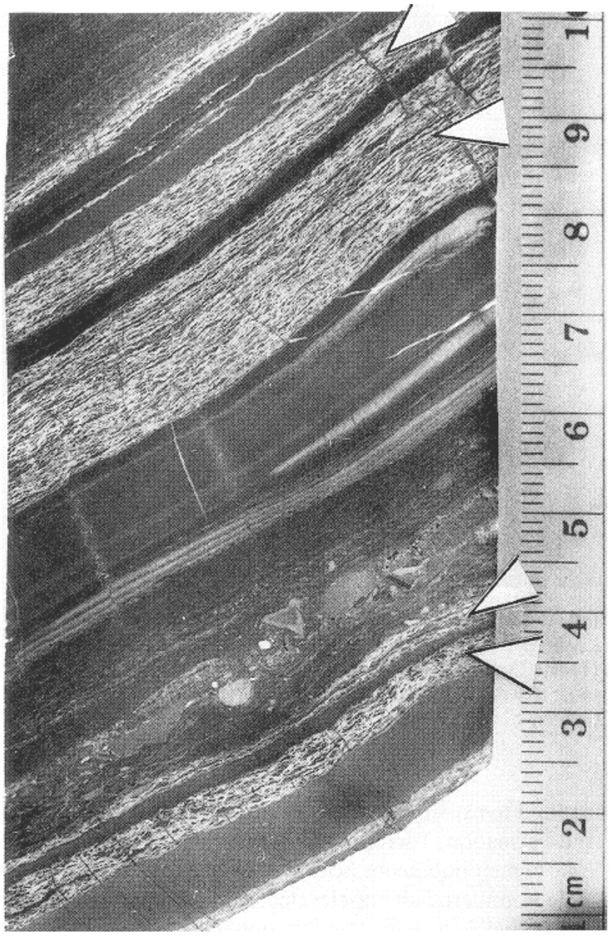

Fig.3. Polished slab of pyretic striped shale. Arrows point out laminated pyrite beds . Note wavy-crinkly laminae within pyrite beds. Scale has mm divisions.

METHODS

Ideally, a clean mechanical separation of all individual diagenetic pyrite generations and their subsequent isotope analyses would have been desirable. However, pyrite occurrences as well as available technical facilities prohibited this kind of initial preparation. A different method was applied in order to achieve the desired resolution.

Samples were split for petrographic and geochemical analyses. Polished thin sections(subsequently also etched with HNO_3) were studied petrographically and different pyrite generations were identified. For all samples the relative proportions of early diagenetic(fine crystalline) and later diagenetic pyrite(overgrowths and cubes) were visually estimated using conventional estimation charts. This enabled us to define not only the two “endmembers” (i.e. samples containing only early diagenetic or only latest diagenetic pyrite, respectively), but also to distinguish a suite of samples with increasing rates of overgrowth from various diagenetic stages.

These petrographically well characterized were subjected to sulphur isotopic analyses. For this, rock powder was generated from the sample splits. The pyrite sulphur was liberated as H_2S gas with Chromic Chloride solution (CANFIELD et. al., 1986), then trapped as ZnS and converted to Ag_2S with 0.1 M $AgNO_3$ solution. Barite sulphur was reduced to H_2S with “Thode-solution” (THODE et.al., 1961) and also trapped as ZnS and later converted to Ag_2S. The silver sulphide was mixed with CuO and combusted on-line at 850 ° C to produce SO_2(FRITZ et al., 1974). The mass-spectrometric analyses were performed on a Nuclide Model 6-60. Sulphur isotope ratios are reported in the standard delta notation as per mil differences against the Canyon the Canyon Diabolo Troilite standard(CDT). Reproducibility was ± 0.5% as determined from duplicate measurements.

RESULTS AND DISCUSSIONS

The analytical results for all samples are presented in Table 1 together with the estimated percentage of early diagenetic pyrite within the samples. The results will be discussed with regard to genesis and timing of pyrite formation, in comparison to other sedimentary sulphides from the Belt Supergroup, to other Mid-Proterozoic sequences, and in the context of the Proterozoic sulphur isotope cycle.

