A model for sulfide band formation under epigenetic conditions — a study based on simulated sedimentary systems

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The formation of sulfide bands in sediments has been investigated in the past, but in all the cases described they have formed by the diffusion of solutes from stationary fluids in the pores of the sediments. Experimental work with liquids flowing through sediments has shown that such bands may be formed even in a dynamic environment. A model based on experimental work with simulated sedimentary systems explaining the mechanism responsible for the formation of such bands under epigenetic conditions is presented in this paper.

Introduction

The investigation of problems associated with various branches of geology, sedimentology and geobiology is usually based on two approaches:

(a) fieldwork; and
(b) laboratory investigation.

The fieldwork approach has, of course, a distinct advantage of direct observation of systems or their results in nature, and usually adequate amounts of material available for studies.

However, field investigations are frequently hindered by the complexity of the systems being studied and the investigator is handicapped by lack of experimental control. Furthermore, although very slow processes may have been operating long enough for the results to be measurable, their original operating environment may have been very different to that at the time of observation.

As the field approach can be disadvantaged by the complexity of systems, laboratory investigation of individual parameters, their evaluation, and significant application to the field may be limited by over-simplification of systems. Individual processes, as studied, do not operate independently in the field, but are highly interactive in their effects. However, one of the primary advantages of laboratory experiments is that the starting conditions of processes being studied are known, which is frequently essential for subsequent evaluation of the systems. In many cases the size of an experiment may be a limiting factor: frequent sampling over a long time may be necessary, for example, or the walls of a small container may affect processes associated with surface tension, microbiological activity, and permeability. On the other hand, such experiments are usually readily monitored and the answers to many basic questions are relatively easy to obtain.

Finally one of the most important advantages of laboratory investigations is the operator's experimental freedom, lacking in most cases of field investigations.

After consideration of all the advantages and disadvantages of the above approaches, an attempt was made to utilise their advantages and eliminate as many of their short-comings as possible, by devising another approach. A concept of a simulating system was formulated.

The simulating system represents an attempt, in the laboratory, to move closer to the field environment, while eliminating some of the non-essential complexity, and facilitating experimental control. There is, of course, no sharp division between laboratory experiments and simulation. Ideally, there should be continuity from the simple laboratory system, through the experimentally manageable simulating system, to the naturally complex field environment.

In the designing of a simulating system, the questions to be answered should be carefully defined. To reduce the complexity of the system as much as possible, the number of parameters to be monitored simultaneously should be limited. Therefore the selection of these parameters is of the greatest importance. The problems of continuous sampling and side-wall effects can be reduced, if not eliminated, with proper planning, although requirements for specific minerals and fluids in quantities of kilograms or even tonnes can create logistic problems, especially where uniformity of chemical composition or mineralogy is important. In the cases where fully automatic monitoring and automatic control are desirable the instrumentation may become very complex. The same would apply to a field study, of course.

History of investigations

Probably the earliest attempt to simulate a geobiological environment was made by Winogradsky (1945) when he investigated the effect of organic material on carbonate mineralogy. Later, Weiss & Amstutz (1966) devised a system to study the extraction of lead and other metals from clay in the presence of sodium sulfide solution.

The genesis of Mansfield copper shale was simulated by Suckow & Schwartz (1968), and the ionic movement of iron through sediments in the presence of organic matter and the diffusion processes involved were simulated by Berner (1969), who also previously worked on the effect of organic matter in carbonates (Berner, 1968). Experimental work simulating multi-ionic diffusion through sediments and the consequent separation of metals into monomineralic strata has been described by Bubela & McDonald (1969), Lambert & Bubela (1970), and by Bubela (1981).

Thorstenson & Mackenzie (1971) and Deelman (1975) investigated, by simulating systems, the effects of microbiological sulfate reduction and carbonate precipitation, and Hargrave (1972) was simulating some aspects of eutropic lakes for his investigation of Eh and O_2 concentration in such a lake.

