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## SMALL SCALE SEDIMENTARY IRON DEPOSITS IN A MID-PROTEROZOIC BASIN: VIABILITY OF IRON SUPPLY BY RIVERS

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### ABSTRACT

The Helena embayment, an eastern extension of the Mid-Proterozoic Belt basin, Montana, U.S.A., contains extensive horizons of pyritic shale along the basin margins. These pyritic shale horizons may contain several hundred million tons of iron in pyrite. The source of the iron is problematic, and it is proposed here that it was introduced into the basin by continental runoff. Pyritic shale units were deposited after major regressions (or pulses of coarse clastic sedimentation), thus suggesting a mode of iron introduction similar to Phanerozoic oolitic ironstones. The sedimentary record of the Beltian sequence indicates semi-arid climate, a hinterland of low relief, and low sedimentation rates. A combination of these parameters with data from recent environments provides physical and chemical constraints on a 'fluvial' model of iron introduction. With such a model the average size of the drainage basin and the amount of introduced iron can be estimated.

Sufficient iron is introduced within the temporal and physical limits that are imposed by data from the sedimentary record and by data on iron transport in recent terrestrial waters, to form the pyritic shale horizons in the Helena embayment.

### ZUSAMMENFASSUNG

Das "Helena embayment", eine östliche Fortsetzung des mittelperozoischen Belt Beckens, Montana, U.S.A., enthält ausgedehnte Horizonte pyritreicher Schiefertone entlang der Beckenränder. Diese pyritreichen Schiefertonehorizonte können einige hundert Millionen Tonnen Eisen in Pyrit enthalten. Die Herkunft des Eisens ist problematisch und es wird hier vorgeschlagen, dass es durch Flusswasser in das Becken eingebracht wurde. Die pyritreichen Schiefertonehorizonte wurden nach grösseren Regressionen (oder nach grobklastischen Sedimentationspulsen) abgelagert. Es ist deshalb naheliegend, dass das Eisen ähnlich wie in phanerozoischen oolithischen Eisenerzen in das Becken befördert wurde. Die Sedimentationsgeschichte des Belt Beckens zeigt ein semi-arides Klima, ein Hinterland mit niedriger Topographie, und niedrige Sedimentationsraten an. Eine Kombination dieser Parameter mit Daten von Rezentbeispielen

liefert physikalische und chemische Rahmenbedingungen eines "Flusswasser"-Modells für die Eiseneinbringung. Mit solch einem Modell kann das durchschnittliche Einzugsgebiet der Flüsse und die Menge des eingebrachten Eisens abgeschätzt werden.

Innerhalb der zeitlichen, chemischen und physikalischen Rahmenbedingungen die von der Sedimentationsgeschichte und von Information über Eisentransport in rezenten terrestrischen Wässern abgeleitet werden können, wird genügend Eisen angeliefert um die pyritreichen Schiefertone des "Helena embayments" zu bilden.

## 1. INTRODUCTION

### 1.1. The Source Problem in Sedimentary Iron-Formations

Precambrian banded iron-formations are the most voluminous iron-rich rocks and are most abundant in the time interval between 2.4 and 1.8 b.y. ago. Individual occurrences of this type of iron formation contain on the order of  $10^{12}$  to  $10^{14}$  tons of iron. Various theories of origin have been proposed to account for these large iron accumulations in sedimentary basins. Iron supply by volcanic emanations (Gole et al., 1981), by rivers (James, 1954; Lepp et al., 1964), and by ocean upwelling (Holland, 1973; Drever, 1974) are the three most popular hypotheses. Quantitative problems with both the volcanic and the river supply model are summarized by Maynard (1983), who suggests that an ocean upwelling model introduces fewer problems than the other two hypotheses.

Phanerozoic oolitic ironstones are of smaller size than Precambrian banded iron-formations. One of the largest oolitic iron formations, the Kerch ironstone, contains between  $10^{10}$  and  $10^{11}$  tons of iron according to Kimberley (1979). There is as yet no generally accepted mechanism for the formation of oolitic ironstone deposits. However, transport of iron by rivers is probably the most popular hypothesis (e.g., Hallam, 1975).

The sedimentary setting and the origin of pyritic shale horizons in the Helena embayment of the Mid-Proterozoic Belt basin was investigated by Schieber (1985) as part of a Ph.D. research project. Individual pyritic shale horizons do not contain more than a few hundred million tons of pyrite iron, and are thus small when compared to banded iron-formations and oolitic ironstones. However, the pyritization of these shales is much too large and extensive to be accounted for by normal processes of sedimentary pyrite formation as described by Berner (1970). Thus, the iron enrichment of these shale horizons requires investigation concerning the source of iron that was added to these sediments.

### 1.2. Geologic Setting of Pyritic Shale Horizons

#### 1.2.1. Stratigraphy

The sediment fill of the Helena embayment, an eastern extension of the Belt basin (Fig.

1), consists predominantly of rocks of the Lower Belt Supergroup (Harrison, 1972). In the south of the embayment the LaHood Formation (McMannis, 1963) is prominent and is exposed in an east-west trending belt along the Willow Creek fault. In the north of the embayment the Newland Formation, which is underlain by Chamberlain Shale and Neihart Quartzite, comprises most of the outcropping Lower Beltian rocks. Figure 2 shows a generalized cross-section of the basin and the relationships between the lithostratigraphic units, based on data from Walcott (1899), Mertie et al. (1951), McMannis (1963), Nelson (1963), Keefer (1972), Boyce (1975), and Schieber (1985). Figure 3 shows generalized stratigraphic columns for the southern Helena embayment (Highland Mountains) and the northern Helena embayment (Little Belt Mountains).



Fig. 1. Location map. Stipple pattern outlines Belt basin. Triangles indicate occurrences of pyritic shale horizons. The upper right triangle also indicates the position of the Little Belt Mountains, whereas the lower left triangle coincides with the location of the Highland Mountains.

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### 1.2.2. Pyritic Shale Horizons

Pyritic shale horizons occur both toward the northern and southern margins of the Helena embayment (Figs. 1 and 2). The pyritic shale horizons in the southern Helena embayment (Highland Mountains) occur above the coarse clastic LaHood Formation, in the transition between LaHood Formation and Greyson Formation (Fig. 3). The pyritic shale horizons in the northern Helena embayment (Little Belt Mountains) are found at the top of the transition zone between the upper and lower member of the Newland Formation (Fig. 3). Pyritic shale horizons are discontinuous in both areas, can be traced laterally for as much as 8 km, reach 60 m thickness, and may cover an area of up to 20 km<sup>2</sup>.

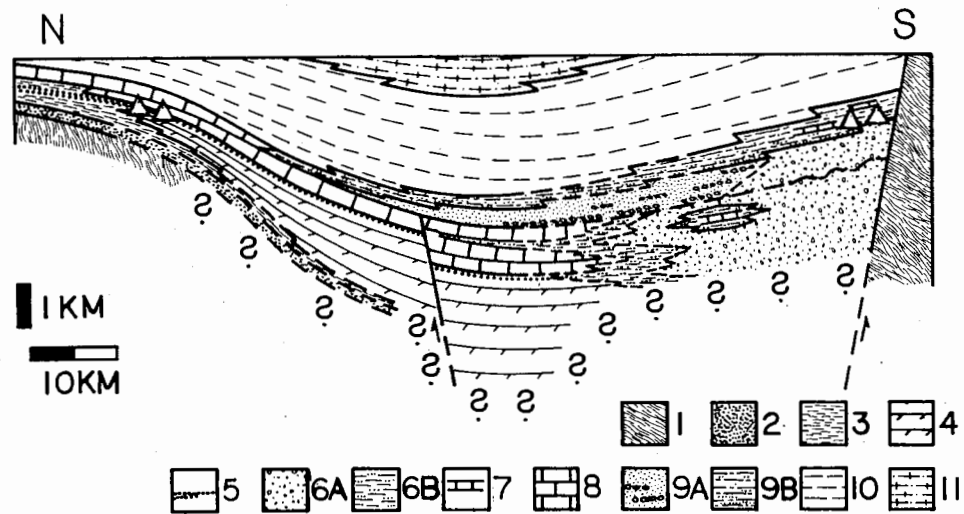


Fig. 2. Generalized cross section of the Helena embayment. Data for the northern part are from the Little Belt Mountains and for the central part from the Big Belt Mountains. The southern part of the cross section is a composite from the various outcrops of the LaHood Formation along the southern embayment margin. Explanation of symbols: 1 = metamorphic basement; 2 = Neihart Quartzite; 3 = Chamberlain Shale; 4 = dolomitic shales of Lower Newland Formation; 5 = sandy transition zone between the Upper and Lower Newland Formation; 6A = arkosic and conglomeratic LaHood Formation; 6B = silty shales with some interbedded arkose, the fine grained facies of the LaHood Formation; 7 = carbonate-rich interval; 8 = interstratified packages of shales and carbonates, the Upper Newland Formation; 9A = arkosic sandstone with some interbedded conglomerate, the Lower Greyson Formation of the Big Belt Mountains (probably lateral equivalent of LaHood Formation); 9B = silty shales of the Lower Greyson Formation; 10 = shales of the Upper Greyson Formation; 11 = red shales and siltstones of the Spokane Formation. Triangles mark occurrences of pyritic shale horizons. Known geologic relationships outlined with solid lines, inferred relationships with dashed lines.