The sulphur isotope values show a broad range from –14 to +18% versus CDT. Distinctly negative values for samples with high content of early diagenetic pyrite(as inferred from petrographic studies) clearly indicates its formation via bacterial reduction of contemporaneous seawater. Its sulphur isotopic composition lies between +14 and +18%(Table 1) as determined during this study from barite within the Newland Formation. Petrographic evidence suggests the barite to be a replacement of early diagenetic calcium sulphate (SCHIEBER, 1985). Values obtained here are close to other isotope data for stratigraphically slightly younger barite from the Belt Supergroup(Spokane Formation, 1250 Ma) between +15 and +20%(Rye et.al., 1983) and are most likely representative of Mid-Proterozoic seawater.

A crossplot of sulphur isotope values versus percentage of early diagenetic pyrite (Fig.6) indicates a clear relation between these two parameters. The δ^{34}S value for early diagenetic pyrite appears to be approximately –14%. Increasingly heavier sulphur isotope values accompany a decrease in percentage of early diagenetic pyrite. The isotopic difference between both “end-members”(as distinguished petrographically) is quite remarkable(around 32%) with values of approximately +18% for “later diagenetic” concretionary pyrite (percentage early diagenetic pyrite approaches zero). Independent additional analyses of pyrite from the Newland Formation yielded δ^{34} S values as heavy as +32% (H>STRAUSS, unpubl. data)

The evolution towards heavier sulphur isotope ratios for sulphides within a given sediment suggests the “classical” interpretation of an evolving diagenetic system where later generations of iron sulphides are being formed in a closed system with respect to sulphate availability. Within such a scenario the amount of sulphate that is being utilized by sulphate reducing bacteria constantly decreases and its isotopic composition becomes progressively heavier (Rayleigh Distillation) as the resulting H_2S is being immobilized as iron sulphide. This development results in isotopically heavy sulphides(JORGENSEN,1979) like those found in this study.

The distribution of δ^{34} S values obtained for the Newland Formation is quite similar to numerous studies of recent sediments displaying an essentially continuous spectrum from open to closed system patterns indicating δ^{34}S enrichment during progressive diagenesis (for a comparative treatment of these data see CHAMBERS, 1982). In an attempt to achieve a sulphur isotopic mass balance in modern sentiments CHANTON et.al., (1987) recently focused on the problem of open versus closed system with respect to sulphate availability. In particular the importance of sulphate supply via diffusion has previously been underestimated. Because of its isotopic difference in comparison

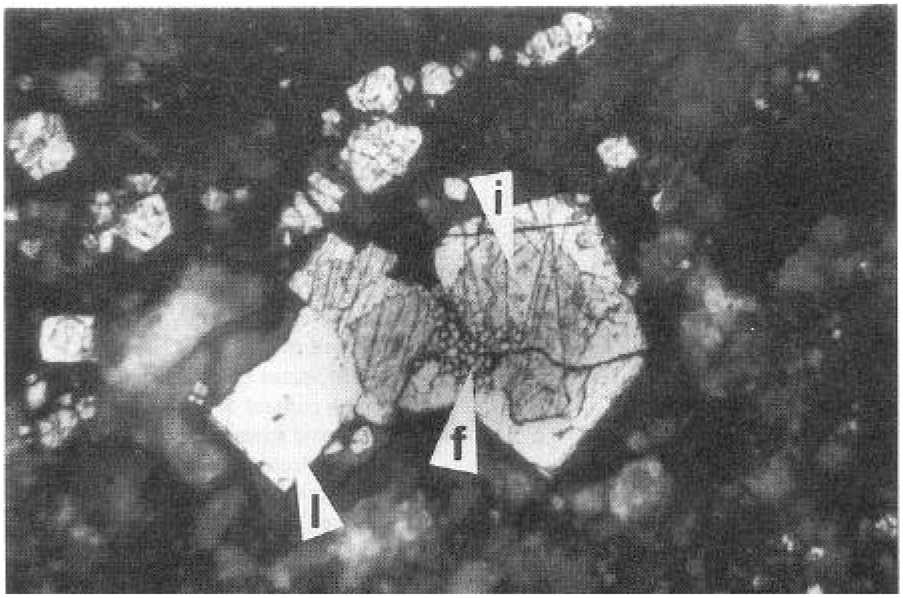

FIG. 4. Photomicrograph of pyrite framboid that is cemented and overgrown by intermediate and late stage diagenetic pyrite. Pyrite framboid consists of a cluster of small early diagenetic pyrite crystals and is pointed out by arrow (f). Intermediate stage diagenetic pyrite is massive, has been etched by HNO3, and is pointed out by arrow (i). Late stage diagenetic pyrite was not attacked by HNO3, forms euhedral crystal faces at the outside of the pyrite overgrowth rim, and is pointed out by arrow (1). The photomicrograph is 0.29 mm wide.

to the ambient seawater (CHANTON et al., 1987), it bears significantly on the isotopic signature of the buried iron sulfides, often causing a greater variety.

