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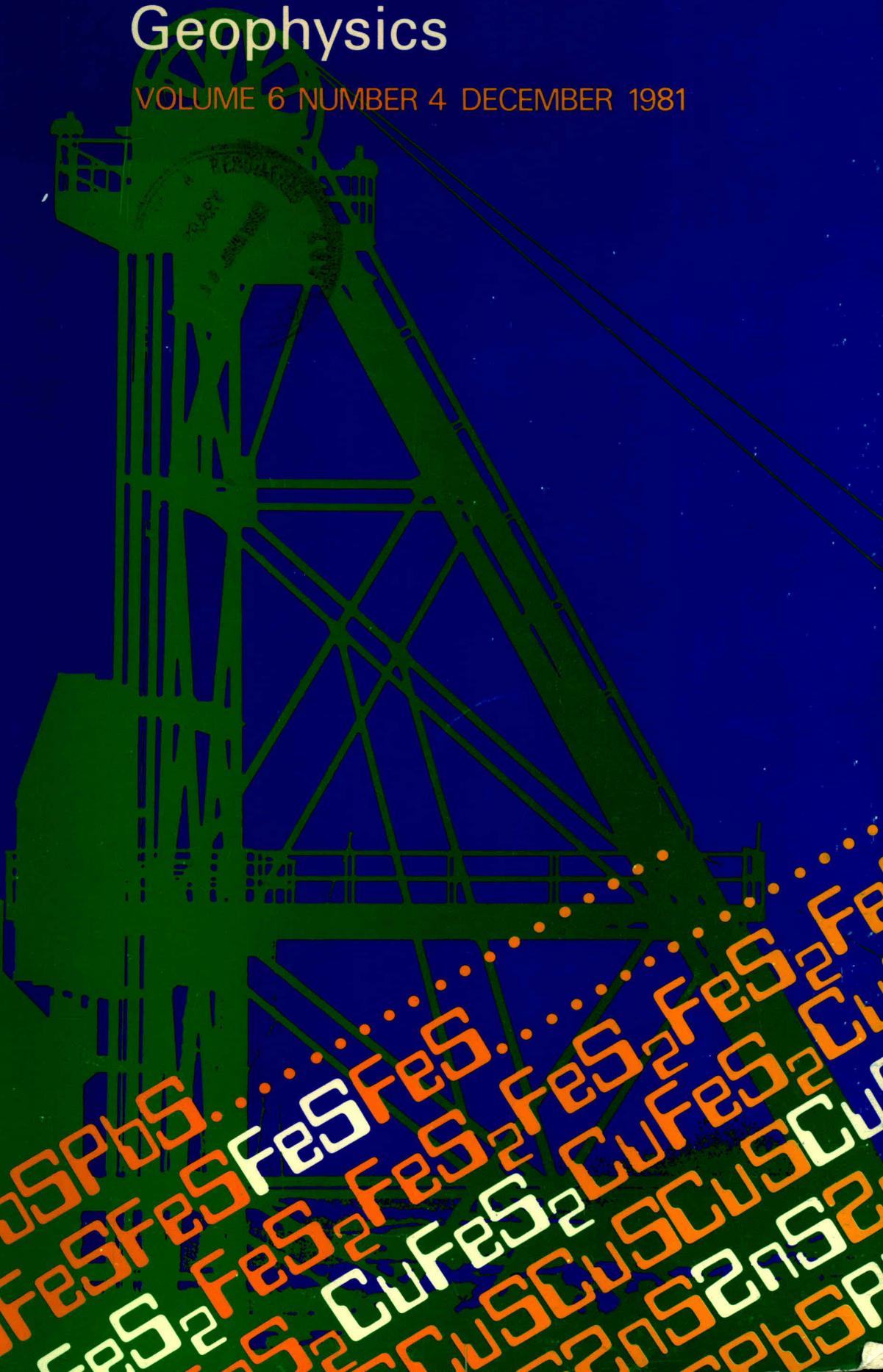
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## Preface

This issue of the Journal is devoted to summaries and some full texts of papers presented to a Symposium on **Sulphide Mineralisation in Sediments: Current Status of Syngenetic Theory**, held in Canberra from March 2-4, 1981. The Symposium was sponsored by the Baas Becking Geobiological Laboratory and formed part of the IGCP Project 157 on **Early Organic Evolution and Mineral and Energy Resources**.

The recognition that present reserves of economic minerals are nearing exhaustion as rates of consumption grow has focussed interest on the part that models of ore genesis might play in the exploration for deep-seated deposits of commercial grade. The idea that some stratabound base-metal sulphide ores may have formed syngenetically by contemporaneous deposition of ore constituents in a sedimentary pile, rather than by hydrothermal replacement, goes back to the early 1950s. Since then, syngenetic models have been proposed for many deposits throughout the world, often implying deposition in low temperature environments, where biological activity may have become involved in mineralisation.

Evidence for and against biological and other syngenetic processes in sulphide ore genesis was reviewed at the Symposium, which was organised around four main themes:

- ancient sulphide mineralisation
- modern settings and processes of sulphide generation and concentration
- the production and diagenesis of organic matter, the driving force for all biogeochemical processes in sediments
- the antiquity of the important biological processes of sulphate reduction and oxygenic photosynthesis.

The Symposium highlighted advances made over the past decade in our knowledge of mineral deposits and modern depositional systems. Problems arose, however, from variable usage of the terms syngeneses, diagenesis, and epigenesis, the boundaries of which seem more a function of discipline than timing.

Nevertheless, there appeared to be a general consensus that few major sulphide deposits are strictly 'syngenetic': low temperature and hydrothermal post-depositional events contribute towards their genesis.

*P. A. TRUDINGER*

*M. R. WALTER*



# Origins of sulphide in sediments

P. A. Trudinger<sup>1</sup>

Sulphide in sedimentary ore deposits may be derived directly from the mantle or by reduction of sulphate. Sulphide in modern hydrothermal deposits is thought to have formed abiologically by reactions between sulphate and ferrous iron or organic matter during deep circulation of sea water and meteoric waters through the crust at temperatures above about 200°C. Below about 70°C sulphate reduction is catalysed by bacteria. This process is widespread in anoxic basins and reducing sediments, and is dependent upon, and often controlled by, the supply of organic matter. The importance of sulphate reduction in carbon turnover has been demonstrated by comparisons of organic carbon production and sulphate reduction in marine sediments and by the discovery of several genera of sulphate-reducing bacteria capable of using a wide range of organic molecules. Recent kinetic studies of sulphate reduction in anoxic marine sediments have confirmed that sulphide accumulations equivalent to those in several major stratiform ores could be generated biologically. Fixed sulphide contents in normal unconsolidated reduced marine sediments, however, are generally an order of magnitude less than those of deposits such as at McArthur River and Mount Isa in the Northern Territory of Australia. The only modern examples of sediments with large fixed sulphide concentrations are those in which sulphide is of hydrothermal origin. One constraint on the concentration of fixed sulphides in sediments is the availability of reactable metals. It is possible that high concentrations of biogenic sulphides can be produced when metalliferous hydrothermal fluids are exhaled into biologically active anoxic basins or depressions.

## Introduction

In the early 1950s the idea developed that some stratiform base-metal sulphide ores may have formed syngenetically by contemporaneous deposition of ore constituents in a sedimentary pile, rather than by hydrothermal replacement (King, 1967). Initially, this concept was applied particularly to the Rhodesian Copper Belt and several base-metal occurrences in Australia, but in the intervening years syngenetic models have been proposed, although not universally accepted, for many deposits throughout the world. The feasibility of low-temperature syngenetic sulphide deposition was suggested by the discovery that several sulphide minerals, previously thought to be exclusively high-temperature forms, can be produced at low temperatures in biological (Baas Becking & Moore, 1961) and chemical (Roberts, 1967) systems.

Determining the source of sulphide in an ore deposit, however, has proved difficult, since there are no unequivocal criteria for distinguishing 'biogenic' from abiogenic sulphide minerals (Trudinger, 1976). The most commonly used criteria, those based on sulphur isotopic data, are often ambiguous: similar isotopic patterns can be generated by biological reactions and high-temperature exchange reactions between sulphide and sulphate (Ohmoto & Rye, 1979).

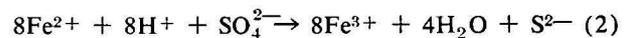
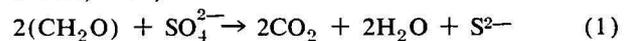
Some insight into environmental controls on mineralisation and processes of ore formation can be gained by studies of modern sedimentary environments (von der Borch, 1981). In this paper I briefly review the known present-day sources of sulphide, and attempt to assess the potential contribution of biologically controlled sources to ore genesis, in the light of information obtained from examinations of Recent sediments. Emphasis is placed on quantitative aspects, since there can be little doubt that biological activity has contri-

buted significantly to 'background' levels of sulphide in sedimentary rocks over much of geological history. The problem is to interpret anomalous sulphide accumulations.

The main sulphur pools from which sulphide in sediments can be derived are the mantle, and seawater or evaporite sulphate, which are reduced by either chemical or biological mechanisms. In hydrothermal situations some sulphide may be derived more or less directly from volatile phases in the mantle (Bonatti, 1975), but there is isotopic evidence that, for about the last 2000 m.y., sulphate has been a major source of sulphide in sedimentary deposits (Sangster, 1968, 1976; Monster & others, 1979; Schidlowski, 1979; Skyring & Donnelly, 1982 — in press).

## Abiological reduction of sulphate

At temperatures above about 300°C, sulphate is chemically reduced, at near-neutral pH values, by organic matter (Equation 1: Dhannoun & Fyfe, 1972; Toland, 1960; Kiyosu, 1980) or ferrous iron (Equation 2: Hajash, 1975; Mottl & others, 1979; Seyfried & Dibble, 1980).



Reactions between ferrous iron in silicate minerals and sulphate were originally proposed by Spooner & Fyfe (1973) to account for the presence of sulphides associated with ophiolitic complexes. The reactions appear to be responsible, at least in part, for the formation of dissolved and mineral sulphides in experiments on the hydrothermal alteration of basalts by sea water (Hajash, 1975; Mottl & others, 1979): alteration minerals identified in various experiments include pyrite, pyrrhotite, chalcopyrite, and acanthite.

During the course of sea water/basalt reactions the original slightly basic Na-Mg-SO<sub>4</sub>-Cl solution changes to a slightly acidic, predominantly Na-Ca-Cl solution

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System	pH	Na	Si	Ca	Mg	SO <sub>4</sub> -S	Fe	Mn	Ca:Mg Mol ratio	Reference
Normal sea water	8.2	10 800	4	410	1300	900	0.02	0.01	0.19	1
Seawater-basalt (1:1)										
300°C, 506 days	5.4	11 300	280	2 000	15	99	11	7	80	
400°C, 272 days	4.0	11 700	740	1 200	11	120	78	53	65	
Reykjanes geothermal brine: drill hole No. 8	6.1	9 610	374	1 530	16	10.3	0.5	2.0	57	4,5
Atlantis II Deep 56°C brine	5.6	92 600	30	5 150	760	280	80	80	4	1
Salton Sea geothermal brine (I.I.D. No. 1 well)	5.2	50 400	187	28 000	54	1.7	2290	1400	311	6

**Table 1. Partial chemical compositions (in ppm) of experimental and modern hydrothermal solutions.**

References: 1, Emery & others (1969); 2, Mottl & Holland (1978); 3, Mottl & others (1979); 4, Björnsson & others (1972); 5, Mottl & others (1975); 6, Muffler & White (1969).