HIGHLAND MOUNTAINS    LITTLE BELT MOUNTAINS

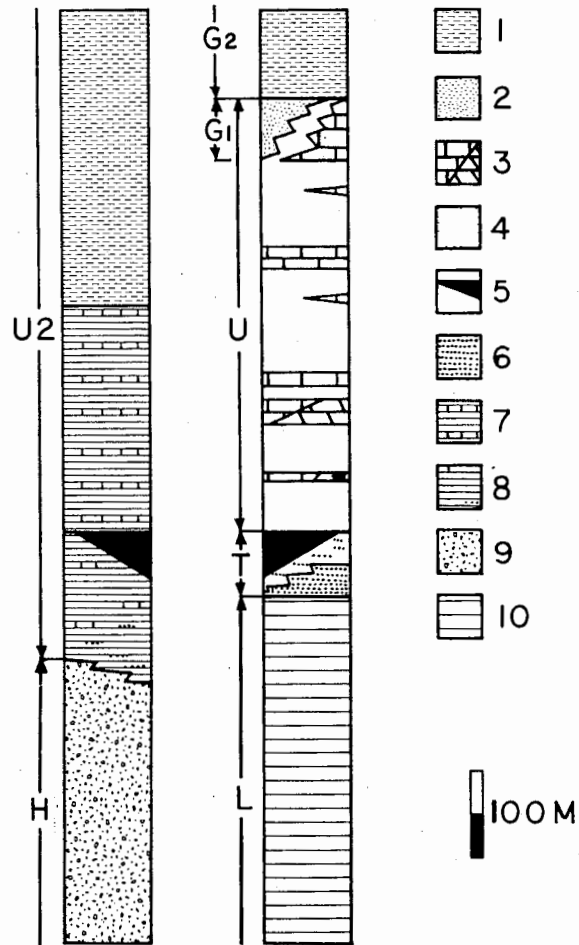
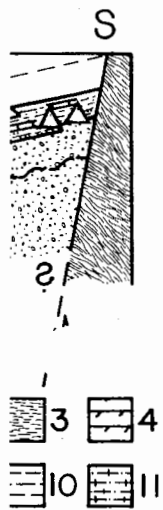


Fig. 3. Partial stratigraphic columns for the Beltian sequence in the Highland and Little Belt Mountains. Explanation of symbols: 1 = shales of the Upper Greyson Formation; 2 = arkosic sandstones of Lower Greyson Formation; 3 = limestones and dolostones of Upper Newland Formation; 4 = banded shales of the transition zone and Upper Newland Formation; 5 = pyritic shale horizons; 6 = sand-rich portions of the transition zone between Upper and Lower Newland Formation; 7 = shale with interbedded limestone beds; 8 = banded shale, may have some interbedded arkose and some limestone beds; 9 = arkose and conglomerate; 10 = dolomitic shale; L = Lower Newland Formation; T = transition zone; U = Upper Newland Formation; G1 = Lower Greyson Formation; G2 = Upper Greyson Formation; H = LaHood Formation; U2 = Unit 2 of McMannis (1963).

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Pyritic shales are banded with alternating pyritic and non-pyritic beds (Fig. 4). Pyritic beds have wavy-crinkly internal laminations (Fig. 5). The banded appearance of the pyritic shales is reminiscent of banded iron-formations, where iron-rich hematitic beds alternate with iron-poor silicic beds.

The pyritic shale horizons are of tabular character and grade laterally into unmineralized shales. Sediment layers within pyritic shale horizons continue into unmineralized surrounding shales. Lateral changes involve a decrease of pyrite content, but no changes in the appearance of the sedimentary facies occur.

For several samples the pyritic and non-pyritic beds were analyzed separately, and the major element composition of samples is given in Table I. The compositional variations of normal, unmineralized shale samples are shown in Figure 6. Illite, quartz, and

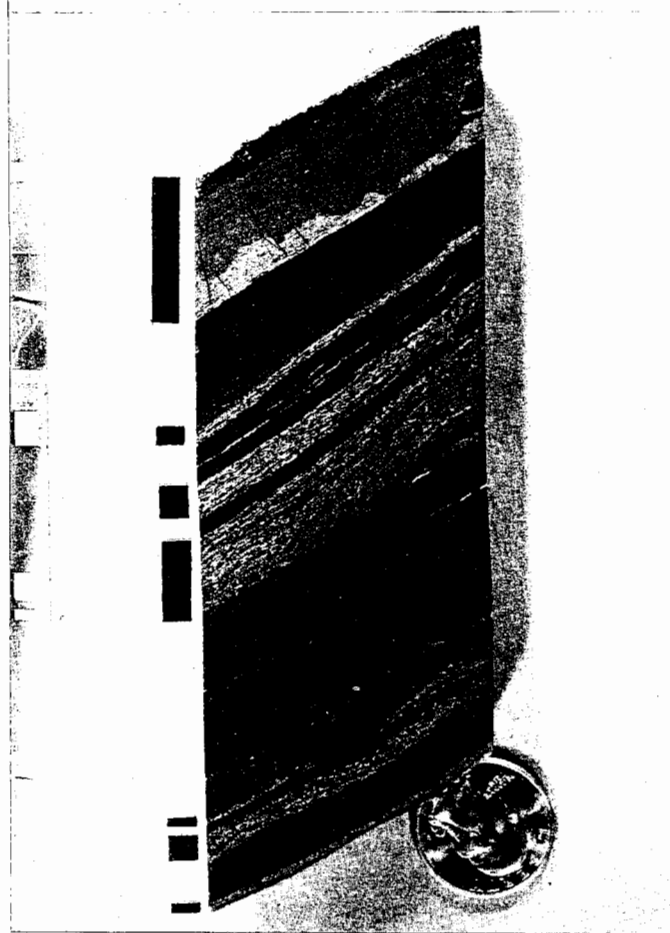


Fig. 4. Drill core specimen of pyritic shale. Coin is 24 mm in diameter. Pyritic beds marked by black bars.

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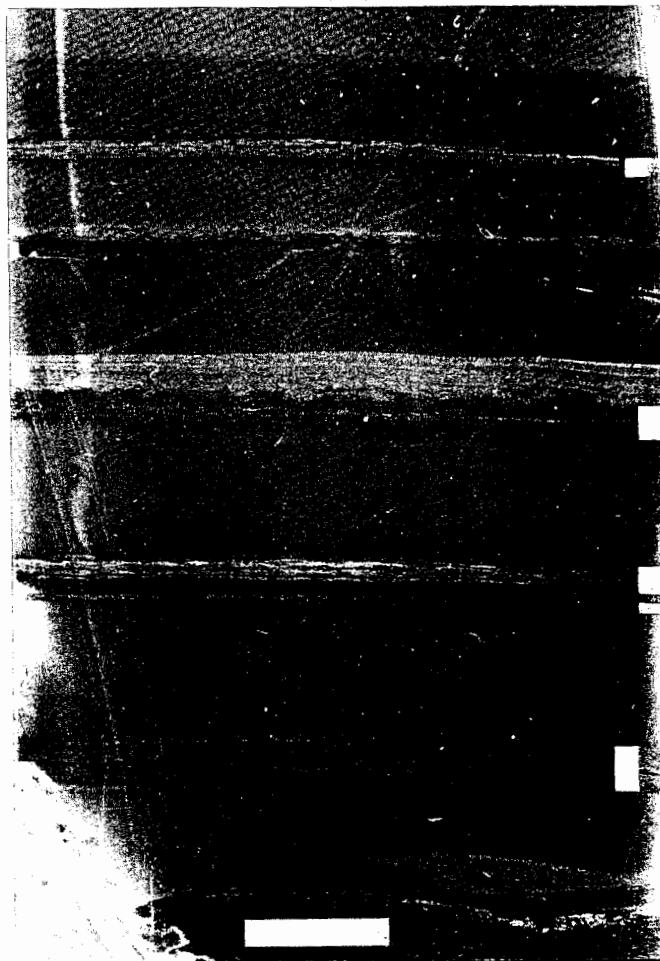


Fig. 5. Photo of polished specimen of pyritic shale (dominated by non-pyritic interlayers). Note wavy-crinkly lamination of pyritic beds. Pyrite beds marked by white bars. Scale bar at bottom is 5 mm long.

dolomite are the main mineral constituents and account for more than 95% of the weight of any given unmineralized shale sample. Mineralized shale samples contain pyrite in addition to illite, quartz, and dolomite.