A more complex system was developed by Graetz & others (1973) to study Eh and nitrogen transformation in lake sediment—water environments, and photosynthetic sulfide oxidation and its response to heat and light were simulated by Blackburn & others (1975).

A more sophisticated system was developed by Bubela & Ferguson (1973) where the relative large

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size of the simulating system (over 1000 litres) permitted continuous sampling and monitoring over a long time without undue disturbance to the system. The system simulated diagenetic processes in unconsolidated sediments in the presence of carbonates, heavy metals, microbiological sulfate reduction and algal growth (Bubela, 1970; Bubela & Powell, 1973; Bubela & others, 1975; Ferguson & others, 1975; Davies & others, 1978).

All of the systems mentioned so far were static, where the systems, except for molecular diffusion, evaporation, and biological activity, were at a steady state.

However, natural systems are usually dynamic, and thus simulation studies have evolved to include dynamic factors such as water movement and varying energy states.

Several systems have been developed where the liquid phase was forcibly circulated. Jorgensen & others (1975) circulated seawater through an experimental column and measured the rate of sulfate reduction and the oxygen uptake by the water of the sediments. A similar system simulating oxygen uptake by sediment waters was constructed by Fenchel (1960).

A high energy environment favourable to the formation of carbonate ooids was simulated and the effect of high molecular weight organic substances on the processes involved was described by Ferguson & others (1978) and Davies & others (1978).

To study the effects of metal chelation on transport and deposition, Hallberg & others (1980) developed a system where continuous sedimentation of mineral particles took place for several months. A mathematical evaluation of such a simulating system was done by Mooney & others (1978).

Movement of interstitial waters through sediments is important during diagenesis of carbonates and organic matter (Bubela, 1980), and a complex system was developed by Bubela & others (1978), to provide horizontal and vertical water movement, climatic simulation and continuous monitoring of a variety of parameters (Johns & Bubela, 1979).

Hydrological studies with simulating systems

The two main areas concerned with the hydrology of sediments as studied with simulating systems are: (a) movement of fluids through sediments and the effect on associated processes; and (b) hydrochemistry.

The movement of water through sediments is influenced by a number of factors. Possibly, the most pertinent is the permeability of the sediments, which is directly linked to the useful porosity of the sediments. The porosity and permeability may be affected in a number of ways, both biological and abiological (Bubela, 1980). Biological factors may be the production of organic matter in pores, development of low-permeability algal mats sealing the water-sediment interface, formation of low permeability strata of high organic content, should such mats become buried in sediments, and diagenesis and cementation processes involving carbonates, owing to the release or consumption of CO_2 by the biological component of the sediments. Abiological processes may consist of compaction of sediments, a decrease of pore space, owing to pressure, diagenetic responses of carbonates to temperature and pressure, and pH changes. Only rarely would any of these factors be involved singularly.

The heteropermeability of sediments is important, as direction of flow of interstitial fluids and the length of the pathway the fluids travel may be altered considerably and result in changes in the chemical and physical properties of the fluids, thus affecting the conditions governing deposition or solution of minerals (Bubela, 1980). Direct evidence of such an influence was obtained by Bubela (1980). While the growth of an algal mat limited free movement of interstitial fluids, it permitted the passage of at least some ions. At pH 7.7 and 20°C and concentration gradient of 500 μmoles over 1 mm of mat thickness, 75 μmoles of copper passed per 1 cm^2 per day. However, no metal passage was detected if the metal was bound as an organo-complex.

To some extent, the composition of interstitial and supernatant waters reflects the biological activity of a system. When the algal mat mentioned above (Bubela, 1980) was active at the water-sediment interface, the Ca/Mg ratio in the interstitial water increased—owing to the relative solubilities of the calcium and magnesium carbonate respectively, the CO_2 concentration decreased—because of its consumption by the algae, and the pH of the system rose to 8.4. During the bacterial decay of the algae mat, the total concentration of CO_2 in the waters increased, the Ca/Mg ratio decreased and the pH value was lowered to 6.5. A similar fluctuation of the above parameters was noticeable during diurnal changes in microbiological activities.