Supplements				Temperature (°C)	Duration (days)
H <sub>2</sub> S (Saturated)	Na <sub>2</sub> S (400 µmol)	S <sup>0</sup> (0.1 g)	FeCl <sub>3</sub> (1.8 µmol)		
NAPHTHENIC-AROMATIC OIL (0.1% S)					
+	—	—	—	80	39
+	—	+	—	80	39
—	+	+	—	80	10
HIGHLY PARAFFINIC OIL (<0.1% S)					
—	+	—	—	80	10
+	—	+	+	80	42
—	+	+	+	80	84
+	—	—	—	120	14
+	—	—	—	190	10
+	—	+	—	120	14
+	—	+	—	190	10

**Table 2. Experimental conditions for attempted abiological reduction of sulphate.**

All mixtures contained oil (4g), 17.5% aqueous NaCl (4 gm) and Na<sub>2</sub><sup>35</sup>SO<sub>4</sub> (0.4 mmol: 2.3 x 10 dpm).

with a high Ca/Mg ratio, low sulphate content, and a significant enrichment in metals such as Fe and Mn (Bischoff & Dickson, 1975; Hajash, 1975; Seyfried & Bischoff, 1977, 1979; Mottl & Holland, 1978; Seyfried & Mottl, 1977; Mottl & others, 1979). The experimentally derived solutions resemble, at least qualitatively, hydrothermal fluids like those of the Atlantis II Deep, and Salton Sea and Reykjanes geothermal fields, which are associated with active oceanic spreading centres and rift zones (Table 1). The results provide an experimental foundation for the hypothesis that hydrothermal fluids in these tectonically active areas are generated during deep circulation of sea water through the crust (see review by Bonatti, 1975). The fluids acquire their characteristic chemistry by interacting with the rocks through which they pass: solution of evaporites will lead to high salinities. Sulphide is formed by high-temperature reduction of sulphate by ferrous iron (or perhaps by organic matter—Kaplan & others, 1969). Two modern deposits to which this model has been applied are the sulphide facies of the Atlantis II Deep sediments (Craig, 1969; Shanks & Bischoff, 1977) and the polymetallic massive sulphides formed on the East Pacific Rise near 21°N (Hekinian & others, 1980).

Abiological sulphate reduction by organic matter at lower temperatures (80-200°C) has been proposed as a source of sulphide in Mississippi Valley-type deposits (Barton, 1967; Dunsmore, 1973), and to account for isotopic changes in sulphide and organic sulphur in oil fields during petroleum maturation (Orr, 1974). Low-temperature abiological sulphate reduction, however, has not been demonstrated experimentally. In unpublished experiments, L. A. Chambers, D. T.

Rickard & P. A. Trudinger heated crude oil fractions with <sup>35</sup>S-labelled sulphate at 80-190°C under several conditions (Table 2). In no instance was the formation of radioactive sulphide demonstrated unequivocally. It would, however, be premature to reject the possibility of low-temperature abiological reduction of sulphate. Very little experimental work has been done: in particular a more extensive range of the organic matter, and potential catalysts, such as metal ions and mineral surfaces, need to be examined.

### Biological sulphate reduction

Below about 70°C, sulphate is readily reduced to sulphide by dissimilatory sulphate-reducing bacteria, which use sulphate for the anaerobic oxidation of organic matter (Postgate, 1979). The process is a characteristic feature of the most anoxic basins and sediments. The rate of sulphate reduction and the extent to which sulphate is reduced is generally controlled by the supply of organic matter. Recent studies have provided quantitative evidence of the importance of microbial sulphate reduction in carbon cycling in marine sediments. From the rates of sulphide formation and carbon dioxide fixation in peritidal, cyanobacterial mat sediments at Mambray Creek, Spencer Gulf, South Australia (Bauld & others, 1980), G. W. Skyring (personal communication) calculated that over 50 percent of the organic matter produced by photosynthesis was degraded during sulphate reduction. Similar results have been reported for the littoral sediments of Solar Lake, a hypersaline, shallow-water pond on the Sinai coast (Jorgensen & Cohen, 1977), for marshland

Organism	Substrate <sup>a</sup>			
	Lactate	Succinate	Aromatic compounds <sup>b</sup>	Fatty acids (Carbon No.)
<i>Desulfobacter postgatei</i>	—	—	—	2
<i>Desulfobulbus propionicus</i>	+	—	—	3
<i>Desulfococcus multivorans</i>	+	—	+	2-14
<i>Desulfonema limnicola</i>	+	+	—	2-14
<i>Desulfonema magnum</i>	—	+	+	2-10
<i>Desulfosarcina variabilis</i>	+	+	+	2-14
<i>Desulfovibrio sapovorans</i>	+	—	—	2-18
<i>Desulfovibrio baarsii</i>	—	—	—	2-18

Table 3. Organic substrates for new isolates of sulphate-reducing bacteria: partial listing (from Widdel, 1980).

<sup>a</sup> complete oxidation is indicated by boldface: incomplete oxidation by medium face.  
<sup>b</sup> e.g. benzoate, phenylacetate.

sediments (Skyring & others, 1979; Howarth & Teal, 1979), and for sediments of Limfjorden, a shallow, brackish-water body cutting through the northern part of Denmark (Jørgensen, 1977).

Until quite recently, the carbon sources used by sulphate-reducing bacteria were thought to be limited to a few simple organic molecules, such as lactate and pyruvate, which were incompletely oxidised to acetate (Postgate, 1979). This was difficult to reconcile with the quantitatively important role played by these bacteria in carbon turnover in anoxic sediments. Widdel (1980), however, has isolated from marine, brackish-water, and fresh-water muds, sulphate-reducing organisms with much broader metabolic capabilities (Table 3). It is now apparent that, as a group, the sulphate reducers can effect the complete oxidation of a wide range of organic compounds, including fatty acids up to C<sub>18</sub>. This provides a biochemical foundation for the field evidence that much of the energy supplied to anoxic marine sediments in the form of photosynthetically derived organic matter is used to drive the reduction of sulphate.

### Quantitative aspects of sulphide deposition

Trudinger & others (1972) and Rickard (1973) concluded that present-day rates of sulphate reduction in marine sediments, for example those of the Black Sea, are sufficient to produce ore-grade sedimentary sulphide accumulations. This conclusion is supported by recent determinations of sulphate reduction rates in shallow-water coastal sediments (Table 4), which are of interest in view of proposed ore-genesis models involving shallow-water or sabkha environments (Renfro, 1974; Smith, 1976). These rates are one to two orders of magnitude higher than those in Black Sea sediments and, if maintained over long geological periods, could provide sulphide concentrations equivalent to those in several stratiform ore deposits (Table 4). Solar Lake and Mambay Creek are particularly relevant in the context of Precambrian mineralisation, since, in these areas, the input of organic matter from higher plant, terrigenous, and anthropogenic sources is minimal, and sulphate reduction is supported largely by authigenic organic matter produced by cyanobacteria. The differences in sulphate reduction rates between shallow-water environments and the Black Sea are almost certainly related to organic matter supply. In the former, zones of sulphate reduction are close to those of primary production, whereas the sediments of the Black Sea are up to 2000 m below the zone of photosynthesis, and about 80 percent of primary

	Rate (g S m <sup>-2</sup> y <sup>-1</sup> )	Reference
MODERN SEDIMENTS <sup>a</sup>		
Black Sea	17	Sorokin (1962)
Mambay Creek	200-400	G. W. Skyring (personal communication)
Limfjorden	100	Jørgensen (1977)
Solar Lake	800	Jørgensen & Cohen (1977)
Salt marsh, New England	2400	Howarth & Teal (1979)
Salt marsh, Essex	99-140	Nedwell & Abram (1978)
ORE DEPOSITS <sup>b</sup>		
McArthur River	12-46	Trudinger & others (1972)
Mount Isa	10-40	Trudinger & others (1972)
Roan Antelope	1-4	Trudinger & others (1972)
Kupferschiefer Mansfeld	3-12	Trudinger & others (1972)

Table 4. Rates of sulphate reduction or sulphide deposition in modern sediments and ore deposits.

<sup>a</sup> Rate of sulphate reduction measured using <sup>35</sup>S-labelled sulphate

<sup>b</sup> Calculated rate of sulphide deposition based on total sulfide and time of ore formation.

organic carbon is degraded by aerobic processes during settling through the water column (Deuser, 1971). The exceptionally fast rate of sulphate reduction in the New England salt-marsh sediments (Table 4) has been attributed; in part, to a large supply of organic matter from the roots of sea-grass (*Spartina*), which dominates this environment.

In modern sediments, however, most biogenic sulphide is rapidly reoxidised to sulphate. In the sediments of Limfjorden and Solar Lake the proportions of biologically produced sulphide fixed as metal sulphides are estimated to be less than 10 percent (Jørgensen, 1977), and about 0.1 percent (Jørgensen & Cohen, 1977), respectively, while at Mambay Creek essentially all sulphide is recycled within weeks or months (Chambers, 1982). This lack of fixation is reflected in low sulphide levels in unconsolidated detrital and bioclastic reducing sediments: maximum sulphide levels are generally below 1.5-2 percent and the mean values are below 1.0 percent (Fig. 1). Higher concentrations (up to 5 percent S) in the form of pyrite have been claimed for salt-marsh sediments colonised by *Spartina* (Howarth & Teal, 1979). However, the analytical method used for pyrite-sulphur (as sulphate after oxidation of HCl-treated samples) would not exclude fixed forms of sulphate, which, in similar *Spartina*-dominated sediments, may reach 30 percent of the total sulphate (Skyring & others, 1979).

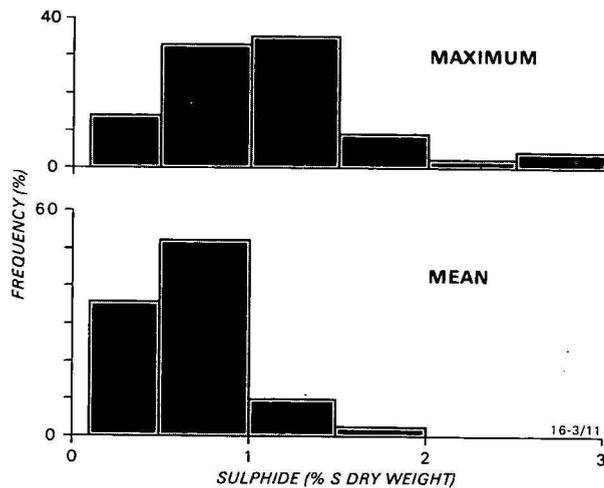


Figure 1. Frequency plots of mean and maximum values for fixed sulphide in unconsolidated, reduced marine sediments (sediments containing an average of less than 0.1% sulphide not included).