The shales of the Newland Formation contain on average between 3 and 4%  $\text{Fe}_2\text{O}_3$ , which is a relatively low iron content when compared with the 6.75%  $\text{Fe}_2\text{O}_3$  of the average shale of Turekian and Wedepohl (1961). Four analyses of granitoid basement rocks below the Beltian sequence allow to calculate an average iron content of 3.6%  $\text{Fe}_2\text{O}_3$  for these rocks. Thus, the average iron content of the unmineralized shales reflects the iron content of the source rocks. Even though the pyritic beds contain ten

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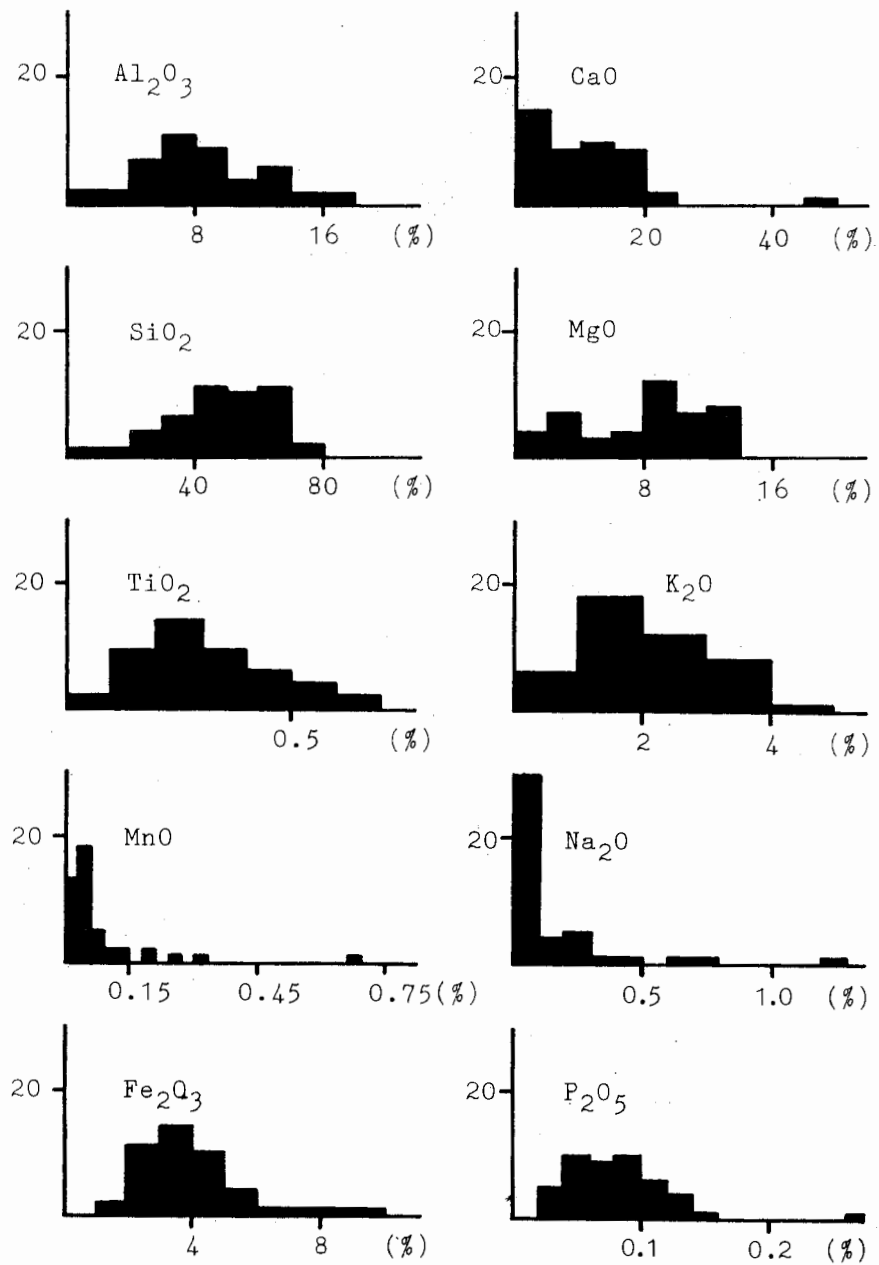


Fig. 6. Major element distribution within unmineralized shale beds. The vertical axis of histograms indicates the number of samples.

TABLE I. SPLIT ANALYSES OF PYRITIC SHALE

SAMPLE #	1122-77		1117-7		1110-8	
	pyrite	shale	pyrite	shale	pyrite	shale
Al <sub>2</sub> O <sub>3</sub> %	1.94	4.74	4.08	6.18	3.28	8.74
SiO <sub>2</sub> %	18.55	31.59	22.31	32.96	24.25	51.67
TiO <sub>2</sub> %	0.07	0.15	0.21	0.22	0.10	0.30
K <sub>2</sub> O %	0.32	1.30	0.51	1.74	0.36	1.71
Na <sub>2</sub> O %	0.02	0.05	0.17	0.27	0.02	0.05
CaO %	3.88	17.45	4.21	16.57	1.52	7.21
MgO %	3.44	13.10	4.87	12.50	4.65	10.77
Fe <sub>2</sub> O <sub>3</sub> %	39.88	1.93	31.30	2.33	37.58	3.61
MnO %	0.07	0.09	0.08	0.12	0.05	0.04
P <sub>2</sub> O <sub>5</sub> %	0.01	0.09	0.05	0.10	0.02	0.05

times as much iron than the average shale of the Newland Formation (Table I), averaging iron enrichment over the whole thickness of a horizon of pyritic shale results in an overall non-lithogenic iron addition of only 7.5% iron.

### 1.2.3. Sedimentary Setting

The sedimentary setting of pyritic shale horizons in the northern Helena embayment (Little Belt Mountains) was examined in detail by the author. A brief overview of the sedimentation history of the Helena embayment is published in Schieber (1986).

The pyritic shale horizons in the northern Helena embayment were deposited on top of the transition zone between the upper and lower member of the Newland Formation. This transition zone marks a major regression. The basin configuration during deposition of the transition zone was an east-west trending half-graben with an active growth fault along the southern basin margin, and a gentle flexure in the north (Fig. 2). Detailed studies indicate that the pyrite beds constitute mineralized algal mats that formed in shallow nearshore lagoons, in proximity to fan-delta complexes.

Thorson (1984), suggested that the pyritic shale horizons in the southern Helena embayment (Highland Mountains), accumulated on the down-dropped blocks of local syndepositional faults. However, this hypothesis remains controversial because, in independent work on the stratigraphy and sedimentology of the Belt Series in the Highland

Mountains, the exploration staff of Anaconda Minerals Co. came to the conclusion that the pyritic shales accumulated in a nearshore lagoonal setting, and that syndepositional faults are not necessary to explain the observed facies pattern. Syndepositional faulting in the southern Little Belt Mountains during deposition of the Newland Formation has been suggested by Godlewski et al. (1984). However, work by the author in the same area shows that the sedimentary record contradicts this suggestion.

In the northern Helena embayment (Little Belt Mountains), the sandstone in the transition zone between the upper and the lower member of the Newland Formation (Fig. 3) is probably related to uplift in the hinterland. Sedimentological as well as chemical data (Schieber, 1986) suggest that weathering during deposition of the transition zone was less thorough than during deposition of the lower and upper members of the Newland Formation. The pyritic shale beds were deposited during the initial stages of the transgression that followed the deposition of the transition zone sediments. Likewise, in the southern Helena embayment (Highland Mountains), pyritic shale horizons are found in the fine grained sediments that were deposited above the arkoses of the La-Hood Formation (Fig. 3). Thus, the pyritic shale horizons of the Helena embayment were deposited after a major regression (Little Belt Mountains), or following a pulse of coarse clastic sedimentation (Highland Mountains).