Mineralogical studies with simulating systems

Weiss & Amstutz (1966) reported that a mixture of metals adsorbed to clay separates into a form of metal sulfide when H_2S is diffused through the clays. Similar results were obtained by Bubela & McDonald (1969) and Lambert & Bubela (1970) when they separated a mixture of lead, zinc, and copper into individual mineral zones by counter-diffusion of metals and hydrogen sulfide through stationary interstitial fluids. The metals did not separate into the zone sequences according to their solubilities, as was expected. Copper with the lowest solubility ($K_S = 8.5 \times 10^{-45}$) spread through the whole zone of observation, while lead ($K_S = 3.5 \times 10^{-28}$) accumulated in the middle of the zone, and zinc ($K_S = 1.2 \times 10^{-23}$) travelled furthest before it precipitated as the corresponding sulfide.

This observation indicates that other factors besides solubility may determine the zone of precipitation. The separation of metal sulfides into individual bands from two converging streams, carrying metal and sulfide ions respectively, was demonstrated by Bubela (1981). The sulfide bands were formed parallel to the resulting flow.

It is evident from the experimental work by Hallberg & others (1980) that organic matter has a considerable influence on metal precipitation, in certain cases even preventing it. It is possible that under some conditions the supersaturation threshold is considerably increased by the presence of organic matter and metal precipitation is delayed until a higher degree of supersaturation is reached.

Diagenetic changes in carbonates have been studied in simulating systems in some detail. The earliest experimental work was concerned with participation of organic matter and the involvement of sulfate reducing organisms in the diagenesis of carbonates (Berner, 1968; Thorstenson & Mackenzie, 1971; Deelman, 1975). Lambert & Bubela (1970) described the participation of carbonates in the formation of framboidal hydrocerussite, which was converted to galena by passing biologically produced H_2S through the sediments.

When deposits of nesquehonite were exposed to biological activity associated with endogenous organic

material in a simulating system (Davies & others, 1973) chemical changes were noted leading to the formation of dypingite, protohydromagnesite, high-magnesium calcite, huntite, and protodolomite. Formation of a crust was observed at the water-sediment interface, composed of monohydrocalcite spherules embodied in nesquehonite matrix (Davies & others, 1973). During this experiment the aqueous phase always covered the surface of the sediments. Under different experimental conditions (Bubela, 1980), when the surface of the sediments was allowed to dry out and the surface temperature was maintained at 30°C, a surface crustation formed of residues of algal mat, halite, gypsum, anhydrite, and high-magnesium calcite. At a later stage the high-magnesium calcite disappeared and dolomite was detected.

The formation of carbonate spherules in the static simulating system of Bubela & others (1975) is important, as general opinion was that such structures are only inorganic precipitates formed during motion in suspension after heterogenous nucleation, and the organic matter found within the ooids (spherules) is an accidental accessory unrelated to their growth (Berner, 1974). Experimental work employing simulating systems (Davies & others, 1978) has shown that ooid formation may take place in both high and low-energy regions, but each will produce a different geometry in the crystals composing the ooids. Ooids formed in a high-energy environment (waves) exhibit a tangential orientation of baton-like crystals and the endogenous organic matter is accidental. Quiet-water ooids have radial arrangement of their crystals, and they are formed from supersaturated seawater containing organic matter. The factors most important in the quiet-water formation are the molecular weight of the organic matter, the presence of carboxyl groups, and an ability of the matter to participate in hydrophobic-hydrophilic interactions. The organic matter has to be able to form organic membranes, which form the bases of concentric shells for the growth of the crystals and induce the periodicity in the carbonate precipitation. The membranes have been shown (Ferguson & others, 1978) to form by association of individual organic molecules through metal bridging and hydrophobic/hydrophilic interactions, which are known to contribute to the stability of biological membranes.