Data sources: Black Sea (Berner, 1974; Migdisov & others, 1974; Calvert & Batchelor, 1978); Baltic Sea (Hartmann & Nielsen, 1969); Great Bay Estuary, NH (Lyons & Gaudette, 1979); Gulf of California (Berner, 1964; Lein & others, 1976; Goldhaber & Kaplan, 1980) Californian off-shore basins (Kaplan & others, 1963; Goldhaber & Kaplan, 1974); Cariaco Trench (Goldhaber & Kaplan, 1974); Pacific Ocean (Lein & others, 1976; Volkov & others, 1976); Long Island Sound (Berner, 1970; Goldhaber & others, 1977); Limfjorden (Jørgensen, 1977); Solar Lake (Jørgensen & Cohen, 1977); Pedernales, Venezuela (Thode & others, 1960); Indian Ocean (Cook & others, 1978), Moroccan Basin (Migdisov & others, 1980).

The concentrations of sulphide shown in Figure 1 compare reasonably well with those of relatively low-grade ores like the Kupferschiefer and Roan Antelope deposits, but are an order of magnitude below those of high-grade ores such as the McArthur HYC and Mount Isa (Table 5). The only known modern examples of high-grade sulphide mineralisation are hydrothermal, exemplified by the sulphide facies of the Red Sea and the precipitates from the Salton Sea geothermal brines (Table 5).

An upper limit on the concentration of fixed biogenic sulphide in a sediment will be set by the supply of reactable metals. Iron is by far the most abundant metal in normal marine sediments, and typically reaches

	Sulphide (%S)	Reference
ORE DEPOSITS		
McArthur (HYC)	14	Trudinger & others (1972)
Mount Isa	12	Trudinger & others (1972)
Roan Antelope	1.1	Trudinger & others (1972)
Kupferschiefer Mansfeld	3	Trudinger & others (1972)
HYDROTHERMAL DEPOSITS		
Red Sea (sulphide facies)	17	Emery & others (1969)
	7.5	Shanks & Bischoff (1980)
Salton Sea precipitate	12	Skinner & others (1967)

Table 5. Average sulphide contents of ore deposits and modern hydrothermal deposits.

2-5 percent in shallow-marine and deep-sea muds (Rösler & Lange, 1972). Thus the theoretical upper levels of fixed sulphide (as  $\text{FeS}_2$ ) would be in the order of 2-6 percent, still well below those required for high-grade sulphide mineralisation. (In fact, the amounts of potentially reactable iron in modern sediments often exceed those fixed as sulphide (Berner, 1974), indicating that other factors are important in limiting biogenic sulphide accumulation).

The question can then be raised whether bacterial sulphate reduction can contribute to sulphide deposition in environments in which anomalous levels of metals are introduced by hydrothermal fluids. Some consider that dual sources of sulphur are required to account for isotopic and other characteristics of, for example, the Rammelsberg deposit (Anger & others, 1966) and sulphide deposits at McArthur River (Smith & Croxford, 1973; Croxford & others, 1975; Williams, 1978a,b).

In the best studied example of modern hydrothermal deposition, the Atlantis II Deep of the Red Sea, the present-day brines and sediments appear to be sterile (Trüper, 1969; Watson & Waterbury, 1969). There is isotopic evidence for biogenic sulphide in the basal detrital-oxidic-pyritic unit of the Atlantis II Deep sediments. However, biological sulphate reduction appears to have ceased, except perhaps around the periphery of the pool, with the onset of hydrothermal activity, leading to the deposition of the first sulphide facies (Shanks & Bischoff, 1980). The hydrothermal fluids of the east Pacific seafloor spreading centres support dense populations of microorganisms and fauna (Jannasch & Wirsén, 1979; Karl & others, 1980), but are discharged into oxygenated ocean waters that are not conducive to the development of anaerobic biological processes.

Two basins, Lake Kivu and Guaymas Basin, display features that might favour deposition of mixed hydrothermal/biogenic sulphides. Lake Kivu is situated in the East African rift valley and is fed from below by metalliferous thermal waters, which cause temperature and salinity stratification (Degens & Kulbicki, 1973; Degens & others, 1973). Its maximum depth is about 500 m and, below about 50 m, the waters are anoxic and contain dissolved sulphide up to  $10 \text{ mg l}^{-1}$  (Degens & others, 1972). The uppermost sediments are finely laminated, rich in organic matter (up to 15 percent organic-C), and contain about 4 percent iron in the form of nickel-rich pyrite: buoyant resinous spheres containing microcrystalline sphalerite occur suspended in the water column (Degens & others, 1972). The primary productivity of Lake Kivu is high (about  $380 \text{ g C m}^{-2} \text{ y}^{-1}$ ) and supports a rich population of methanogenic bacteria in the anaerobic surface sediments (Degens & others, 1973). The sediments of Lake Kivu contain 10-15 percent sulphides on a dry-weight basis (Deuser & others, 1973). However, no data on bacterial sulphate reduction or the sources of sulphide have been reported.

The Guaymas Basin, Gulf of California, is part of the system of spreading centres and transform faults that extends from the East Pacific Rise to the San Andreas Fault system (Moore, 1973). The basin includes two spreading rift valleys, about 2000 m in depth (Einsele & others, 1980), and a white sulphide-rich talc deposit was discovered in the northernmost valley (Lonsdale & others, 1980). The deposit appears to have precipitated from fluids with temperatures of

about 280°C, which the authors suggest were generated during intrusion of basaltic magma into soft sediments, causing compaction of the sediments and expulsion of heated pore waters on the sea floor. The talc deposit overlies an organic-rich diatomaceous mud that contains widespread pyrite and free hydrogen sulphide, probably of biogenic origin. The main sulphide phase in the talc is pyrrhotite with a  $\delta^{34}\text{S}$  value ( $-4\%$ ) intermediate between those characteristic of modern hydrothermal and biogenic sulphides (Table 6). This result is consistent with a dual sulphur source for pyrrhotite mineralisation (Lonsdale & others, 1980), but it may be noted that a similar  $\delta^{34}\text{S}$  value ( $-5\%$ ) is exhibited by pyrite concretions in the 7000-m deep Romanche fracture zone (equatorial Atlantic), where scarcity of sediments and lack of organic matter render bacterial sulphate reduction unlikely (Bonatti & others, 1976).

Source	$\delta^{34}\text{S}(\%)^a$	Reference
Biogenic sulphides in surface marine sediments	-40 to -6	Chambers (1981)
Experimental basalt-seawater interactions	+8 to +21	Ohmoto & others (1976)
Abiological reduction of sulphate by organic matter <sup>b</sup>	+10 to +20	Kiyosu (1980)
East Pacific Rise	+2 to +3	Hekinian & others (1980)
Atlantis II Deep (sulphide facies)	+2 to +14	Shanks & Bischoff (1980)
Guaymas Basin	-4	Lonsdale & others (1980)

**Table 6.** Sulphur isotope compositions of modern hydrothermal and biogenic sulphides.

<sup>a</sup>Relative to meteoric.

<sup>b</sup>Sulphate normalised to  $\delta^{34}\text{S} = +20\%$ .

## Conclusions

In the modern marine environment, there are several examples of high-grade sulphide deposition from abiogenic sulphide exhaled in hydrothermal fluids at oceanic spreading centres and rift zones. Bacterial sulphate reduction is a potential source of high sulphide concentrations in normal marine sediments, but fixation is limited by lack of reactable metals, and could lead, at best, to the formation of relatively low-grade ores of the Roan Antelope and Kupferschiefer types. The formation of high-grade deposits from purely biogenic sulphide would appear to require a set (or sets) of circumstances for which no modern analogue is known, but which may have existed in the past. Biogenic sulphide might also contribute to mineralisation in hydrothermal situations: while there are, as yet, no clear-cut examples in the modern environment, further detailed chemical, isotopic, and biological studies on rift-related basins such as Lake Kivu and Guaymas Basin could well prove rewarding.

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## Organic matter in ancient ores and sediments

J. D. Saxby<sup>1</sup>

Organic material incorporated in an ore or a sediment may represent the resistant parts of organisms, organic compounds adsorbed on inorganic minerals, organic precipitates from chemical reactions in basin waters, or detrital grains eroded from older carbonaceous rocks. In addition, hydrocarbons may be generated elsewhere in a basin before migrating into and being retained in the rocks under consideration. During diagenesis and metamorphism under non-oxidising conditions, the chemical composition of organic matter from all sources progressively changes as volatile compounds (including carbon dioxide, water, and hydrocarbons) are evolved. All types of carbonaceous source material give graphite as the final solid product, but in various amounts, depending on their initial composition and subsequent history. Bacterial or aerial oxidation of solid organic materials is most rapid at low ranks and initially causes an increase in oxygen/carbon ratios before complete removal of carbonaceous matter is achieved. At high temperatures, oxidation by water can completely convert graphite to carbon dioxide. Data are given on the insoluble organic matter isolated by demineralisation of samples from the Red Sea, Julia Creek, McArthur River, Mount Isa, Broken Hill, Cobar, Woodlawn, Kambalda, Rum Jungle, Alligator River (Australia) and the Witwatersrand (South Africa). Most of these samples contain material, probably of algal origin, that is now at the graphitic stage of metamorphism. Organic matter from recent sediments in the Red Sea and ore-related rocks from McArthur River, Mount Isa, and Broken Hill show a progressive change in rank consistent with a syngenetic theory of ore formation. The presence (or even the absence) of carbonaceous material in an ore or sediment is a valuable parameter in reconstructing the chemical and biological environment of genesis and subsequent geological changes.

### Introduction

The origin of organic matter in certain ore deposits and its role in the diagenesis and metamorphism of metalliferous sediments are often poorly understood (Breger, 1963; Saxby, 1976). In fact, carbonaceous material has been suggested as the 'principal stumbling block' in reconstruction of the environments of ore genesis (Krauskopf, 1955). The following questions can be of importance to geophysicists and processing engineers, as well as geologists and geochemists involved in exploration: (1) What can be deduced about the origin and properties of an ore when organic matter is present? (2) What does the absence of carbonaceous material in an ore reveal about its genesis and history?

Much has been written regarding organic matter in certain ores and its geochemical significance (for example: Connan & Orgeval, 1976; Macqueen, 1976; Estep & others, 1980; Landais & Connan, 1980). This paper does not seek to review the whole field, but simply to outline some general principles, and present and briefly discuss data for organic material isolated from a variety of Australian ores.

### Incorporation of organic matter in sediments

Five basic mechanisms are recognised through which carbonaceous matter can become part of a sediment.

#### *Direct supply of organisms*

The simplest incorporation mechanism is for the organic parts of macro- or microorganisms to accumu-

late along with inorganic material as part of the bottom mud in a sedimentary basin. The proportions of carbohydrate, protein, lignin, and lipids in the original living organisms will vary greatly, and these in turn will suffer various degrees of solution in the water column, principally as a result of bacterial activity. The extent of this microbial reworking will determine whether the physical shapes of the original organisms are retained or whether only biologically resistant fragments become buried below the sediment/water interface. Bacterial solution can occur under both oxic and anoxic conditions. In general, lignin and lipids are more resistant than carbohydrates and proteins, but all four classes of compounds can be rendered soluble if conditions are suitable for sufficiently rapid oxidation. Figure 1 shows the approximate composition of these chemical precursors expressed in an atomic hydrogen/carbon versus oxygen/carbon diagram.

An association between metals and organic matter may be established at this early stage if resistant metal-organic compounds are present or are formed. For example, chemical entities in which metals are bonded through carboxyl, sulphide, amine or, particularly, porphyrin groups may survive from the original organism.