VanHouten (1984a, b) points out that many Phanerozoic oolitic ironstones formed in association with regressive sedimentary cycles, that most oolitic ironstones occur above a coarsening or shoaling upwards sequence, and that most are overlain by transgressive facies. Thus, even though there is an obvious difference in mineral composition between oolitic ironstones and the pyritic shale horizons of the Helena embayment, there are also noteworthy parallels. Both types of iron occurrences formed in shallow water along the basin margins and the position of iron-rich sediment horizons in the stratigraphic succession is the same in both cases (see Figs. 3 and 7).

#### *1.2.4. Timing of Pyrite Formation*

Soft sediment deformation and load structures in pyrite beds indicate that the pyrite was present very early after burial of the sediment. Sandstone and conglomerate beds that are interbedded with pyritic shales contain fragments of pyrite beds, also indicating early formation of pyrite. Conformable fine internal laminations of the pyrite beds (Fig. 5) suggest a syngenetic or very early diagenetic origin of these beds. Soft sediment deformation of pyrite beds and detrital pyrite in sandstone and conglomerate beds indicate that pyrite formed within the uppermost few meters of the accumulating sediment pile.

## 2. THE ORIGIN OF THE PYRITIC SHALE HORIZONS

Any genetic model for the formation of these pyritic shale horizons has to explain

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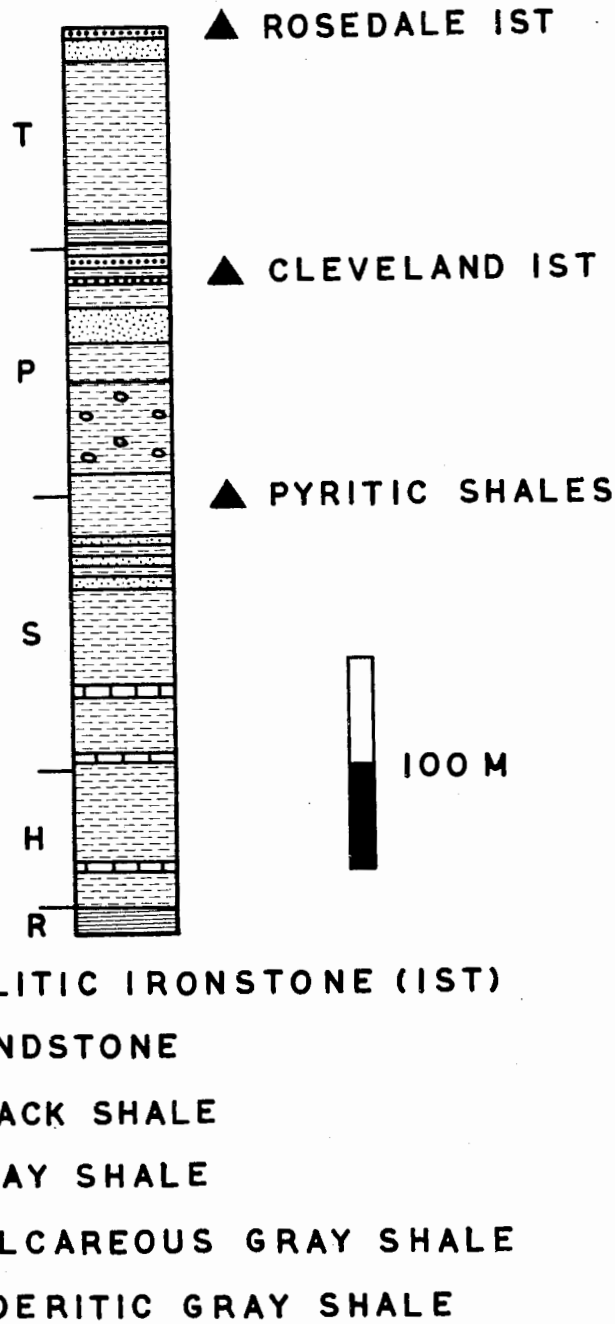


Fig. 7. Partial stratigraphic section of Lower Jurassic from Yorkshire (data from Maynard, 1983). Explanation of symbols: R = Rhaetic; H = Hettangian; S = Sinemurian; P = Pliensbachian; T = Toarcian. Triangles indicate location of iron-rich sediments.

where the large amounts of iron that were added to these sediments came from. For the reasons given in the preceding discussion on timing of pyrite formation, only syngenetic and diagenetic models need to be considered.

Syngenetic sulfide accumulations in shales are in many cases thought to be related to the exhalation of metal bearing fluids on the basin floor (Ramdohr, 1953; Gwosdz et al., 1974; Russel et al., 1981; Lambert, 1983). Fluid expulsion is thought to be driven by compaction of the sediment pile or by thermal convection cells (Russel, 1978; Hamilton, 1984). Another type of syngenetic model, which has been proposed for the copper shales of the African Copper Belt, suggest introduction of metals into the basin by rivers and nearshore precipitation of metals by  $H_2S$  in the water column (Garlick, 1981). Iron introduction by ocean upwelling (Holland, 1973) also belongs into the group of syngenetic models. In diagenetic models it is assumed that metal bearing fluids migrate through the sediment pile and that metals are precipitated when these fluids encounter reducing and  $H_2S$  producing horizons (Tourtelot et al., 1976; Samama, 1976; Hayes, 1984). The exhalative syngenetic and the diagenetic models require the basin itself to be the source of metals in sedimentary sulfide accumulations, whereas an extrabasinal source is assumed in the 'copper shale' model and in the 'ocean upwelling' model.

A good way of approaching the question of the most likely genetic model is to investigate whether the iron source was intra- or extrabasinal. In the case of an intrabasinal iron source, the iron would have to be mobilized from the basin sediments, and carried to its site of deposition by formation waters. Fluid release from compacting sediments happens during several stages of burial history. In a shale dominated sediment pile, 75% of the initial pore waters are lost during shallow burial from 0-100 meters (Perrier and Quibilier, 1974; Rieke and Chilingarian, 1974). Additional fluids are released during the smectite-illite transformation at deeper burial (Johns and Shimoyama, 1972; Burst, 1969; Powers, 1967).

The pore waters that are expelled during early burial (0-100 meters) can not be important for the formation of a pyritic shale horizon. If one for example assumes the mineralizing fluid to contain 1000 ppm Fe, then one would need  $1.5 \times 10^{15}$  litres of this fluid to produce a pyritic shale horizon with 150 million tons of pyrite iron. It may be noted here that the highest iron concentration that Carpenter et al. (1974) found in oil field brines was 440 ppm Fe. If one further assumes an initial shale porosity of 80%, and if the fluid comes out of the uppermost 100 meters of the sediment pile, an area of 25000 km<sup>2</sup> would have to be dewatered (that is a square 158 km by 158 km). If these compaction fluids were to supply the iron for a sulfide horizon, they would have to migrate laterally for about 80 kilometers on average. At the same time, however, they would have to travel no more than 100 meters vertically to escape from the compacting sediment. Thus, the fluid migration during early compaction will be vertical, and thus can not contribute to form a pyritic shale horizon.

The fluids that are released by the smectite-illite transformation are probably im-

portant for flushing hydrocarbons out of sedimentary sequences (Powers, 1967), and probably form a large portion of the present day oil field brines. These brines can be metal bearing, and metal leaching from shales has been called upon to explain the metal concentrations in these brines by Carpenter et al. (1974). However, when one examines their data, it is apparent that the brine samples with high metal values come from formations that have abundant red beds, whereas the low-metal brines are from units that consist mainly of reduced sediments. Thus it appears that the metal content of the brines is related to the oxidation state of the host rock, rather than to the metal content of the host rock. Red beds seem to be a good metal source, whereas reducing sediments seem to be a poor metal source. During the formation of red beds, a redistribution of metals occurs from detrital mineral phases to iron oxide grain coatings (Zielinski et al., 1983). These metals can be mobilized when the red beds are flushed with low-sulfide brines. High-sulfide brines would cause in situ precipitation of metal sulfides, meaning that no metals would be mobilized. Carbonaceous shales are therefore a poor source for metals because the decay of organic matter causes production of  $H_2S$  and in situ precipitation of any mobilized metals.

In unpublished theoretical calculations by Dr. M.H. Reed of the University of Oregon, diagenetic processes in carbonaceous shales were simulated. These calculations showed that  $H_2S$  production, related to the presence of organic matter and sulfate, effectively prohibits mobilization of metals from carbonaceous sediments. Metals mobilized from detrital grains are immediately reprecipitated as metal sulfides. Carbonaceous sediments are therefore a poor source rock for metals during diagenesis.