Simulating studies of diagenesis of organic matter

The diagenesis of organic material has been simulated in several systems. The organic content of the sediments undergoes a number of changes, both qualitatively and quantitatively. It is at least partially biodegraded, which results generally in the evolution of gases, mostly a mixture of methane and carbon dioxide. A system operating under highly saline conditions and being anaerobic (approx.—150 mV) produced a mixture of gases containing hydrogen (80%), carbon dioxide (5%), methane (2%), and cyclobutane, n-butane, isobutane, n-pentane, and isopentane (13%) (Bubela & others, 1975). Such short paraffines have been detected frequently in natural gases, but their presence has been attributed to the catagenetic processes acting at high temperatures on type-2 kerogen (Tissot & Welte, 1978). The system described by Bubela was operating at temperatures around 20°C and at a pressure not exceeding 100kPa above atmospheric pressure. The biodegradation of organic matter under extremely halophilic and anaerobic conditions is not well

known. Significant changes in biological activity due to environmental stresses have been described (Bubela, 1970). It is therefore feasible that such hydrocarbons may be produced directly at low temperatures and pressures from biopolymers without them first being changed into geopolymers (Tissot & Welte, 1978).

An increase in organic matter in sediments has been described by Bubela & others, 1975; Bubela, 1980. Such an increase is primarily due to fixation of carbon dioxide by photosynthetic organisms in the water column above the sediments or the biological population at the water-sediment interface. The biomass produced by such a process is not confined to the region of its genesis, but is transported by diffusion or water movements down into the sediments, where it serves as a substrate for development of the endogenous biological population. Therefore, the organic matter in the sediments consists at any time of the residual syngenetic component, material introduced by diffusion or water movement, the biomass that developed in the sediments after their deposition, and finally, the metabolic by-products of the biological activity taking place.