#### *Adsorption*

Organic matter dissolved in the waters of a basin can be adsorbed by particulate inorganic material and carried down into the sediment. Weak physical adsorption or strong chemical adsorption can lead to thin films of organic material on particles of large surface area, such as colloids. Adsorbed organic molecules will tend to be relatively small. Whether or not they survive subsequent bacterial reworking will depend on conditions within the basin.

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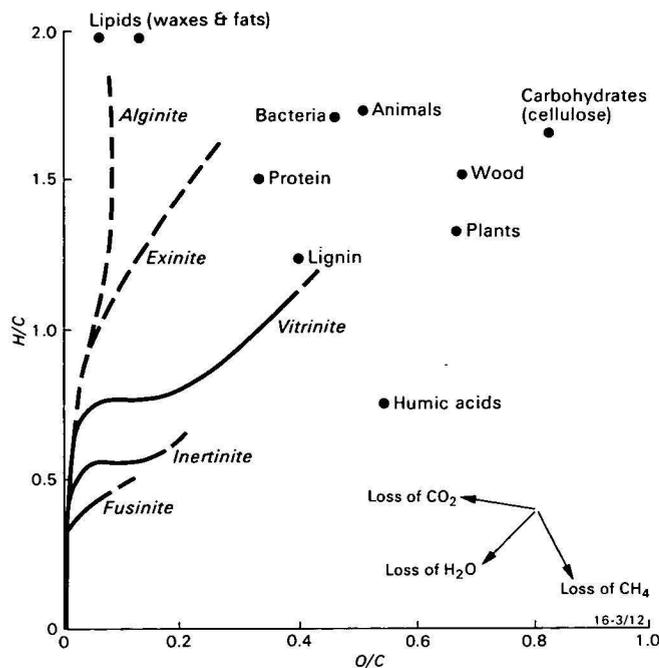


Figure 1. Atomic hydrogen/carbon versus oxygen/carbon, showing average values for precursors of sedimentary organic matter and lines of increasing diagenesis/metamorphism for coal macerals.

**Precipitation**

In certain cases, dissolved organic matter may precipitate from the water column or from pore waters in a sediment by reaction with metal ions or as a result of changes in pH. The precipitation of some metal-organic compounds may be accompanied by changes in the oxidation state of the metal. Precipitated material, which is resistant to bacterial attack, may fall directly into the sediment pile or first be adsorbed on the surface of a suitable inorganic particle.

**Detrital supply**

Organic material eroded from coal seams and other carbonaceous rocks may survive transport to a new basin and be redeposited as particulate matter. This is most likely to occur where the rank of the carbonaceous material has progressed sufficiently towards graphite for rates of solution during transport to be relatively slow. Detrital organic matter in a sediment is often indicated by the presence of microscopically distinct grains; these may show higher reflectivities than the original coal, owing to oxidation of the particle or its surface.

**Hydrocarbon migration**

At any time after consolidation of a sediment, liquid or gaseous hydrocarbons generated elsewhere in the basin may migrate into sufficiently porous and permeable rocks located in a suitable structure. There are at least two ways in which such organic fluids can give rise to a solid carbonaceous component in the sediment:

(1) Slow loss of the more volatile components through the 'cap rock' will tend to concentrate a solid fraction of high molecular weight hydrocarbons. This residue ('bitumen') may be virtually immobile (unless temperatures are increased), occupying mainly voids and fissures in the rock and exhibiting no biological structure except at the molecular level.

(2) If conditions are suitable for bacterial growth at hydrocarbon/water interfaces, hydrocarbons will gradually be converted to carbon dioxide and water, until only the most resistant high molecular weight 'tarry' components remain. This organic residue will contain some contribution from bacterial remains and may coexist with secondary carbonates in cracks or previously porous 'reservoirs'.

Often processes (1) and (2) occur simultaneously.

**Effect of diagenesis and metamorphism on organic matter**

As indicated above, major changes take place in the composition of sedimentary organic material in the first few metres below the sediment/water interface. More than 90 percent of the carbon in a living organism may be lost by bacterial oxidation and solution. Chemically resistant carbonaceous material, related in many cases to lignin or polymerized unsaturated lipids, may survive in the solid form. With increasing temperature and depth of burial this material will undergo changes analogous to coalification or to the maturation of oil shales and petroleum source rocks.

Figure 1 shows diagrammatically how the compositions of coal macerals are progressively altered. The most precisely defined line is that for vitrinite. Organic matter in most sediments and ores consists of a mixture of maceral types, and bulk compositions will always represent average values. The change from low-rank to medium-rank material is principally accompanied by the loss of carbon dioxide and water (Fig. 2). The subsequent conversion to higher ranks and, finally, graphite occurs with the evolution of mainly methane and other hydrocarbons. At any stage of this progression, if the organic matter encounters oxidising conditions, partial

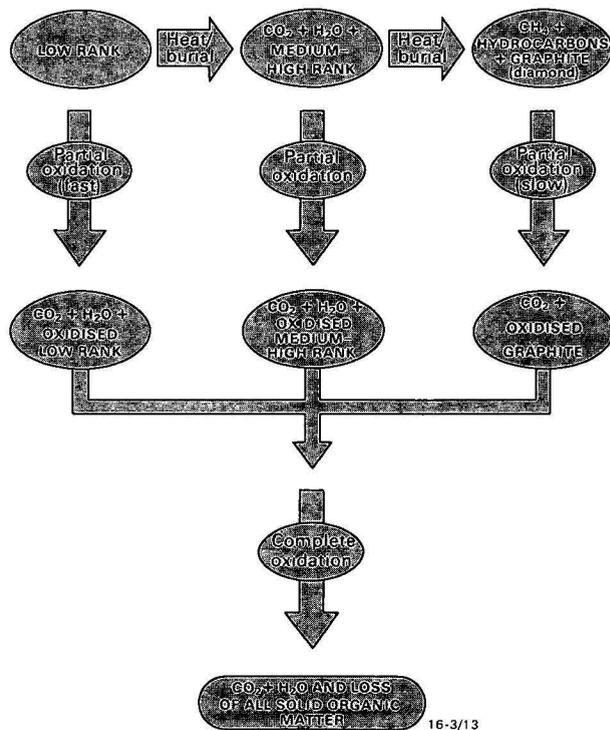


Figure 2. Fate of solid organic material during diagenesis and metamorphism.

Sample	Organic carbon (%)	Elemental composition (%; dry, mineral-free basis)					Ash (%)
		C	H	N	O	S	
Metalliferous Red Sea sediment (Recent)	0.5	66.0	6.5	3.1	21.4	3.0	3.1
Julia Creek oil shale (Cretaceous)	15.0	74.6	8.0	2.2	9.8	5.4	2.4
McArthur River: HYC ore	0.4	84.2	5.3	1.3	6.9	2.3	3.8
shale (57 m)	4.5	83.5	6.4	1.3	7.1	1.7	8.1
Coxco ore (178 m)	0.9	88.8	6.5	0.7	0.9	3.1	34.5
Karns Dolomite (outcrop)	0.1	71.2	3.8	1.3	23.0	0.8	4.2
Mount Isa: Black Star ore	0.6	95.0	1.5	<0.5	1.5	2.0	9.8
Black Rock ore	0.9	95.6	1.2	<0.5	3.0	0.2	11.9
1100 ore	0.4	92.9	1.5	<0.5	1.0	4.6	31.8
Hilton ore	0.3	93.6	1.8	0.4	2.4	1.8	30.1
Mount Oxide shale	1.5	91.0	1.7	0.2	3.6	3.5	11.7
Spinifex Queen shale (309 m)	1.2	95.2	1.8	1.0	2.0	0.0	41.1
Gunpowder Creek shale (113 m)	3.5	93.5	1.0	1.0	4.4	0.0	15.0
North Broken Hill shale	1.0	99.9	0.1	<0.1	<0.1	<0.1	7.9
Cobar ore (Silurian)	<0.1	96.7	1.2	<0.1	2.1	<0.1	12.4
Woodlawn ore (480 m) (Silurian)	2.1	91.5	0.6	0.8	1.5	5.5	5.6
Kambalda shale (288 m)	0.6	98.4	0.8	0.2	0.3	0.3	34.0
Rum Jungle: Woodcutters ore (104 m)	1.2	96.9	0.7	0.1	2.3	<0.1	8.7
shale	2.2	98.9	0.1	<0.1	0.6	0.4	6.3
South Alligator River shale (dump)	1.7	84.8	1.5	1.2	12.1	0.4	5.3
South African thucholite	47.3	91.0	3.3	0.6	4.0	1.2	12.9

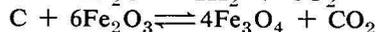
**Table 1. Carbonaceous material obtained by demineralisation of ores**

Ages are Precambrian unless shown otherwise

Depths (where known) are in parentheses; most other samples are from mines

(or even complete) loss of carbon as carbon dioxide is a possibility.

Under more extreme metamorphic conditions, graphite itself participates in reactions that effectively remove all organic matter from the sediment or ore. Possible reactions include:



Hence, under oxidising or aqueous conditions at high temperatures, an initial association of organic matter with a sediment can be destroyed. This is most likely where carbon dioxide can be removed as a gas, in solution, or as a metal carbonate. It is thus conceivable that some metamorphosed ore bodies that now contain no organic carbon were originally formed with carbonaceous matter playing a major role.

### Organic matter in ores

The level of organic carbon is often low (<1%), even in relatively carbonaceous ores, and the separation and characterisation of such material can be difficult. Usually, soluble organic compounds (if present) are removed with a solvent such as chloroform and the insoluble organic material (kerogen) is recovered by demineralisation. Treatment with dilute hydrochloric acid removes most carbonates and oxides, a mixture of hydrofluoric and hydrochloric acids dissolves most silicates, and hydrochloric-resistant sulphides (particularly pyrite) are best removed with lithium aluminium hydride. Repeated treatment with these reagents under the mildest possible conditions is usually necessary to obtain kerogen with a minimum of mineral matter.

Insoluble organic matter has been isolated from a variety of Australian and overseas ores and ore-related shales, using chemical demineralising techniques (Table 1). Details of the geology of the Australian deposits are included in Knight (1975). Most of the samples were selected because of their apparent organic content, and may, therefore, be richer in organic matter than the average ore. Atomic ratios for each of the isolated kerogens are plotted in Figure 3.

Since most of the ores in Table 1 are Precambrian, bacterial and algal remains must constitute the main biological precursor to the organic material remaining in each sample. It is thus instructive to study how a solid residue from algae can change in composition (Fig. 4). Under non-oxidising conditions, lipid-rich algal remains with a hydrogen/carbon ratio greater than ~1.2 will initially mature through the loss of carbon dioxide and water. When the burial temperature is adequate for the cracking of carbon-carbon bonds at a significant rate, oil will be generated (Tissot & Welte, 1978). The composition of the solid residue will change rapidly, until oil formation is complete (hydrogen/carbon ~0.6). Gas generation (methane and, finally, hydrogen) will continue at higher and higher temperatures, until only a small graphitic residue remains.