Bacterial sulfate reduction ceases when sediments are heated above approximately  $100^\circ C$  (Trudinger, 1979). Thus, upon deeper burial there is a potential of mobilizing metals from carbonaceous sediments. The center of the Helena embayment most likely did not contain much more than 2 or 3 km of sediments when the sulfide horizons in the transition zone between the lower and upper member of the Newland Formation formed. At a geothermal gradient of  $3^\circ C/100$  m, the base of the section would have been at a temperature between 60 and  $100^\circ C$ . It may be noted in this context that a geothermal gradient of  $2.6^\circ C/100$  m is reported for the North American Basin and Range Province (in Condie, 1983), which is an area of high continental heat flow.

The sedimentary sequence below the pyritic shale horizons in the northern Helena embayment was studied in detail by the author, and consists essentially of medium to dark gray shales with variable contents of organic matter (as much as 2% organic carbon). Thus, because of the abundance of organic matter in the Newland shales and because of the relatively low temperatures that can be expected due to burial (see preceding paragraph), one should expect that bacterial sulfide production was in progress throughout the sediment pile at the time the pyritic shale horizons were deposited. This assumption is supported by petrographic evidence. In fresh shale specimens disseminated fine crystalline pyrite is ubiquitous. Framboidal pyrite is also present. From the presence of organic matter and pyrite one can presume that reducing conditions prevailed

during diagenesis. A detailed study of diagenetic minerals in these sediments showed that five successive generations of diagenetic pyrite can be documented, and that formation of diagenetic pyrite continued well into late diagenesis. These observations indicate that bacterial sulfate reduction was active within the whole sediment pile when the sulfide horizons formed. Because of the presence of  $H_2S$  in the pore waters, metals that entered the pore solutions of these sediments during diagenesis were reprecipitated as sulfides close to their place of origin (now visible as fine grained pyrite). The only way that sulfate reduction would cease would be if the supply of either sulfate or organic matter were exhausted. Because there is plenty of organic matter left in the shales organic matter apparently was not a limiting factor. The formation of late pyrite shows that  $H_2S$  was still present in the pore fluids during later stages of diagenesis, and thus indicates that there was no shortage of sulfate. Dolomite and calcite are very common diagenetic minerals in the Newland Formation. If one assumes for a moment that for some reason  $H_2S$  was absent in the pore waters, and that iron could therefore go into solution in relatively large amounts, one would expect to find siderite or at least ferroan dolomite among the diagenetic minerals of the Newland Formation. This, however, is not the case. An investigation of diagenetic dolomites with SEM and attached EDAX analyzer did not reveal any significant amounts of iron in the dolomites. Therefore it is most likely that no significant amounts of iron moved within the reducing sediment pile of the Newland Formation at any time of burial history. Metals were redistributed locally during diagenesis, but could not leave the reducing environment.

The sedimentary sequence of the Helena embayment is strongly dominated by shales, and that is another reason why metal bearing fluids were most likely not derived from basinal sediments. Fluids that are expelled during early stages of compaction were ruled out as a potential contributor of mineralizing fluids earlier in this discussion. During later stages of compaction shales have very low permeability, and the very large quantities of mineralizing fluids that are required to supply the iron for the pyritic shale horizons could not have migrated to the trap environment during the time interval in which the pyritic shale horizons were deposited. The sandstone bearing transition zone between the lower and upper member of the Newland Formation could have acted as an aquifer for basinal brines and could have accelerated fluid migration. However the cumulative sandstone thickness of this unit does not exceed 10 m and the sandstone beds are lenticular, discontinuous, and separated by shale beds. The sandstone bearing unit has therefore a low overall permeability, and this, together with its small cumulative sandstone thickness, makes it quite unlikely that sufficient amounts of fluid could have moved through this unit to supply iron for the pyritic shale horizons. Furthermore, no evidence of a feeder pipe or stringer zone through which such metal bearing fluids might have ascended to the basin floor has been found.

Upwelling of iron-rich deep-ocean waters has been proposed as an iron source for Precambrian iron-formations by Holland (1973). However, it is most likely that the Belt basin was an enclosed epicontinental basin (Stewart, 1976; Sears et al., 1978; Piper,

1982), and therefore it is quite unlikely that iron-rich deep-ocean waters could have entered the Belt basin by ocean upwelling.

As outlined above, petrographic evidence and chemical considerations as well as the fine grain size of the underlying sediments make it appear quite unlikely that the iron content of the pyritic shale horizons was derived from the underlying Beltian sediment pile. Because it seems that the basin itself was not able to supply the iron, an extrabasinal iron source should be considered. Considerations of the paleogeography of the Belt basin essentially prohibit iron introduction by ocean upwelling. Terrestrial waters are therefore the only remaining extrabasinal iron source. We must therefore ask if it is possible that terrestrial waters could have supplied sufficient iron to nearshore areas of the basin under the given conditions.

## 2.1. Evaluating a 'Fluvial' Model

### 2.1.1. Size of Basin Marginal Drainages

In order to estimate amounts of iron introduced through basin marginal drainages, their average size has to be estimated. Sediment that is deposited within a basin is supplied by the drainages that surround the basin, and thus the sedimentary record of the basin may provide information to estimate the width of the drainage belt around the basin. The best data on the stratigraphic record of the Helena embayment are available from the northern half of the embayment, and therefore a 'fluvial' model will be tested for the pyritic shale horizons in the Little Belt Mountains, which are found in the transition zone between the upper and lower member of the Newland Formation.

If we assume a trough shaped basin, a relatively simple relationship between basin and hinterland results (Fig. 8). The mass  $M_s = V \times \rho$  of a basinal sediment wedge of volume  $V$

$$V = 0.5 \times H \times d \times \Delta W$$

that is deposited during the time interval  $T$  is equal to the sediment mass  $M_e$

$$M_e = E \times \Delta W \times L \times T$$

that is eroded from a strip of hinterland adjacent to this sediment wedge. The sediment wedge in Figure 8 is approximated by a sediment wedge with triangular cross section. The density of the sediment is denoted by  $\rho$ , and  $E$  is the erosion rate of the hinterland in tons per year per square kilometer. For explanation of other symbols see Figure 8. Because the amount of erosion in the hinterland generally equals the amount of sedimentation in the basin ( $M_s = M_e$ ), the length of the hinterland strip (or the width of the



drainage belt) that supplies one half of the basin with sediment can be calculated as

$$L = 0.5 \times H \times d \times 2.7 \times 10^9 \times (\text{ExT})^{-1} \text{ km}$$

A sediment density of 2.7 tons per cubic meter is assumed, T is in years, H and d are in kilometers. The dimensions H and d of a sediment wedge that includes all the sediment below the Newland Formation/Greyson Formation contact can be estimated from the sedimentary record of the Helena embayment. The results for two possible basin reconstructions are 2 and 3 km for H, and 110 and 75 km for d respectively. The cross section area ( $0.5 \times H \times d$ ) of the basal sediment wedge that results from above figures is approximately 110 square kilometers in both cases. The time span T during which this sediment wedge was deposited can be estimated by combining geochronologic data with data on sediment thickness. Harrison (1972) assumes beginning of Belt sedimentation at around 1450 m.y.b.p., and my own research indicates that Belt sedimentation in the Helena embayment probably did not start before 1400 m.y.b.p. Beltian sediments from Neihart Quartzite to Greyson Formation give a Rb-Sr isochron of 1325 m.y.b.p. (Obradovich et al., 1986). The 1325 m.y. age probably represents the time of the smectite-illite conversion in these sediments, and is therefore a minimum age. From above data we may assume that about 75 to 125 million years passed while the Beltian sequence including the Greyson Formation was deposited. With an approximate sediment thickness of 6500 m in the centre of the basin (Greyson Formation = 3000 m, Upper Newland Formation and transition zone = 900 m, Lower Newland Formation = 2000 m, 'esti-

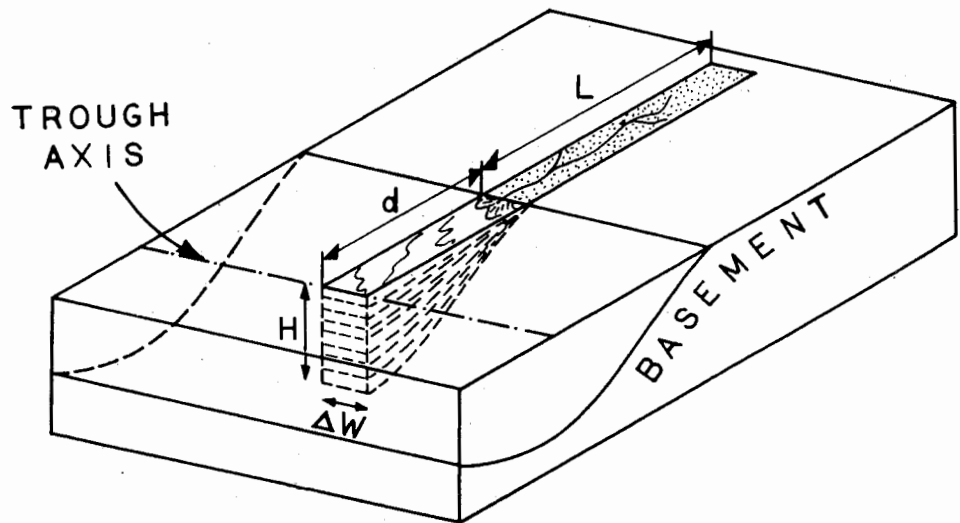


Fig. 8. Relationship between dimensions of sedimentary trough and sediment source area. Explanation of symbols: H = thickness of sediment wedge in depocentre of basin; d = distance between basin margin and depocentre; W = width of sediment wedge; L = length of hinterland strip that supplies sediment to the sediment wedge. A long, trough-shaped basin is assumed.

mate' of Chamberlain Shale and Neihart Quartzite = 600 m), an average sedimentation rate of 0.09 to 0.05 mm/year can be calculated. Because the 1325 m.y. age is probably a minimum age, the total time of deposition may well have been less than 75 m.y. Therefore, for the purpose of this discussion we will assume that the average sedimentation rate was somewhere between 0.2 and 0.05 mm/year.