Alternatively to this constant evolution of a single sulfur source utilized to form all pyrites present, the mixing between two isotopically different sources should be addressed. In particular the addition of isotopically heavy sulfur would be be required to explain the δ^{34}S signature observed for the Newland Formation. Thereby, an isotopically heavy sulfur source (e.g., contemporaneous seawater) would be reduced most likely nonmicrobially at elevated temperatures (80-120°C) with negligible isotopic fractionation (ORR, 1974). Resulting pyrite would display heavy isotope values similar to its parental sulfate. Such a process could account for the isotopic signature of the "later diagenetic" pyrites analyzed

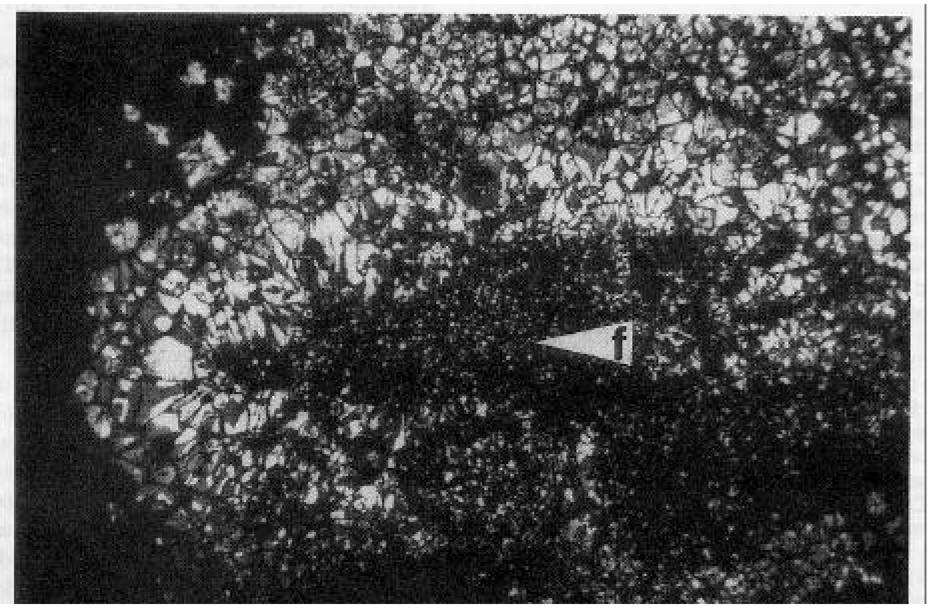

FIG. 5. Photomicrograph of intermediate stage pyrite (coarse crystalline) encrusting an early diagenetic accumulation of fine crystalline pyrite. Early diagenetic pyrite is pointed out by arrow (f). The photomicrograph is 0.29 mm wide.

Table 1. Sulfur isotope results and petrographic characteristics for sulfides

Pyrite Type	Sample No.	$ 34S	Pyrite A
Concretionary	10/20/80-19	+18.1	3
	11/3/80-48	+15.1	3
	11/3/80-13	+ 9.5	7
Laminated	12/01/80-34A	+ 1.6	30
	12/01/80-28	+ 5.2	60
	11/17/80-16A	+ 0.3	70
	11/17/80-25	- 0.8	70
	7/17/82-2	- 5.0	70
	11/17/8o-3oA	- 3.0	80
	11/1o/8o-82A	- 4.1	80
	11/10/80-25A	- 5.3	80
	11/10/80-74A	- 7.1	80
	11/22/80-77A	- 9.7	85
	11/10/80-89	-10.4	85
	11/1o/ao-8A	-10.6	90
	11/17/80-7A	-10.6	95
Striped Shale	11/22/80-77B	- 5.2	85
	11/17/8o-7B	-14.0	95
Barite	8/30/81-12	+13.6	
	6/28/81_4	+14.4	
	6/28/81_1	+18.3	