This pattern can be altered considerably if oxidising conditions are introduced through surface weathering, and could lead to oxidation of aliphatic groups and partial oxygenation of residual organic matter by bacteria in near-surface groundwaters. If oxidation occurs before the oil generation stage, aliphatic groups or components in the organic matter will be preferentially removed. As a result, the composition of the residue will move towards the more aromatic vitrinite line and exhibit lower hydrogen/carbon and higher oxygen/carbon values (Fig. 4). If oxidation occurs after the loss of oil, the main effect will be the addition of oxygen to the periphery of large planar aromatic structures. Oxygen/carbon values will increase with little change in hydrogen/carbon ratios. If either of the oxidation mechanisms goes to completion, no organic matter will remain. Similarly, as discussed earlier, the high-temperature reaction of graphite with water, ferric oxide, etc. can remove all traces of carbonaceous material.

When radioactive elements such as uranium are associated with organic matter, another mechanism for changing kerogen compositions must be considered. Alpha particles have sufficient energy to break carbon-hydrogen bonds, resulting in the release of hydrogen. In the case of aliphatic algal material, high hydrogen/carbon ratios can be significantly reduced (Fig. 4) without appreciable release of hydrocarbons or change in oxygen/carbon values (Francis, 1961).

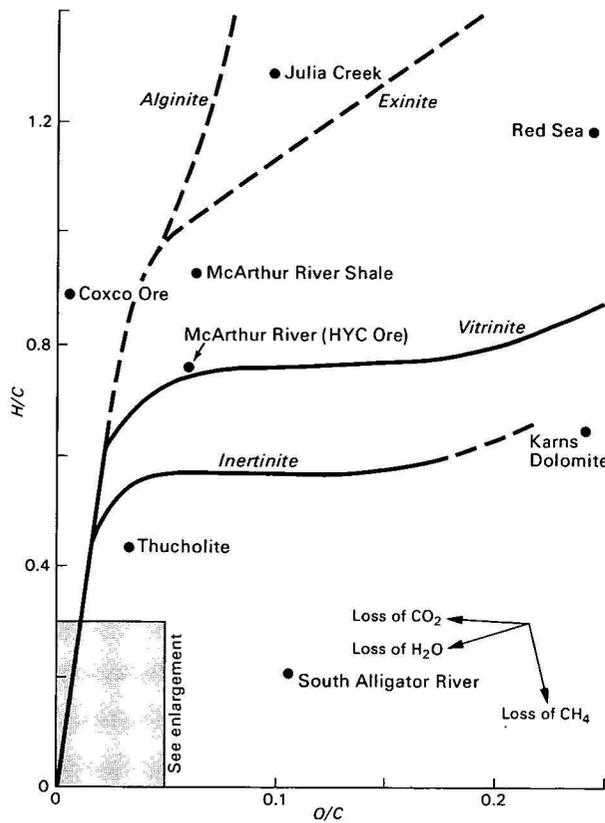


Figure 3. Atomic hydrogen/carbon versus oxygen/carbon for organic matter isolated from metalliferous ores and associated rocks.

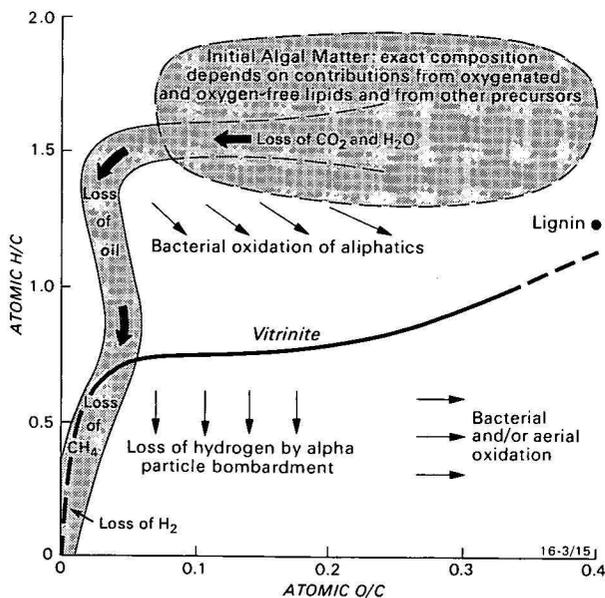
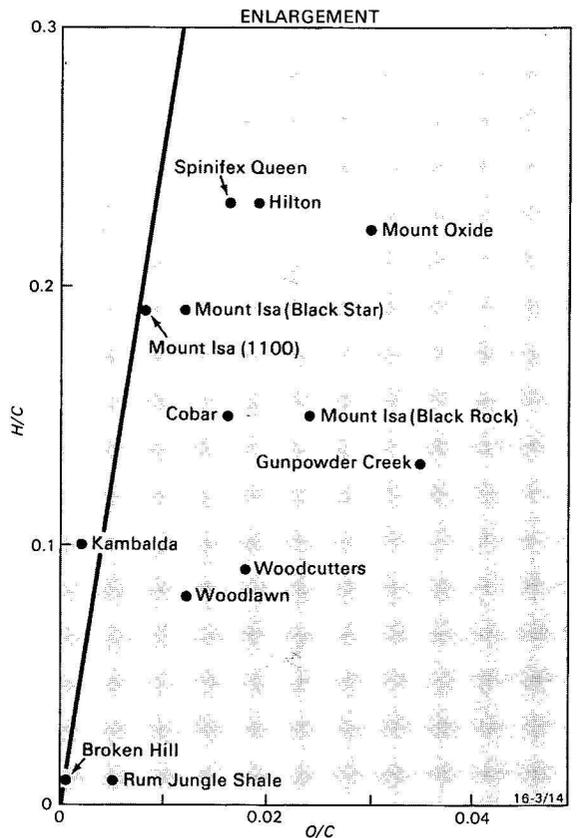


Figure 4. Composition of solid residue and main volatile products of maturation of algal-rich material in a sediment. At any point on the main pathway, oxidation (through addition of oxygen) or loss of hydrogen (through breakage of carbon-hydrogen bonds) will tend to change compositions in the directions shown.

*McArthur River, Mount Isa and Broken Hill*

Organic geochemical studies support the suggestion that these Precambrian mineral deposits are at three different stages in the metamorphic history of somewhat similar original metalliferous sediments. In other words,

a syngenetic mechanism of sediment deposition (followed by differing maximum temperatures achieved during burial) is sufficient to account for the carbonaceous material in these deposits. Algal and bacterial remains (which may have resembled the organic matter in present-day Red Sea sediments) have reached the high-volatile bituminous (medium rank) stage of maturity at McArthur River. More extensive metamorphism at Mount Isa has resulted in recrystallisation of fine-grained sulphides, as well as cracking of the kerogen at the stage where hydrocarbons are generated. Organic matter in ores and shales at and near Mount Isa is past the stage of hydrocarbon generation and is, in fact, approaching graphite in structure. Differences in oxygen/carbon ratio probably reflect various degrees of recent near-surface oxidation. At Broken Hill, more extreme metamorphic conditions have led to the loss of virtually all graphite, presumably by reaction with water (or ferric oxide). X-ray diffraction data show that traces of graphite in shales north of Broken Hill are well crystallised. There is a virtual absence of hydrogen, oxygen, nitrogen and sulphur (Table 1).

Organic matter from the Coxco lead-zinc deposit and the Karns Dolomite (both from the McArthur River district) make an interesting comparison (Walker & others, 1977). The Coxco organic material, which occurs in irregular collapsed brecciated rock, is 38 percent soluble in chloroform, and is probably a predominantly aromatic residue from a crude oil that was generated from an algal source deeper in the basin. The aliphatic compounds have probably been lost by biodegradation and/or water-washing. A similar type of bitumen occurs in the Looking Glass Formation of

the McArthur Basin (Muir & others, 1980) and, in both cases, there are associated sulphides, such as pyrite and marcasite. Oxidation of the Coxco material, which was sampled at a depth of 180 m, has not been extensive. Compared with the Coxco material, the organic matter in an outcrop sample of Karns Dolomite is less soluble, even more aromatic, and much more extensively oxidised.

#### Thucholite

Organic material from the Witwatersrand, rich in gold and uranium, is believed to have originated from Precambrian algae (Hallbauer, 1975). The observed composition of the thucholite kerogen (Table 1) is consistent with such an origin, an initially higher hydrogen/carbon ratio having been lowered by alpha particle bombardment. A significant aliphatic fraction in the isolated thucholite kerogen is indicated by X-ray diffraction and a volatile matter content of 17 percent. However, aromatic compounds still dominate chromatograms of pyrolysis products from this kerogen (Zumberge & others, 1978). The uranium-associated Australian samples from Rum Jungle and South Alligator River are of much higher rank (as revealed by hydrogen/carbon ratios). Although oxygen contents are difficult to measure accurately by difference or direct methods, the high value for the South Alligator River kerogen is probably due to bacterial weathering of aromatic material during recent surface exposure.

#### Julia Creek

The Julia Creek oil shale occurs within the Cretaceous Toolebuc Limestone, and contains up to 0.5 percent vanadium. The kerogen composition (Table 1) is noteworthy for its high organic sulphur content. In unweathered shale, part of the vanadium occurs in both high and low molecular weight porphyrin complexes. On weathering, the organic content of the shale decreases progressively, presumably as a result of bacterial solution of the kerogen (Leythaeuser, 1973). Demineralisation of an outcrop sample containing less than 1 percent organic matter gave a kerogen with a hydrogen/carbon ratio of 0.57. This is in keeping with the mechanism proposed in Figure 4 where bacterial oxidation of lipid-rich material can lower hydrogen/carbon values and, finally, remove all organic carbon. By way of contrast, retorting of Julia Creek shale produces a char with a hydrogen/carbon value (0.54) much lower than the original shale (1.29), but without any appreciable oxidation (oxygen/carbon = 0.06).

### Conclusions

A systematic study of Australian ore deposits reveals that many contain carbonaceous material. Although this material varies widely in abundance, chemical structure, and crystallinity, much of the variation can be accounted for by post-depositional metamorphism and weathering. This study has not been sufficient to establish any genetic links between the

carbonaceous material and mineral deposition, but it has indicated that the carbonaceous material is, potentially, a useful source of information. It is, for instance, a sensitive indicator of the thermal and weathering histories of a rock sequence.

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# Water depth—a critical factor for exhalative ore deposits

I. R. Plimer<sup>1</sup>

If it can be ascertained from sedimentological, palaeontological and/or fluid inclusion evidence that sea water at the site of exhalation was shallow (<500 m) or deep (>1000 m), then predictions can be made on the style of mineralisation expected in the facies present. Shallow-water deposits most commonly contain stratiform Fe-Mn, Ba, Zn-Pb (usually pyritic) ore underlain by, or associated with, a footwall alteration zone of vein, disseminated, or stockwork ore (Cu ± Au, Sn, quartz, tourmaline, carbonate, fluorite). In deep-water settings, stratiform Fe-Mn-Ba, Cu-Zn-Pb (commonly pyrrhotite-bearing), Sn and W ore is not usually underlain by a footwall alteration pipe, and the stratiform ore contains quartz, tourmaline, carbonate or fluorite. In shallow-water deposits, boiling, fluid mixing, or other mechanisms could cause a temperature decrease and resultant mineral precipitation beneath the sea water/rock interface. In deep water, fluid mixing with resultant temperature decrease takes place primarily in sea water and not beneath the sea water/rock interface.