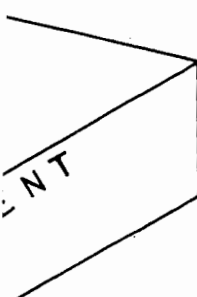
The sedimentary sequence to the top of the Newland Formation in the northernmost exposures of Proterozoic sediments in the Helena embayment (near Neihart, Montana) is about 1000 m thick, and one may assume that at the basin margin a lower net sedimentation rate (say 0.05 mm/year) applies than in the basin centre. With such a sedimentation rate it would have taken about 20 m.y. to deposit Neihart Quartzite, Chamberlain Shale and Newland Formation.

Harrison (1972) stated that the hinterland of the Belt basin was probably of low relief. Predominance of shales, as well as a remarkable mineralogical uniformity of sediments suggests that the same was also true for the Helena embayment (particularly the northern portion of it). The erosion rate  $E$  can only be estimated by means of recent analogues. Because the hinterland was probably of low relief, one may use the average erosion rate of present day continents with low mean elevations, such as Europe ( $E = 31$  tons/year per  $\text{km}^2$ ) or Australia ( $E = 40$  tons/year per  $\text{km}^2$ ; data from Holland, 1978).

The formula to calculate the average width  $L$  of the drainage belt along the northern half of the Helena embayment (see above), contains as variables the distance  $d$  between depocentre and basin margin, the thickness  $H$  of the sediment pile in the depocentre, the erosion rate  $E$ , and the time interval of deposition  $T$ . The size of these variables is assessed in preceding paragraphs. Estimates of  $H$  and  $d$  may easily vary by as much as 30%. However, because low estimates of  $H$  tend to lead to larger estimates of  $d$  and vice versa, inaccuracies are partially compensated for in the product  $H \times d$  of above formula. Therefore the  $H \times d$  term of the formula is not a very sensitive variable and will not be influenced strongly by the various configurations of the sedimentary wedge that are permitted by the available data. The application of present day erosion rates to a Proterozoic basin/hinterland model is hazardous because of the lack of land vegetation during the Proterozoic. We selected average erosion rates from Australia and Europe as recent analogues because both continents have low mean elevations. These two continents differ strongly in their climate and in the density of their vegetation cover, but have surprisingly similar erosion rates. Thus we may assume that erosion rates of low relief Proterozoic continents were similar to those of present day continents with low mean elevation. In that case the erosion rate is probably not a very sensitive variable as well and can reasonably be bracketed between 30 and 40 tons per year per  $\text{km}^2$ . The most critical variable is probably the rate of sedimentation, or in other words the time span during which the sediment wedge was deposited. Because times of deposition for the Beltian sediments can only be crudely bracketed, sedimentation rates could easily have ranged from 0.05 to 0.2 mm per year. Thus the Beltian sequence including the Newland Formation (using the section at Neihart) could have been deposited in as little

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as 5 m.y. or as much as 20 m.y. Harrison (1972) estimates that it took about 600 m.y. to deposit the Belt Series as a whole (about 20 km of sediment), and therefore I assume that the 0.05 mm/year sedimentation rate is more realistic for the Belt Series in the northern Helena embayment. Therefore, the drainage belt width that is calculated for a 0.05 mm/year sedimentation rate should be preferred over the one calculated for a sedimentation rate of 0.2 mm/year. For  $T = 20$  m.y. (small sedimentation rate of 0.05 mm/year) one may also assume a relatively small erosion rate of 30 tons/year per  $\text{km}^2$ . A larger erosion rate of 40 tons/year per  $\text{km}^2$  may be assumed for larger sedimentation rates like 0.2 mm/year ( $T = 5$  m.y.). Together with  $0.5 \times H \times d = 110 \text{ km}^2$  one can then calculate a drainage belt width of  $L = 500 \text{ km}$  for slow sedimentation (0.05 mm/year) and of  $L = 1500 \text{ km}$  for relatively fast sedimentation (0.2 mm/year).

During the time interval that is represented by the transition zone between the upper and lower member of the Newland Formation, the northern shoreline of the Helena embayment was constructive, as is evidenced by regression during that time. Therefore the drainages were probably of elongate shape (Davies, 1885). Hock (1957) investigated the relationship between stream length  $L'$  and drainage area  $A$  and found that these two parameters are related by the empirical expression

$$L' = 1.4 \times A^{0.6}$$

We may assume that in an elongate drainage  $L'$  is close to the length  $L$  of the drainage basin, and if we use  $L$  within the above limits of 500 to 1500 km, then the result is that an average drainage basin within the drainage belt along the northern margin of the Helena embayment was somewhere between 18000 (slow sedimentation) and 112000 square kilometers (fast sedimentation) in size. To assume  $L = L'$  is of course a simplification inasmuch as  $L'$  will always be larger than  $L$  because of river sinuosity and topographic irregularities. The consequence of this simplification is that the drainage areas calculated above are smaller than they realistically should be. They are therefore only minimum estimates.

### *2.1.2. Supply of Iron*

The next question is, are drainage basins of above size able to supply sufficient iron for sulfide horizon formation to the basin? In order to evaluate this question we have to examine how much iron can be carried by terrestrial waters, how much water can be expected under the given climate conditions, whether the water will travel mainly as groundwater or as surface runoff, whether the granitoid basement rocks can supply the necessary amounts of iron, and how terrigenous sedimentation can be decoupled from iron input into the basin.

### 2.1.2.1. *Climate and Water Supply*

The great abundance of carbonates in the Newland Formation indicates a warm climate during Newland deposition (Wilson, 1975). Barite is found in some places within the transition zone sediments. The barite occurs as rosettes, nodules, and scattered crystals that resemble gypsum occurrences in recent sabkhas. The barite may be a diagenetic replacement of precursor gypsum, and may indicate evaporitic conditions during deposition of the host sediments. Similar occurrences of baritized gypsum have been reported from other Precambrian sedimentary sequences (Barley et al., 1979; Groves et al., 1981). Sediments of carbonate mudflats with a predominance of fine crystalline (probably penecontemporaneous) dolomite occur along the margins of the Helena embayment. At present penecontemporaneous dolomite formation is almost exclusively observed in sea-marginal, carbonate-producing environments under semi-arid (evaporitic) climate conditions (Wilson, 1975). Therefore, the general occurrence of carbonates in conjunction with early dolomite formation and probably gypsum precipitation indicates a warm, semi-arid climate during deposition of the Newland Formation.

Under such climate conditions, annual precipitation can be expected to be small, and annual runoff is most likely minimal. As a recent example for the water balance of a semi-arid region, consider the Australian continent, which has extensive coastal regions of semi-arid climate. According to a compilation by Baumgartner et al. (1975), these areas have roughly 60 cm/year annual precipitation. Evaporation is high, and only approximately 3 cm/year of annual runoff reach the ocean. For drainages of 18000 to 112000 km<sup>2</sup> in size this means an annual runoff of 540 x 10<sup>6</sup> to 3360 x 10<sup>6</sup> m<sup>3</sup> respectively. It is important to estimate how much of this water will travel in the subsurface, because only groundwater will remain in contact with crustal rocks and their weathering products long enough to mobilize appreciable amounts of iron.