Pyrite A (%) represents the relative amount of early diagenetic pyrite

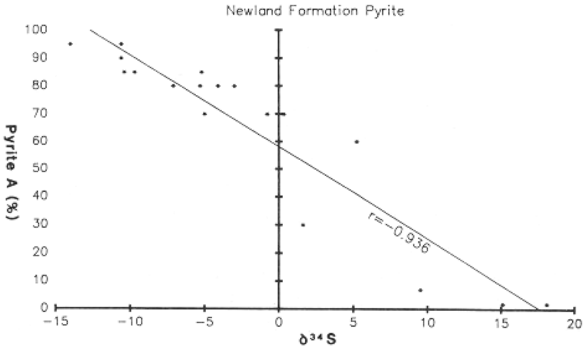

FIG. 6. Plot of δ values in Newland pyrites versus relative amounts of early diagenetic pyrite (pyrite A). Correlation coefficient (r) for regression line was calculated as Pearson's product-moment coefficient.

in this study. Similar results have been reported for some Red Sea sulfides (KAPLAN et al., 1969) where the sulfur source was suggested to be evaporitic sulfate and its reaction with organic compounds to produce HZS. The latter process has also been suggested by ORR (1974) and KROUSE et al. (1988) for thermal maturation of hydrocarbon-rich strata with sulfates present. SASSANO and SCHRIJVER (1989) clearly show the formation of late diagenetic ("hydrothermal") framboidal pyrite.

A number of other sedimentary sulfide occurrences have been described from different stratigraphic levels within the Belt Supergroup. Several of these deposits have been investigated for their sulfur isotopic composition (CAMPBELL et al., 1978; MORTON et al., 1974; RYE et al., 1983; LANCE and SHERRY, 1987; LANCE et al., 1987).

The large Sullivan orebody, British Columbia, hosted in metasediments of the Aldridge Formation (1450-1700 Ma) has been studied by CAMPBELL et al. (1978) and its sulfur isotopic composition ranges from -10.4 to +4.7%0. The sulfur source has been interpreted to be seawater sulfate. The isotopic variation for sulfide sulfur has been suggested to reflect changing basin conditions (e.g., chemistry, temperature) which would have affected the rates of HZS supply through chemical and/or bacterial sulfate reduction.

The Middle Belt copper sulfides have been interpreted as syngenetic (GARLICK, 1988) to diagenetic (LANCE and SHERRY, 1987). Some deposits show an additional phase of clearly later, vein-type sulfides with an independent sulfur source (LANCE and SHERRY, 1987). The syngenetic fine grained sulfides are thought to have formed in the overlying, anoxic water column (GARLICK, 1988), whereas two slightly different diagenetic models have been proposed to explain the observed mineral assemblages (RYE et al., 1983). Metalbearing, possibly oxidized fluids entering permeable units would form copper sulfides either by direct reaction with biogenic HZS or by replacement of earlier pyrite under preservation of the initial (biogenic) isotopic composition. The sulfur isotope values for the Belt copper sulfides are shown in Fig. 7. The broad range is consistent with the interpretation of the initially biogenic signature derived from bacterial reduction of seawater sulfate. Subsequent alteration during later replacement and partial oxidation of earlier pyrite and/or a possible addition of a different sulfur source account for the variation. The isotope ratios obtained for the slightly older Newland Formation are fairly similar to these copper sulfide values.

The pyritic shales within the Newland Formation have been compared to the somewhat older Australian Mid-Proterozoic sediments

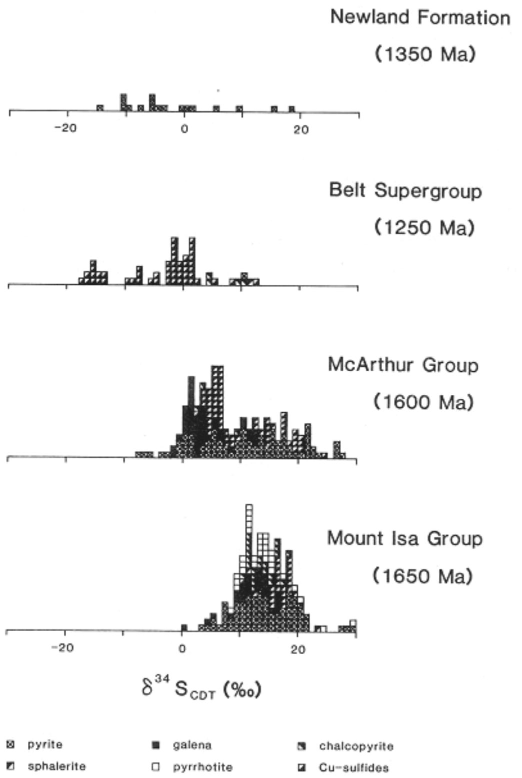

FIG. 7. Sulfur isotopic compositions for some Mid-Proterozoic sedimentary sulfides. Squares represent individual analyses.