## Introduction

The purpose of this paper is to attempt to ascertain the water depth at the site of deposition of a submarine exhalative ore from features that are recognisable in the field. These features include the morphology of the stockwork and stratiform ore, the ore minerals present, and the mineral species in alteration zones and exhalites. In this paper, the term *exhalative ore deposits* is used to describe those deposits that precipitated from hydrothermal fluid exhaling onto the sea-floor. Although most of these deposits are associated with submarine felsic and mafic volcanism, it is difficult in some areas to prove that the source of metals is volcanism, because a local increase in geothermal gradient (e.g. cooling of an underlying pluton, cooling of a volcanic dome, metamorphic dehydration of a very thick pile of underlying rocks) may result in exhalation of non-magmatic ore-bearing hot fluids onto the sea-floor.

A generalised model for the formation of an exhalative deposit is as follows. Hydrothermal fluids ascend to the sea-floor via a fluid conduit, which in many deposits is now an alteration pipe (e.g. Canadian Archaean deposits—Sangster 1972; Kuroko deposits—Lambert & Sato, 1974), an adjacent penecontemporaneous fault (e.g. McArthur River, Australia—Lambert & Scott, 1973), or the axis of a monoclinial flexure (e.g. Rammelsberg, Federal Republic of Germany—Large, 1980). Fluid-rock interaction and/or boiling in and around the conduit results in footwall vein, stringer, or stockwork mineralisation, and exhalation of fluid onto the sea-floor results in the precipitation of stratiform ore. Ore deposits herein termed submarine exhalative ores have been the subject of much controversy and refinement of models, and type examples have undergone recent reinterpretation as epigenetic (e.g. McArthur River—Williams 1978).

## Water depth

Few reliable criteria exist for the quantification of water depth for exhalative deposits: palaeontological, sedimentological, and geochemical criteria can only provide an indication of water depth. The host rocks

for exhalative deposits commonly lack appropriate criteria for ascertaining water depth and, although those from enclosing rocks can be used as a guide, they can be misleading, because of rapid depth changes before and after ore precipitation (e.g. Broken Hill—Stevens & others, 1980). The almost universal lack of fossils in exhalative ores means that the more commonly acceptable depth terms of neritic (0-200 m), bathyal (200-2000 m) and abyssal (> 2000 m) have limitations and, therefore, depth estimates based on depth salinity boiling curves (Haas, 1971) are used to give some quantitative guide to water depth, especially in the bathyal zone.

Ophiolite-related exhalative deposits (e.g. Cyprus) clearly formed at the sites of sea-floor spreading, in water depths of at least 2-3 km, and data from the black smokers of the East Pacific Rise support great depths.

Evidence for deep-water settings of exhalative deposits (> 500 m) is generally the lack of shallow-water features, although deposits present in thick sequences that display graded bedding (e.g. Broken Hill—Laing, 1980) are probably the best examples of deep-water deposits.

The presence of associated fossiliferous clastic rocks (e.g. crinoidal carbonates at Tynagh and Silvermines—Russell, 1975), stromatolitic carbonates (McArthur River—Murray, 1975, Walker & others, 1978), evaporites (McArthur River—Williams, 1978), reefs (Meggen—Gwosdz & Krebs, 1977), and arkoses and conglomerate (Queen Bee—Sangster, 1979) provides evidence of shallow-water settings.

The intimate association of acid pyroclastic rocks (e.g. Iberian Pyritic Belt—Strauss & Madel, 1974; Kuroko deposits—Lambert & Sato, 1974; Canadian Archaean deposits—Sangster, 1972) may be taken to indicate that hydrothermal phreatic explosions took place when the total vapour pressure exceeded the total confining pressure plus the mechanical strength of the rocks. Some workers have suggested that such explosions took place in shallow water (e.g. Sangster, 1972; Carvalho & others, 1976; Finlow-Bates & Large, 1978). Such explosions would certainly take place in shallow water, where the total confining pressure is low, but, even at depths at or below the carbonate compensation depth (presently ~4000 m), the hydrostatic pressure

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of sea water is only in the order of 0.5 kb, and, hence, such explosions could still take place in very deep water.

Burnham (1979) has shown that large amounts of mechanical energy are released when a hydrous magma exsolves water during solidification. This energy derives from a great increase in volume of the system and, hence, intensive fracturing results. Burnham (1979) suggested that the average kinetic energy associated with explosive volcanism is less than that produced by exsolution of water from 1 km<sup>3</sup> of water-saturated melt. He showed that explosive separation of fluids from water-saturated magmas takes place when external pressures are 0.4-1.6 kb, i.e. lithostatic head of 1.5-6 km or water depth of 4-16 km. Using these data and field relationships (e.g. time specificity of sea water circulation systems associated with Kuroko deposits, benthic faunal assemblages, rapid subsidence structures, presence of high temperature ores near the sea floor, mineral zoning), Ohmoto (1978) suggested that Kuroko deposits formed in association with large submarine calderas at water depths of about 4 km.

If the felsic magma that was the precursor to the felsic pyroclastic rocks associated with submarine exhalative deposits (e.g. Woodlawn, NSW—Malone, 1979) was initially undersaturated with respect to water, phreatic explosion could occur at water depths much shallower than 4000 m. Furthermore, some thermodynamic and isotopic data for Kuroko and other exhalative deposits show that the ore-forming fluid was derived from sea water or was a sea water/magmatic fluid mixture (Kajiwara, 1975; Sheppard, 1977; Hattori & Sakai, 1979; Hattori & Muehlenbachs, 1980), thus indicating that the initial water content of the parental magma could have been very low.

Harley (1979) suggested that the exhalative deposits in the Bathurst-New Brunswick mining district formed in association with a large resurgent caldera that was, only in part, submarine (and hence possibly shallow water depths prevailed). Similarly, the volcanic-siliceous complex of the Iberian Pyrite Belt is in part submarine and in part subaerial, and submarine volcanism was along strike fissures and not in calderas (Carvalho & others, 1976).

On the basis of radiolaria and foraminifera (which were probably planktic species), maximum sea water depths of 300-500 m have been suggested for the Kuroko deposits (Ishikawa, 1964; Tatsumi & Clark, 1972), although more recent studies (Guber & Ohmoto, 1978) on the benthic forams from the Matsuki Mine indicate much greater depths. The calcareous *Melonis* assemblage at Matsuki alternates with the arenaceous *Martinottiella* assemblage and, by comparison with the Deep Sea Drilling Project data, the former assemblage formed at a depth of 2500-4000 m, whereas the latter was at or below the carbonate compensation depth (Guber & Ohmoto, 1978). Palaeontological data on the benthic fauna from the Iberian Pyrite Belt indicate that water depths associated with these submarine exhalative massive pyrite deposits (associated with felsic volcanism) were shallow (Carvalho & others, 1976).

The filling temperatures of fluid inclusions in samples of Kuroko ores are typically in the range of 150-250°C (Tokunaga & Honma, 1974). The inclusions are commonly < 5 weight percent equivalent NaCl and show evidence that the ore fluid was in the liquid rather than the vapour phase. If the fluid

temperatures are in the order of 250°C, then these data indicate that Kuroko deposits formed at depths greater than 400 m (Fig. 1). Fluid inclusions in stockwork ore from the Kosaka Mine (Marutani & Takenouchi, 1978) have filling temperatures of 280-320°C and salinities of 2.5-5.5 weight percent, and these workers suggest that the depth of formation of the stockwork ore was, therefore, > 1000 m (Fig. 1).

The above data suggest that some exhalative deposits associated with felsic volcanism probably formed at seawater depths greater than 1000 m, whereas some associated with mafic volcanism formed at depths greater than 2000 m. Deposits associated with thick sequences of sedimentary rocks (e.g. Irish deposits, Rammelsberg, McArthur) probably formed over a very narrow depth range (Russell & others, 1981), whereas other 'shale hosted' deposits (e.g. Gamsberg, South Africa; Broken Hill, Australia; Sullivan, Canada) probably formed over a greater range.

It has been argued by Finlow-Bates & Large (1978), using the boiling point curve data of Haas (1971) (Fig. 1), the thermochemical data of Large (1977), and sedimentological associations, that deposits underlain by a footwall stringer, disseminated, vein, or stockwork zone rich in chalcopyrite formed in relatively shallow

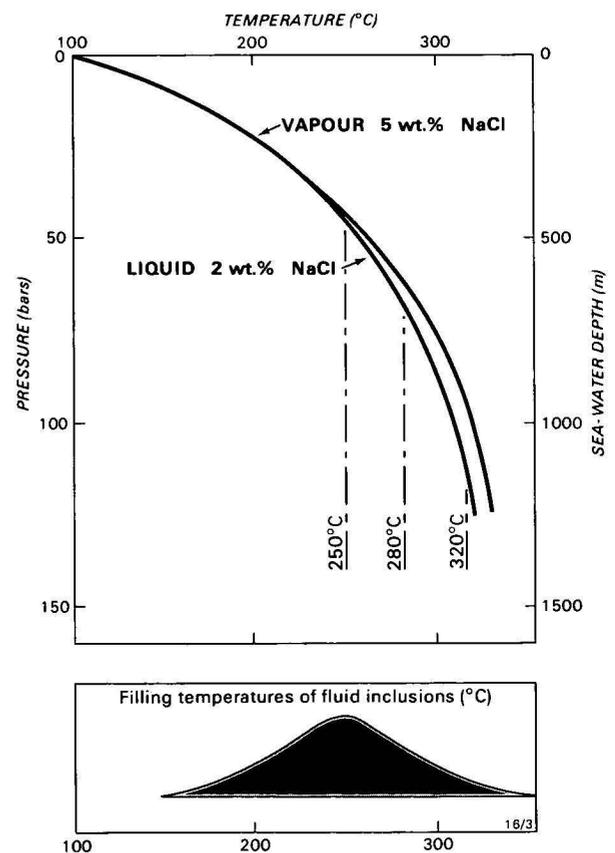


Figure 1. Fluid inclusion filling temperatures of the Kuroko deposits (from Tokunaga & Honma, 1974) and the phase diagrams of 2 weight percent and 5 weight percent NaCl solutions (from Haas, 1971).

The minimum depth of seawater required to prevent boiling of ore-forming fluids on the seafloor at 250°C is approximately 400 m. A minimum depth of 800-1200 m is required for Kuroko deposits with fluid inclusion filling temperatures of 280-320°C (Marutani & Takenouchi, 1978).