Rainfall in semi-arid climates is sporadic and often occurs in short violent rainstorms. Present day experience with ephemeral streams shows that their flood stages last only a short time, usually some hours to days (Glennie, 1970; Reineck et al., 1980). Infiltration competes with flood discharge for the water that is supplied by rainstorms in semi-arid regions. Babcock et al., (1942) found that about 50% of the total streamflow during floods infiltrates close to its origin and adds to the groundwater. Besides recharge in streambeds, additional infiltration occurs over the whole area that receives rainfall. Furthermore, rainstorms occur only locally within a drainage basin, and the surface runoff from a flood-area has to pass through non-flooded areas before it can reach the basin. This means further diminishing of surface runoff by infiltration. Thus, most of the water that finally reaches the sedimentary basin travels underground most of the way, and enters streams in the coastal regions where the groundwater table reaches the surface. It is probably a fair assumption that in the semi-arid setting envisioned here, only approximately 20% of the annual runoff would travel as pure surface runoff. The other 80% would travel mainly as groundwater and would enter surface drainages in

coastal areas. Thus about 80% of the annual runoff can be expected to interact with detrital crustal rocks to mobilize iron. For the drainage sizes envisioned above that would amount to between  $430 \times 10^6$  and  $2690 \times 10^6 \text{ m}^3$  of annual groundwater discharge to the basin. This water is contained in a pediment of sand and gravel. In order to estimate the average flow velocity of the groundwater in the pediment we would need to know the average permeability and the slope of the pediment. We might try to get an estimate of the permeability by comparison with recent alluvial sediments, but it is practically impossible to estimate the slope of the pediment. However, if we take for example a relatively high groundwater flow velocity of 25 m/year it would take an average of between 10000 (500 km drainage belt) and 30000 (1500 km drainage belt) years for a complete turnover of the groundwater in the alluvium of the drainage. Thus we may safely assume that there is sufficient time for the groundwater to mobilize iron from the aquifer.

#### *2.1.2.2. Source of Iron*

Crustal rocks are the source of iron in terrestrial waters. The pre-Beltian granitoid basement gneisses of the Helena embayment contain about 3% iron oxide, half of which is in the ferrous state (1.5% FeO). The iron that is available for leaching is the ferrous iron in mafic minerals of the alluvial cover of the hinterland. Mafic minerals, such as biotite and altered hornblendes are found in the sediments of the transition zone between the lower and upper member of the Newland Formation, an indication that mafic minerals were also present in the alluvial equivalents of these sediments. If, for simplicity, we assume an average alluvium thickness of 100 m over the whole drainage (that estimate is fairly low, particularly for the time after a regression), and further assume that about 1% FeO is available in the immature alluvium for leaching (after uplift and regression), then, at a density of  $1.8 \text{ g/cm}^3$  for the alluvium, we could potentially leach  $25 \times 10^9$  ( $18000 \text{ km}^2$  drainage) to  $157 \times 10^9$  ( $112000 \text{ km}^2$  drainage) tons of iron from the alluvial cover. These figures clearly show that there probably was by no means a shortage of leachable iron in the drainages around the Helena embayment. The pyritic shale horizons contain on the order of some hundred million tons of pyrite iron. Thus, the potentially available amount of iron may have exceeded the amount of iron needed for formation of pyritic shale horizons by as much as two or three orders of magnitude. The only remaining problem is to move the iron to the basin.

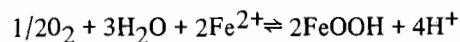
#### *2.1.2.3. Transport of Iron*

Iron concentrations found in filtered river-water samples have been reported to range from 30 to 1670 ppb (Durum et al., 1963). However, most of this 'dissolved' iron consists of iron colloids of very fine particle size (less than  $0.45 \mu\text{m}$ ; Boyle et al., 1977), rather than being in true solution. The bulk of the iron that is transported by present

day rivers is not transported in solution or as a finely disperse colloid, but rather as a constituent of particulate matter, either in iron bearing minerals, or as iron oxide coatings on mineral grains (Carroll, 1957). Iron transport as grain coatings however means that large iron supply is coupled with large sedimentation rates, and the dilution of iron by terrigenous sediments in the sedimentation basin would preclude the formation of a strongly iron enriched sediment horizon. Thus we need a mechanism for transporting large amounts of iron without moving large amounts of detrital matter at the same time. One possibility would be to transport iron in true solution, but the problem is that the Beltian sequence contains red beds (Harrison, 1972). The red beds are evidence that during Beltian times the Precambrian atmosphere contained free oxygen and was already oxidizing enough to cause formation of goethite and hematite in surface environments (Schidlowski et al., 1975).

The conservative nature of the composition of shales through time shows that nature and intensity of near-surface chemical processes has changed little between Archean and recent (Holland, 1984). The partial pressure of CO<sub>2</sub> was probably higher in the Precambrian, and the partial pressure of O<sub>2</sub> lower than today (Holland, 1984). These characteristics, however, had little influence on iron transport on the surface of the earth, because the concentration of ferrous iron in surface waters can only be significant when oxygen is practically absent.

Groundwaters have a much better chance to move large quantities of iron. Present day oxygenated surface waters contain 8.2 ppm O<sub>2</sub> (Carpenter, 1966), and when they come in contact with mafic minerals they oxidize these minerals. One litre of present day surface water contains  $2.56 \times 10^{-4}$  mole (or 8.2 ppm) of O<sub>2</sub>, and it follows from a reaction of ferrous iron to goethite



that only  $1.024 \times 10^{-3}$  moles of ferrous iron (or 0.057 grams) would be needed to bind that amount of O<sub>2</sub> in goethite. At 35% porosity of the alluvial aquifer, 5 kg of rock material (density 2.7 g/cm<sup>3</sup>) would surround one litre of water. Assuming the immature aquifer sediments contain 1% FeO (see above), then about 40 grams of ferrous iron would be available to bind the O<sub>2</sub> that is dissolved in each litre of groundwater. Because only 0.057 grams of Fe<sup>2+</sup> are needed to bind the dissolved oxygen, oxygenated water that enters an aquifer containing mafic minerals will become oxygen-free after only a small amount of interaction with the aquifer has taken place. Oxygen can still enter the groundwater by diffusion from above, but access is strongly restricted by the sediment between surface and groundwater table. As soon as oxygen is depleted, ferrous iron can go into solution in considerable quantities. Iron also forms secondary iron minerals like chlorite and siderite.

Coastal aquifers of Coos Bay, Oregon, are feldspathic sandstones and contain a few percent of mafic minerals. Dissolved iron concentrations in groundwaters from these a-

quifers range from 2-40 mg/litre (Luzier, 1982). Additional sampling by M. Magaritz (pers. comm.) produced samples with peak values of 100 mg/litre dissolved iron. If these waters were in equilibrium with the atmosphere, they should have only on the order of some  $10^{-6}$  mg/litre of dissolved iron.

High values of dissolved iron were also found in low-pH saline groundwaters from the Yilgarn Block, Australia. The Yilgarn Block is dominated by granitoid basement, has drainage basins with low gradients, and is characterized by large areas of colluvial and alluvial slopes (Mann, 1984). Playa lake systems and a semi-arid climate are characteristic for most of the Yilgarn. Groundwaters contain up to 204 mg/litre of dissolved iron, and the average of the measured values is 36 mg/litre (Mann, 1984).

Groundwaters of near neutral pH were investigated by Kraynov et al. (1982), who found that iron in groundwaters is present in dissolved and colloidal form. In oxygenated groundwaters  $\text{Fe}(\text{OH})_3$  greatly predominates as the dissolved form of iron, and when the solubility product of  $\text{Fe}(\text{OH})_3$  is reached, polymerization produces a colloid. In oxygen- and sulfide-free groundwaters  $\text{Fe}^{2+}$  is the most abundant dissolved iron species, but additional iron is found as  $\text{Fe}(\text{OH})^+$ ,  $\text{FeHCO}_3^+$ , and  $\text{FeSO}_4$  (Kraynov et al., 1982). The dissolved iron content of above waters ranges from some mg/litre to 100 mg/litre.

Thus present day groundwaters are obviously capable of carrying significant quantities of iron, and the same should be true for Proterozoic groundwaters. In the Proterozoic the lower oxygen content of the atmosphere (Holland, 1984) should have helped to make oxygen-free groundwaters even more common than they are today. In such groundwaters high dissolved iron contents may have been common as long as mafic minerals were present in the aquifer.