The composition of the organic matter changes quite rapidly. Bubela & Philips (in prep.) have observed that the buried organic matter, which originally exhibited an abundance of hydrocarbons of about C_{17}, thus demonstrating its algal origin, altered significantly after 18 months. The algal characteristics of the organic matter decreased, and hydrocarbons in the C_{20-30} range became predominant, thus indicating its predominantly bacterial origin. The significance of this observation lies in the fact, that it was the bacterial and not algal material, which, at least to some degree, underwent further diagenetic changes, leading eventually to the formation of geopolymers. As the original sediments become more and more covered by new sediments, the introduction of fresh organic matter suitable as the substrate for the endogenous population diminishes and the chemical, abiological changes become more and more predominant, resulting eventually in the formation of kerogen type-1 (Tissot & Welte, 1978).
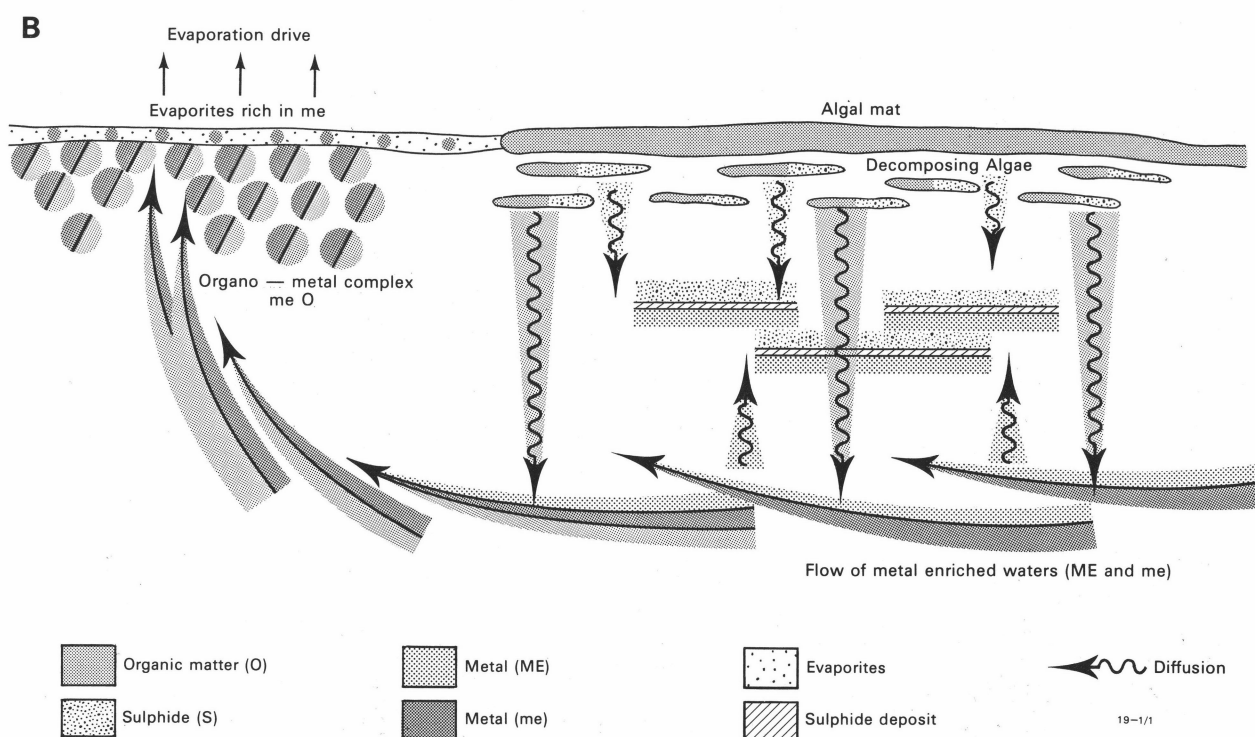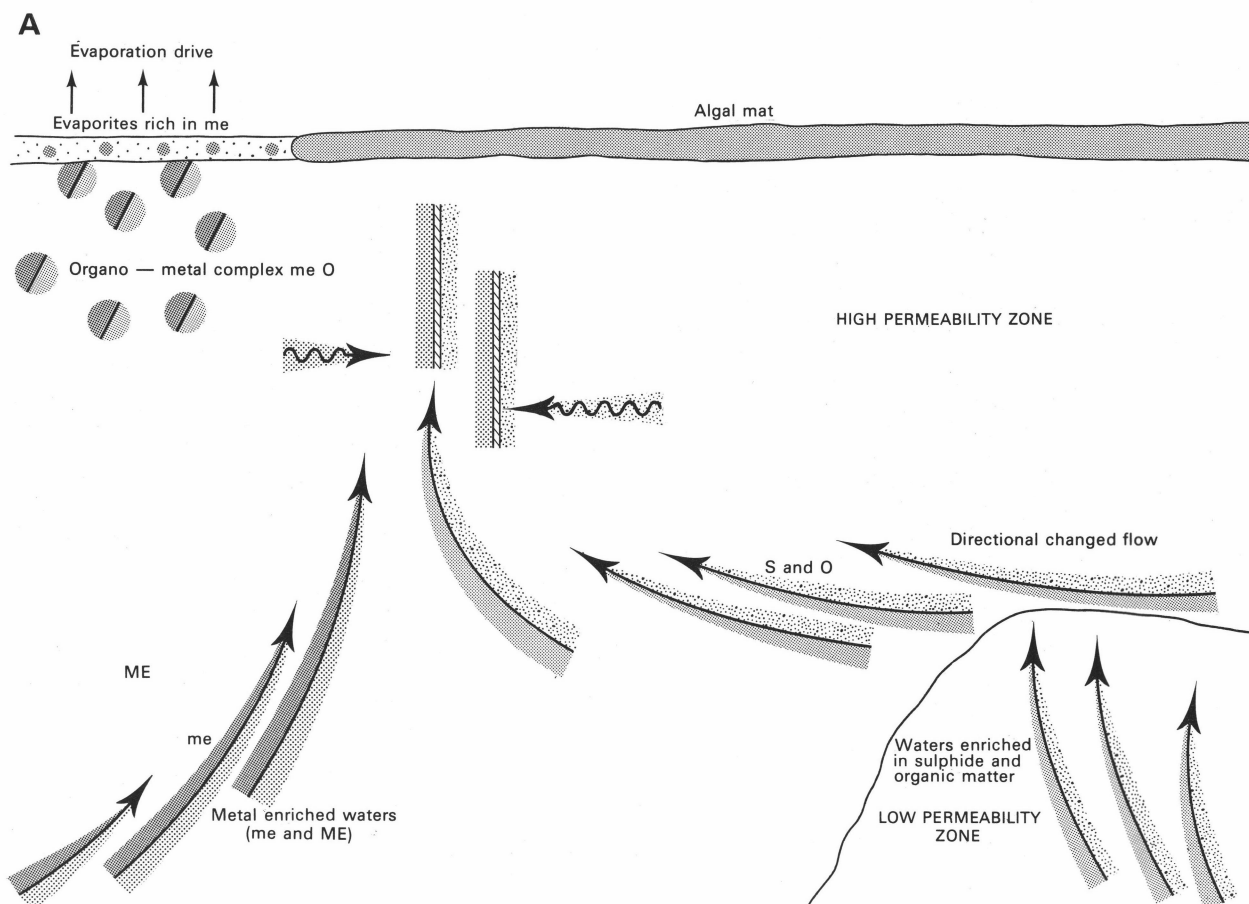
Some conclusions from simulating studies