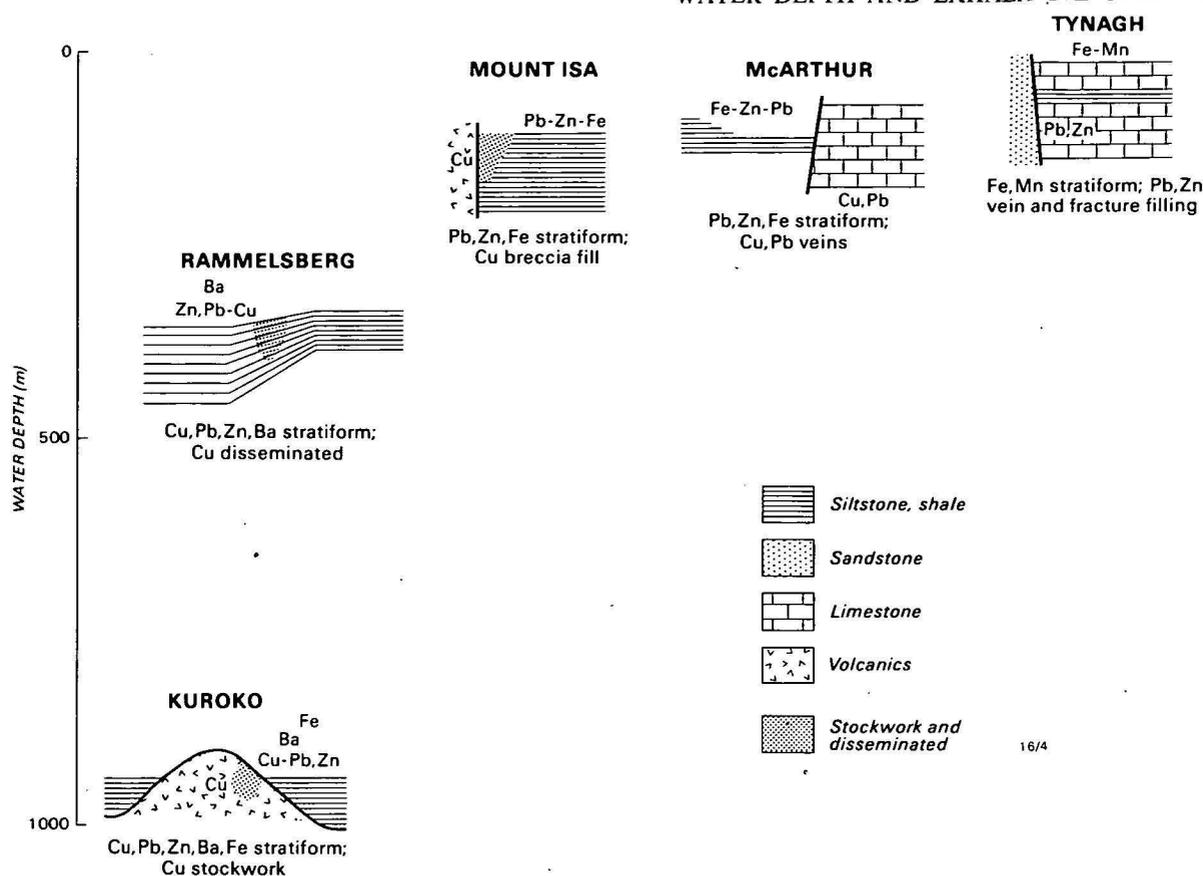


Figure 2. Schematic relation between water depth at the site of exhalation, the style of mineralisation, and zonation of Cu-Zn-Pb-Ba-Fe-Mn ore (modified from Finlow-Bates & Large, 1978).

water (Fig. 2). Water depth, and, hence, hydrostatic pressure, controls boiling and, at shallow depths (< 500 m), typical hydrothermal solutions boil before reaching the sea floor, and the least soluble species (chalcopyrite) precipitates as a result of the temperature decrease. In deep-water settings, chalcopyrite precipitates as stratiform ore and not as transgressive ore in the fluid conduit.

The unmetamorphosed deposits of Cyprus and the Japanese Kuroko deposits lack evidence of boiling in the fluid inclusions (Spooner & Bray, 1977; Marutani & Takenouchi, 1978). Boiling is not expected in the Cyprus deposits, which formed in a mid-oceanic ridge environment, nor is it observed associated with the black smokers of the East Pacific: but boiling may well have occurred in many other shallower metamorphosed exhalative deposits (e.g. Rosebery—Solomon & Walshe, 1979) for which no primary fluid inclusion data exist. Solomon & Walshe (1979) suggested that ascending hydrothermal fluids may boil during ascent (with a minor loss of  $H_2S$ ,  $CO_2$  and  $CH_4$ ), and that such boiling would cool the solution, and chalcopyrite and pyrite would precipitate beneath the sea water/rock interface. The problem of boiling remains unresolved and variation in the degree of boiling possibly results from fluid mixing and water/rock interaction.

### Mineral species of alteration zones and exhalites

It has been suggested (Finlow-Bates & Large, 1978) that in shallow water, sulphides are deposited as footwall stockwork, disseminated and transgressive minerali-

sation (Fig. 3). Examples given were the copper ores of Mount Isa, the Keiko ores of the Kuroko deposits, and the transgressive Pb-Zn mineralisation at Tynagh (Eire) and McArthur River (Australia). This concept is extended here to show that the phases present in the footwall alteration zones of deposits considered to have formed in shallow water are also present in stratiform ore formed in deep water. These phases are cobaltian pyrite, tin minerals, tourmaline, quartz, fluorite, and carbonate.

The presence of pyrite with anomalously high Co values and abundant chalcopyrite in the footwall-altered felsic volcanics in the shallow-water deposits of Rosebery (Green, 1976) and Rio Tinto (Kersabiec & Roger, 1976) is in contrast to the stratiform cobaltiferous pyrite ore formed in deep water at Broken Hill (Plimer, 1977) and Outokumpu (Peltola, 1978). Metamorphism of pyrite-bearing chloritic footwall alteration zones produces a distinct change in the Co/Ni ratio of pyrite (Mookherjee, 1976). Ni partitions from pyrite into ferromagnesian silicates and, hence, with increasing metamorphic grade, the Co/Ni ratio of pyrite in the alteration zone increases.

In the shallow-water Kidd Creek (Walker & others, 1975) and Iberian pyrite deposits (Aye & Picot, 1976), tin-bearing phases (cassiterite, stannite, tetrahedrite), together with tourmaline, are present in the footwall alteration zone or the stratiform ore. Tourmaline is an unusual phase associated with submarine exhalative ores, but, at Sullivan, BC, Canada, a tourmaline-bearing alteration pipe and some of the stratiform ore contain cassiterite (Freeze, 1966). The sedimentological data indicate that the Sullivan deposit formed in deeper

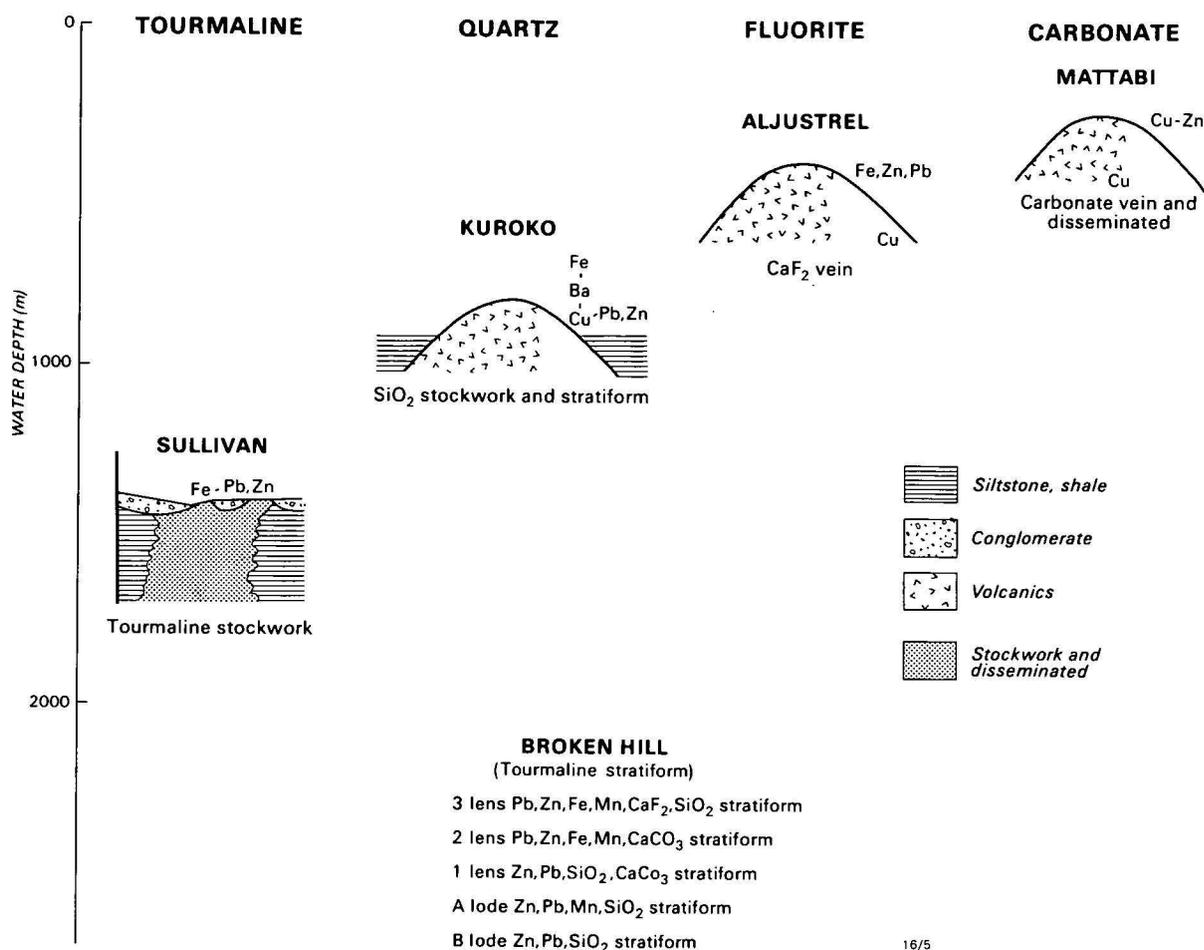


Figure 3. Schematic relation between water depth at the site of exhalation and the species present in the footwall alteration zone and exhalites.

water than Kidd Creek or the Iberian pyrite deposits (Ethier & others, 1976).

Tourmaline may occur disseminated in sulphide rocks (e.g. Elizabeth Cu deposit, Vermont, USA—Slack & Taylor, 1980), in footwall alteration zones (e.g. Sullivan, BC—Ethier & Campbell, 1977; Black Hawk Zn-Cu deposit, Maine, USA—Slack & Taylor, 1980), and as tourmalinites (bedded units with greater than 20 percent tourmaline by volume). Tourmalinites are most commonly associated with deep water 'shale-hosted' exhalative base-metal sulphide deposits (e.g. Black Hawk Zn-Cu, Maine, USA—Slack & others, 1980; Bleikvassli Pb-Zn, Norway—Vokes, 1963; Broken Hill, NSW—Barnes, 1980), whereas disseminated tourmaline and tourmaline-bearing footwall alteration assemblages are more common in deposits associated with shallower-water submarine felsic volcanism (e.g. Kidd Creek, Canada—Walker & others, 1975; Pyhasalmi, Finland—Helovuori, 1979; Vihanti, Finland—Rouhunkoski, 1968; Rosebery, Tasmania—Brathwaite, 1974). Tourmalinites are also associated with stratabound Au deposits (e.g. Passagem de Mariana, Brazil—Fleischer & Routhier, 1973), stratabound W deposits (e.g. Zimbabwe—Cunningham & others, 1973; Broken Hill, NSW—Barnes, 1980) and stratabound Sn deposits (e.g. Bolivia—Schneider & Lehmann, 1977; Broken Hill, NSW—Plimer, 1980).