When such iron-rich groundwaters enter the surface drainage system the dissolved iron will be oxidized in the presence of an oxidizing atmosphere. However, oxidation to ferric oxide and hydroxide does not necessarily mean precipitation of iron. When conditions are right for iron oxide and hydroxide to precipitate, it often forms instead a stable sol, and as such, may be carried for long distances (Krauskopf, 1967; Kraynov et al., 1982). In fact, aside from iron transported as a constituent of particulate matter (Carroll, 1958), this is the chief method of transportation of iron in present day surface waters (Krauskopf, 1967; Boyle et al., 1977). The iron colloid is flocculated by electrolytes, particularly where streams enter the sea (Boyle et al., 1977; Fox and Wofsy, 1983). With above mechanism the iron can be transported on the last leg of its journey in oxygenated surface waters and finally be deposited in basin marginal areas as iron hydroxides. The great lateral extent of the pyritic shale horizons is a circumstance that may be related to the formation of ferric hydroxide floccules in nearshore areas. Because these floccules are of relatively low density, moderate currents and wave stirring in nearshore areas will cause large lateral dispersal of iron collide floccules.

Now we have to examine whether we can get enough iron out of the envisioned drainage areas to account for the iron in the pyritic shale horizons. Using the range of sedimentation rates established above, it should have taken about 50000 (0.2 mm/year)

to 200000 (0.05 mm/year) years to deposit 10 m of a pyritic shale horizon. With an areal extent of 20 km<sup>2</sup> and 7.5% added iron in the average pyritic shale, 10 m of such a pyritic shale horizon (average density 2.96 tons/m<sup>3</sup>) should contain roughly 50 million tons of iron in pyrite. One year's average subsurface runoff amounts to between 430 and 2690 million m<sup>3</sup>, and if these groundwaters were to contain a relatively low iron concentration of 5 mg per litre (or 5 ppm), one could expect from 430 million tons (200000 years, 18000 km<sup>2</sup> drainage) to 670 million tons (50000 years, 112000 km<sup>2</sup> drainage) of iron to be delivered to the basin. We assume here that the iron forms a stable sol upon entering oxygenated surface waters. As we see, even with minimum estimates for the drainage basin size, and with relatively low values of dissolved iron, between 8-13 times more iron can be delivered to the basin than is actually needed for the formation of a large pyritic shale horizon (20 km<sup>2</sup>). If we consider that colloidal iron concentrations in excess of 1 mg per litre are not uncommon in present day rivers (Durum et al., 1963; Boyle et al., 1977), and if we further consider that with just 1 mg of iron per litre our above envisioned drainage would still contribute sufficient iron to the basin to form a pyritic shale horizon, then continental runoff as an iron source for these pyritic shale horizons should be an even more plausible proposition.

### 3. SUMMARY

Above considerations of a 'fluvial' iron source for the pyritic shale horizons of the Helena embayment show:

- A) That the average drainage size around the Helena embayment can be estimated using the available data on stratigraphy and sedimentology.
- B) That the prevailing climate was probably semi-arid.
- C) That the runoff from the drainages probably travelled as groundwater most of the time.
- D) That at least an order of magnitude estimate of the annual runoff is possible.
- E) That aquifers which contain mafic minerals will cause depletion of dissolved oxygen in groundwaters.
- F) That recent oxygen-free groundwaters can carry significant quantities of iron in solution.
- G) Iron that is mobilized by groundwaters can be transported in surface waters as iron colloids and can thus reach the basin.
- H) Amounts of iron that are vastly in excess of the iron found in the pyritic shale horizons can be mobilized from a relatively thin cover of immature alluvium in the drainage area (assuming a granitoid basement).
- I) That only relatively small amounts of iron (less than 1 ppm) need to be carried in groundwaters and related surface waters, in order to create pyritic shale horizons of the observed size.
- J) And that a system as it is envisioned above is capable to produce much more vol-



uminous pyritic shale horizons when conditions are optimal.

Two more questions remain to be settled. First, why pyritic shale horizons in the Helena embayment are only observed after major regressions and pulses of coarse clastic sedimentation, and second, the cause for the decoupling of terrigenous sedimentation from iron deposition. The answer for the first question lies probably in the sedimentary history of the basin and the granitoid basement rocks. Intense pyritic shale deposition in the northern Helena embayment occurred over a stratigraphic interval of about 70 m, just above the deposits of a major regression (the only major regression in the northern Helena embayment). That regression produced a cover of immature alluvium in the hinterland, containing mafic minerals. Because of the 70 m thickness of the pyrite-rich interval, iron leaching from that immature pediment lasted for about 0.35-1.4 m.y. (sedimentation rates between 0.2 and 0.05 mm/year). During this time interval, more and more of the primary mafic minerals in the alluvium were destroyed until the alluvium could no longer act as an iron source. In addition, the pyritic shale horizons were deposited in the early stages of a transgression, and this transgression drowned more and more of the mafic-rich alluvial aquifer until it finally could no longer function as a conduit for groundwaters to the basin margins. Before and after the regression that is marked by the 'transition zone' sediments, sedimentation was slow and the hinterland of muted relief. Erosion was therefore slow as well, and the small amount of mafic minerals that was present in the granitoid source rocks was oxidized early in the weathering cycle. Erosion was more rapid when uplift occurred in the hinterland, and a blanket of immature alluvium with mafic minerals was spread out. Thus, in the case of a granitoid basement, the potential of iron leaching from alluvial sediments is greatly enhanced after uplift and regression. If there had been a basement dominated by mafic rocks, pyrite enrichment in nearshore shales might have been much more common, and regressions might have been marked by a peak in pyrite deposition.

The circumstances of a semi-arid climate probably furnish the answer to the second question. As noted above, major surface runoff in a semi-arid climate is restricted to periods of strong rainfall and flooding. During those periods, relatively large amounts of water leave the drainage basin within a matter of days, and pulses of sediment are contributed to basin marginal lagoons and to the basin. Most of the time however, only groundwater-derived waters (with colloidal iron) would have entered the nearshore areas. Water discharge into the basin would have been quite slow and not much sediment would have been transported. Thus, only minor dilution of the iron flocculate by terrigenous sediment would have occurred. Dilution of flocculate-rich nearshore waters would have been retarded in nearshore lagoons, and iron floccules would have been trapped by benthic microbial mats (see introduction). Reducing conditions and  $H_2S$  production prevail in microbial mats immediately below the surface (Bauld, 1981), thus iron oxide and hydroxide floccules that are trapped by the mat surface would be transformed into pyrite after burial. This would create laminated pyrite beds as observed in the pyritic shale horizons (Figs. 4 and 5).

#### 4. CONCLUSION

The large amounts of iron that are contained by the pyritic shale horizons in the Proterozoic sediments of the Helena embayment can not be explained with an exhalative or early diagenetic model that requires the iron to be derived from within the basin. The reducing character of the basinal sediments below the pyritic shale horizons, as well as pyrite formation throughout most of the diagenetic history of the sediments make it appear unlikely that significant quantities of iron could have been mobilized from within the basinal sediment pile. An alternative model in which iron is brought into the basin by continental runoff is clearly feasible and in accord with the sedimentary history of the basin. Iron was mobilized from immature alluvium containing mafic minerals, and was probably transported into the basin as iron oxide and hydroxide sols. Iron colloids were flocculated upon mixing with electrolyte-rich basin waters and deposited in basin marginal lagoons. These flocculates were incorporated into benthic microbial mats, where laminated pyrite beds formed by reduction shortly after burial of the mats.

The position of the pyritic shale horizons within the sedimentary context of the basin (nearshore, following regression) is comparable to that of most oolitic ironstones in the Phanerozoic. Only the trap environments of these two types of sedimentary iron enrichment are different. Therefore, the approach that was used to constrain a 'fluvial' model of iron introduction by means of information derived from the sedimentary record of the basin, might also be applied to test the feasibility of fluvial iron supply for oolitic ironstone deposits. The approach taken in this paper might also be applied to pyritic shale units in other sedimentary basins in order to evaluate the origin of the 'excess' iron that is accumulated in such sediments.

Phanerozoic oolitic ironstones contain iron accumulations of comparable or larger magnitude than found in the pyritic shale horizons of the Helena embayment. Thus, from the standpoint of sedimentary iron accumulations, the occurrences in the Helena embayment are far from exceptional and probably owe nothing to 'different' conditions in the Precambrian atmosphere-ocean system. There is a resemblance in appearance between Precambrian banded iron-formations and the pyritic shale horizons of the Helena embayment. However, because of differences in mineralogy and size, the pyritic shale horizons do not fit the standard definitions of an iron-formation (Stanton, 1972). The only truly 'Precambrian' feature of these pyritic shale horizons is probably the microbial mat lamination that is exhibited by the laminated pyrite beds. This morphological type of sedimentary pyrite should be quite rare in Phanerozoic sediments, because grazers had greatly reduced the preservation potential of microbial mats in post-Precambrian times.

#### 5. ACKNOWLEDGEMENTS

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