From data obtained from the above simulation studies it is possible to derive some conclusions regarding the behaviour of natural marine evaporative sedimentary systems.

(a) The movement of interstitial waters through sediments may be greatly influenced by biological activity, the major effect of which is to change permeability. Such changes affect not only the quantitative aspect of flow, but the directional component as well, and may result in the alteration of conditions governing the mechanisms of deposition and/or solution of components of the sediments. An example would be chemical and physico-chemical changes in the fluid composition, a decrease in the evaporation drive through the surface of the sediments and selective passage of metals through algal mats (Bubela, 1980).

(b) The mineralogy and morphology of sediments becomes affected by the presence and composition of organic material, and may, in certain cases, such as in the presence of dolomite or ooids, be used as indicators of the environmental conditions during their formation (Davies & others, 1978; Ferguson & others, 1978).

(c) The production of cyclic and iso-paraffines of 4-carbons by biological processes makes their value as

A

Evaporation drive

Evaporites rich in me

Algal mat

Organo — metal complex me O

HIGH PERMEABILITY ZONE

Directional changed flow

S and O

ME

me

Metal enriched waters (me and ME)

Waters enriched in sulphide and organic matter

LOW PERMEABILITY ZONE

B

Evaporation drive

Evaporites rich in me

Algal mat

Decomposing Algae

Organo — metal complex me O

Flow of metal enriched waters (ME and me)

	Organic matter (O)		Metal (ME)		Evaporites		Diffusion
	Sulphide (S)		Metal (me)		Sulphide deposit		

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indicators of high temperatures and pressures in the sediments during their formation rather questionable (Bubela & others, 1975).

(d) Biological processes resulting in the production and/or consumption of CO_2 affect the Ca/Mg ratio in interstitial waters, and therefore directly influence the solution and deposition of carbonates and their mineralogy. These processes, frequently observed during diurnal changes in nature, are even more active during the establishment of algal mats and their subsequent biological decomposition (up to several months), when their effect can be very pronounced. The effects of diurnal changes tend to be mutually cancelling (Bubela, 1980).

(e) The formation of predominantly monomineralic sulfide deposits is not necessarily a manifestation of subsequent changes in the depositional environment (sequential introduction of metals, changes in pH and Eh, etc), but may be the result of diffusion in stationary interstitial fluids or converging and/or parallel flow patterns (Bubela & McDonald, 1969; Lambert & Bubela, 1970; Bubela, 1980, Bubela, 1981).

(f) The distribution of metals through sediments will be affected by their capacity to form organic complexes and the relative stability of such complexes compared with that of their corresponding sulfides (Hallberg & others, 1980).