which host extensive mineral deposits (ZnS, PbS, FeS, FeS_2, $CuFeS_c$) at McArthur (1600 Ma) and Mount Isa (1650 Ma) leading to significant exploration activities during the last few years. SCHIEBER (1985) addresses the geological, textural, and genetic relationships between these settings with regard to the likeliness of a similar ore deposit within this part of the Belt Supergroup.

Isotopically, the Australian deposits are quite different compared to the results obtained during this study. The McArthur and Mount Isa deposits and sedimentary sulfides related to the particular basins display a range of isotope values which are relatively heavy (McArthur: -8 to +28%o, mean value at +7.95 ± 8.54%o; Mount Isa: 0 to +30%o, mean value at +14.24 ± 4.61%o) (Fig. 7). These results have been attributed to bacterial sulfate reduction (SOLOMON, 1965; STANTON and RAFTER, 1966; SMITH and CROXFORD, 1973, 1975; CARR and SMITH, 1977; SMITH et al., 1978 WALKER et al., 1983; MUIR et al., 1985). However, WILLIAMS (1978a, 1978b) and RYE and WILLIAMS (1981) clearly distinguish an early diagenetic pyrite generation (Py,) formed by bacterial sulfate reduction and a second stage of mineral precipitation (Py, PbS, ZnS) deriving from mineralizing fluids.

The striking isotopic difference between pyrite from the Newland Formation and the Australian deposits, although of similar, biogenic origin, may be in part the result of paleoenvironmental differences. The sediments of the McArthur Group for example consist of evaporitic and stromatolitic cherty dolostones, dolomitic siltstones, and shales indicating environments like marginal marine, lacustrine, and fluvial (POWELL et al., 1987).

The Newland Formation on the other hand lacks extensive stromatolitic carbonates of the type observed at McArthur River and contains in contrast a large proportion of fine grained terrigenous clastics. Sedimentologic observations by SCHIEBER (1985, 1986a, 1986b, 1987b, 1987c, 1989b) indicate that the bulk of the Newland Formation was deposited in a shallow epicontinental setting. Terrigenous muds that were deposited in subaqueous portions of the basin were in many places colonized by benthic microbial mats (SCHIEBER, 1986b, 1989b). Examination of storm deposits indicates that the water depth in the central portions of the Helena embayment was probably on the order of tens of meters (SCHIEBER, 1978b). Very shallow water deposits with intraformational conglomerates and mudcracks occur along the northern margin of the Newland Formation outcrop belt. Thus, in comparison with the Australian examples, environmental conditions during Newland deposition were probably somewhat deeper and more open marine. The pyritic striped shales of the Newland Formation have been envisioned as mineralized microbial mats in partially enclosed lagoons along the basin margin (SCHIEBER, 1985, 1987a, 1989a). However, these lagoons were connected to the remainder of the basin and the system must have been open with respect to sulfate as can be inferred from the sulfur isotope values of early diagenetic pyrite.

The question of whether the Belt "sea" was connected to the Proterozoic ocean, or if it was a large restricted inland sea, has occupied researchers since the beginning of this century. Early investigators predominantly preferred a lacustrine interpretation of the Belt basin (WALCOTT, 1914) whereas later on an open marine interpretation became widely accepted (PRICE, 1964; HARRISON, 1972). Recent paleogeographical reconstructions (STEWART, 1976; SEARS and PRICE, 1978; PIPER, 1982) suggested an epicontinental setting for the Belt basin, and have led to a resurrection of the lacustrine interpretation by WINSTON (1986). Even though an epicontinental setting is indicated, the sulfur isotope data presented here indicate that the Belt "sea" was nonetheless connected to the Proterozoic ocean rather than being an isolated inland basin.