Model for sulfide band formation under epigenetic conditions

A number of models have been suggested for environments where, owing to an evaporation drive, underground supply of metals and biologically or abiologically produced S^{2-}, metal sulfides are deposited. One such model has been described by Renfro (1974). This model describes the formation of mixed sulfide deposits, but cannot explain the formation of predominantly monomineralic strata in the sediments. Considering some of the observations described above and demonstrated in and by the simulating systems, it is possible to construct a model that does explain simply the separation of individual metals into distinct zones, not necessarily conforming to the direction of the sedimentary beds.

Basically, the model starts from the same concept as Renfro's, visualising an environment where metals and sulfide ions are supplied from their individual sources. The first modification of Renfro's model is to take into consideration the heteropermeability of the sediments. It has been shown that, owing to differences in permeability, significant directional variation of fluid movement will result. The second modification is due to the fact that algal mats may considerably reduce the evaporation drive and therefore alter the directional components of flow of the interstitial fluids. The next difference in the concept is due to the observation that organic complexing of metals may influence their availability to be precipitated as sulfides. Finally, the formation of banded sulfides from converging or parallel-moving fluids is taken into account.

The model is presented in Figure 1A. The surface of the sediments is partially covered by low-permea-bility algal mat. Interstitial waters emerging from a low-permeability zone of buried organic matter, where biological activity results in the production of S^{2-}, are enriched in organic complexing matter and S^{2-}. Owing to the change in permeability, the S^{2-}-rich waters deviate from their original direction. This trend is further enhanced by the evaporation drive operating at the mat-free surface. The metal-enriched waters, from their separate source, converge on the sulfide/organic matter stream. Because of the negligible compressibility of liquids, these streams eventually run parallel to each other with limited mixing, if the flow rate is sufficiently slow, to result in laminar flow. The same mechanism (Liesegang phenomenon) responsible for the formation of monomineralic sulfide bands during counter-current diffusion (Bubela & McDonald, 1969) will be operative and sulfide bands parallel to the flow will be formed. The orientation of the bands may be at a variety of angles to that of the sedimentary layers.

A variation to the above model is presented in Figure 1B. In this case, the metal-bearing waters move parallel to the sedimentary layers. The decomposing buried algae produce sulfide, which, owing to its concentration gradient, diffuses in a direction perpendicular to the flow of the metal enriched waters. Similarly to the situation described in Figure 1A, metal-sulfide bands will form parallel to the flow and the bedding.

The system on which this model is based varies significantly from that described by Bubela & McDonald (1969) and Lambert & Bubela (1970), where, in all the cases investigated, only the molecular movement of the solutes (metals and sulphide) was considered, and the solvent (water) was stationary. Therefore, in principle, the process leading to banding as described previously (Bubela & McDonald, 1969; Lambert & Bubela, 1970) may be classified as a diagenetic process, while the present model describes the formation of bands under epigenetic conditions. In both cases, these terms are used as defined by Williams (1979). In many instances it may be difficult to decide by which of these two processes the sulphide bands were formed. The epigenetic model indicates the feasibility of the processes envisaged by Williams (1979) for the McArthur River deposits: if some of the metals form organocomplexes of sufficient stability, they may be moved for a considerable distance from the precipitation zone and may eventually follow the evaporation drive, finishing as an enrichment in the surface evaporites.

In summary, the model presented here is capable of explaining certain problems associated with sulfide deposits in sediments and is believed to complement Renfro's model by providing plausible mechanisms for the formation of banded metal deposits at various angles to the sediments.

Acknowledgements

Figure 1. Models of sulphide band formation under epigenetic conditions.
A: Waters enriched in S= and organic matter (O) converge on metal-bearing waters (ME and me); ME does not form an organo-complex and is precipitated as a ME sulfide band. Metal me forms a stable organo-complex and is not readily precipitated as a sulfide, but is removed from the zone of precipitation and accumulates in the evaporites.
B: Sulfide ions produced by decaying algal mat diffuse down into the sediments' metal-bearing waters, and produce sulfide bands parallel to the bedding.

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