In comparison to the sulfur isotope age curve (SCHIDLOWSKI et al., 1983; LAMBERT and DONNELLY, 1989), the dataset presented in this study represents one of the few Mid-Proterozoic units with predominantly negative 83°S values, in particular when considering the early diagenetic values. Table 2 lists the sulfur isotope distributions for middle Proterozoic sedimentary sulfides. The results from the Newland Formation are in marked contrast to many other Mid-Proterozoic units which display much heavier values. As outlined above, one possible reason could be paleoenvironmental differences in between these units. The predominantly negative sulfur isotopic signature for the Newland Formation could be interpreted as a clearly open marine sulfur isotope signal.

Table 2. Sulfur isotopic compositions of Mid-Proterozoic sulfides

Geologic Unit	Age (Ma)	Isotopic Value				
		Mean	Min.	Max.	N	Ref.
Bijaigarh Shale Formation	950	9.34	4.52	19.96	36	1
Central African Copperbelt	1000		-15.30	19.20	374	2
Grenville metasediments	1050	4.68	-16.40	18.80	67	3
Nonesuch Formation	1050	4.48	-15.83	31.26	86	4
Eurelia Beds	1100	-3.23	-16.40	15.80	29	5
Gap Well Formation	1100	20.70	20.20	21.20	2	6
Shicaohe Formation	1150		18.91	27.93		7
Middle Belt Supergroup	1250	-2.47	-17.00	12.50	59	8
Newland Formation	1350	-0.34	-14.00	18.10	18	9
Taizi Formation	1400	24.11				10
Gaoyuzhuang Formation	1450		-13.00	24.00		11
McArthur Group	1600	7.95	-8.00	28.00	181	12
Mount Isa Group	1650	14.24	0.00	30.00	185	13

References: 1: GUHA (1971); 2: DECHOW and JENSEN (1965); 3: BROWN (1973), BUDDINGTON et al. (1969); 4: BURNIE et al. (1972); 5: LAMBERT et al. (1984); 6: VOGT and STUMPFL (1987); 7: QIN et al. (1985); 8: LANGE and SHERRY (1987), LANGE et al. (1987), MORTON et al. (1974), RYE et al. (1983); 9: This study; 10: QIN et al. (1985); 11: QIN et al. (1985); 12: MUIR et al. (1985), RYE and WILLIAMS (1981), SMITH and CROXFORD (1973), SMITH et al. (1978), WALKER et al. (1983); 13: CARR and SMITH (1977), SMITH and CROXFORD (1978), SOLOMON (1965), STANTON and RAFTER (1966).

Many of the other middle and late Proterozoic units analysed display an isotopic pattern that suggests pyrite formation under more restricted conditions as far as sulfate availability is concerned. This sulfur isotope imbalance (lack of 3'S depleted sulfides) presents an enigma which has to be addressed by future detailed geochemical, petrographical, and paleoenvironmental studies. In addition, the general trend towards 34S enriched sulfides during the middle and late Proterozoic might be partially the result of a biased sampling predominantly from mineralized areas as noted by LAMBERT and DONNELLY (1989). It is quite difficult to estimate the effect that hydrothermal emanations which have supplied metal cations like Zn, Pb, or Cu had on the isotopic signature of the original sulfides. Also, the analysis of the total sulfur fraction without distinguishing early versus late diagenetic pyrite could result in heavier values if late diagenetic sulfides are the dominant phase in a given sample.

CONCLUSIONS

Sulfur isotopic compositions presented in this study for early diagenetic pyrite from the Mid-Proterozoic Newland Formation clearly indicate its formation via bacterial reduction of contemporaneous seawater sulfate. The evolution from an open to a closed system with respect to sulfate availability is favored in order to explain the isotopic signature across different diagenetic pyrite generations. However, a mixing with an isotopically different (heavy) sulfur source for late diagenetic pyrite cannot be ruled out.

Compared to many other middle Proterozoic sedimentary sulfides as well as the overall Proterozoic sulfur isotope record and its generally 3'S enriched nature, the early diagenetic pyrite studied during this investigation is characterized by negative values indicating predominantly open system conditions with respect to sulfate. This also bears on recently proposed lacustrine interpretations of the Belt basin.

The good resolution obtained here shows the usefulness and necessity of combined petrographic and isotopic geochemical analyses while studying pyrite genesis and its paleoenvironmental implications in sedimentary basins.

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