Quartz is a common phase in footwall alteration zones and rare in stratiform sulphide ores. Fluid in-

clusion data from quartz (Tokunaga & Honma, 1974; Spooner & Bray, 1977), S isotope geothermometry (Kajiwara, 1971) and oxygen isotope data (Ohmoto & Rye, 1974) indicate that the hydrothermal fluids that formed exhalative ore deposits were at temperatures of 250-300°C immediately before debouchment onto the sea floor. Temperatures in excess of 350°C have been observed for the black smokers of the East Pacific (Francheteau & others, 1979). The solubility of silica in aqueous solution is virtually independent of the concentration of dissolved salts and pH, over the range of interest to geology and, in the range of 25-250°C, amorphous silica is more soluble than quartz (Holland & Malinin, 1979). Quartz solubility is increased by increasing pressure and temperature, but, in the T-P conditions for exhalative ore deposits and footwall alteration pipes, the most important variable is temperature (Holland & Malinin, 1979). A decrease in temperature would result in the precipitation of quartz and, hence, silica alteration zones and pipes (e.g. Keiko ore of Kuroko deposits—Lambert & Sato, 1974) are an expression of a high thermal gradient. The temperature decrease could be a result of either boiling or fluid mixing. Further cooling of the hydrothermal fluid, after debouchment, results in the formation of siliceous exhalative ore. Siliceous exhalites associated with shallower-water deposits are generally restricted in occurrence (e.g. jaspers in the Iberian Pyrite Belt—Strauss & Madel, 1974), whereas siliceous exhalites associated

with deep-water deposits have a great strike continuity (e.g. Skorovas—Halls & others, 1977). For example, the quartz-gahnite horizons at Broken Hill (interpreted as a metamorphosed silica-clay-zincian carbonate exhalite) are a slightly shallower-water and/or more oxidised equivalent to the deep-water Pb-Zn exhalative ore, and these horizons have a total outcrop length of > 300 km.

Fluorite is a minor phase in the alteration zone of some exhalative deposits (e.g. green tuff at Aljustrel Portugal—Carvalho & others, 1976). In aqueous solution, fluorite is sparingly soluble and, because it is partially ionised, its solubility is dependent upon the presence of other electrolytes, temperature, pressure, ionic strength, and the  $\text{Ca}^{2+}/\text{F}^-$  ratio (Holland & Malinin, 1979). Fluorite solubility below 200°C increases with temperature and NaCl concentration (Holland & Malinin, 1979), whereas, above 200°C, complexes (which can be neglected at low temperatures) may be important, especially in low-density fluids (Strubel, 1965). Cooling of fluid precipitates the maximum amount of  $\text{CaF}_2$  when the  $\{\text{Ca}^{2+}\}/\{\text{F}^-\}$  ratio is 0.5 and the amount of  $\text{CaF}_2$  precipitated decreases sharply when the ratio varies from 0.5 (Holland & Malinin, 1979). Fluorite can precipitate as a result of an increase in pH of solutions that were initially acid ( $\text{pH} < 3$ ), but most commonly precipitates as a result of decrease in temperature and pressure along the flow path for hydrothermal solutions, e.g. by fluid mixing (Richardson & Holland, 1979). Fluorite precipitation in the footwall alteration zone of exhalative deposits probably results from rapid temperature decreases, resulting from boiling or fluid mixing. Some deep-water submarine exhalative ores contain a significant fluorite content in the stratiform Pb-Zn ore (e.g. No. 3 lens, Broken Hill; Stållberg, central Sweden) or in time-equivalent calc-silicate horizons (e.g. Broken Hill—Barnes, 1980).

Although  $\text{CaF}_2$  is the most common F-bearing phase, exhalites with uraniferous fluorapatite (e.g. banded iron formation at Broken Hill, NSW—Plimer, unpublished data, and Gamsberg, South Africa—Rozendaal, personal communication) and alteration zones containing fluoromicas (e.g. Salgadoinho, Portugal—Plimer & Carvalho, 1981) are characteristically associated with exhalative ore deposits.

Carbonate minerals are uncommon phases in alteration zones, but, where present, they are generally mixtures of calcium, magnesium, iron, and manganese carbonates (e.g. Mattabi—Franklin & others, 1975; Michipicoten iron formations—Goodwin, 1962). The solubility of calcite in aqueous fluid decreases with increasing temperature (which is the inverse for quartz and fluorite), and increases with increasing  $\text{P}_{\text{CO}_2}$  and NaCl concentration, in the temperature range expected for exhalative deposits (Ellis, 1959, 1963; Holland & Malinin, 1979). Boiling and removal of  $\text{CO}_2$  from solutions would greatly reduce  $\text{P}_{\text{CO}_2}$  and carbonate would be precipitated in the alteration zone. Fluid inclusion studies of altered rocks associated with exhalative deposits show that boiling is rare and, hence, carbonate precipitation could be related to the loss of  $\text{H}^+$  by base-leaching reactions and the release of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . A rise in pH would lead to an increase in  $\text{CO}_3^{2-}$  concentration and, hence, precipitation of carbonate minerals. In deep water, carbonate minerals associated with exhalative ores are stratiform and not present in footwall alteration zones. Carbonate

and calc-silicate exhalites (e.g. Broken Hill district; central Sweden) contain minor  $\text{CaF}_2$  and, in places, scheelite. The presence of Fe carbonates in iron formations associated with submarine felsic volcanism and of manganese cherts (quartz-Mn carbonate) associated with both felsic and mafic submarine volcanism indicates that precipitation was at water depths less than the carbonate compensation depth. Although carbonate of hydrothermal origin is most common in deeper water, rare manganese carbonate is present in some shallow-water settings (e.g. Rosebery, Tasmania—Brathwaite, 1974).

## Discussion

It is suggested that the principal mechanism for precipitation of mineral phases in footwall zones and fluid conduits is rapid decrease in temperature. Mineralogical and chemical variation between exhalative ore deposits is probably caused by differences in the chemical parameters (e.g. pH,  $f_{\text{O}_2}$ ,  $f_{\text{S}_2}$ ,  $\Sigma\{\text{S}\}$ , salinity of sea water) resulting from diverse interactions between relatively cold sea water and hydrothermal fluids at the site of debouchment. Changes in the physical parameters of the hydrothermal fluid at the site of exhalation (e.g. boiling, temperature decrease due to fluid mixing) are clearly important, and it is suggested that these changes, together with the topography and stability of the sea floor, control the shape of exhalative ore deposits.

Although there is some evidence from primary fluid inclusions of boiling associated with unmetamorphosed submarine exhalative ores, it is also evident that boiling is associated with deposits with a low hydrostatic load (i.e. shallow-water deposits). Boiling produces an increase in the concentration of dissolved species and a decrease in temperature—both of which would cause mineral precipitation. Mixing of cold sea water with hydrothermal fluid in the conduit (especially immediately after phreatic explosions) could also cause a great temperature decrease. Interactions between hydrothermal fluid and rock would result in a change in the concentration of hydrogen and other ions and, although high geothermal gradients are expected at the site of exhalation, the low thermal conductivity of silicate rocks suggests that little heat would be lost from the ascending hydrothermal fluid into the enclosing rocks and, hence, the fluids would not greatly decrease in temperature. The inverted conical shape and brecciation of footwall alteration pipes (e.g. Kuroko deposits—Lambert & Sato, 1974; Canadian Archaean deposits—Sangster, 1972) indicate a rapid or explosive expansion in the volume of the hydrothermal fluid with resulting cooling.

Unequivocal sedimentological and palaeontological evidence for water depth at the site of exhalation is only present in a few exhalative deposits (e.g. Meggen, Tynagh, Cyprus). For most other exhalative deposits, the depth can only be approximated from sedimentological criteria. If approximate water depth at the site of exhalation can be established, even as simply as shallow or deep, then predictions can be made on the style of mineralisation to be expected in the facies present and, hence, exploration targets can be narrowed. Vein, disseminated, or stockwork ore could represent feeder zones to undiscovered, eroded or weathered stratiform ore (especially in deformed rocks). Older and deeper-water submarine exhalative ores, empirically, tend to be pyrrhotite-bearing, whereas pyrite is

favoured in recent shallower-water deposits (Plimer & Finlow-Bates, 1978), but such concepts must bear in mind the evolution of sea water, and the variations in the Fe-S-O system during ore-mineral precipitation, as a result of decreasing temperature and increasing  $f_{O_2}$ .

### Conclusions

The chemistry and physics of exhalative systems are considered important for the fluid behaviour (e.g. possible boiling, cooling, fluid mixing, fluid/rock interaction) and resulting exhalative deposit (e.g. shape of alteration zone, morphology of ore, zoning of ore, etc.). Hydrostatic pressure is probably one of the principal controls on the ore solution during ascent beneath the sea floor. An attempt to ascertain the relation between hydrostatic pressure (i.e. water depth) and exhalative deposits is based on the assumption that the water depth has some control on the volcanic and sedimentary facies.

Submarine exhalative deposits are hosted by ultramafic volcanics (e.g. Outokumpu, Finland), mafic volcanics (e.g. Cyprus), intermediate volcanics (e.g. Viti Levu, Fiji), acid volcanics (e.g. Iberian Pyrite Belt, Spain-Portugal), ruditites (e.g. Queen Bee, Cobar, NSW), arenites (e.g. Broken Hill, NSW), argillites (e.g. Sullivan, Canada) and carbonate rocks (e.g. Tynagh, Eire). It is, therefore, not surprising that the water depth at the time of exhalation is rarely manifest unequivocally in the exhalative ores. Lithological associations, together with the associated mineralisation and alteration, can only give some guide to the water depth.

Shallow-water deposits contain stratiform ore (Fe-Mn, Ba, Zn-Pb) associated with a footwall alteration zone of vein, disseminated, or stockwork mineralisation (Cu  $\pm$  Au, Sn). This indicates that boiling, fluid mixing, or other mechanisms that could cause a temperature decrease and resultant mineral precipitation took place beneath the sea water/rock interface. Quartz, cassiterite, tourmaline, carbonate or fluorite may be present in the alteration zone of shallow-water deposits. In deep-water deposits, the mineralisation is not underlain by a footwall alteration pipe, and the exhalites containing Fe-Mn, Ba-Zn-Pb-Cu, quartz, cassiterite, tourmaline, carbonate, phosphate, uranium and fluorine are stratiform. The concordance of deep-water exhalative deposits suggests that fluid mixing with the resultant temperature decrease took place primarily in sea water and not beneath the sea water/rock interface.

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## Diagenetic organic matter in Recent sediments and environments of deposition

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Organic geochemical studies of the reduced organic material in sedimentary rocks provide a valuable insight into the origin and history of the sediments. Information on the source of the organic matter (marine or non-marine), the depositional environment (oxic or anoxic), whether or not biodegradation has occurred, and the maturity of the organic matter can be obtained by studying the distribution of various organic compounds, known as biological markers, in extracts from these sediments. Selection of environments with a fairly narrow range of source material allows more direct correlations to be made between source material and specific biological markers.

### Introduction

Studies of organic matter deposited in contemporary environments are of practical importance in obtaining a better understanding of the formation of coals, oil shales, crude oils, natural gas deposits, and, possibly, to a lesser extent, ore deposits. Correlations between specific organic compounds in Recent sediments and particular source organisms or plants permit information to be obtained on the type of organic matter deposited in ancient organic-rich sediments (Philp & others, 1976). Stereochemical changes occurring in molecules from Recent sediments can be extrapolated to provide information on the maturational history of ancient sediments (Mackenzie & others, 1980). Biodegradation of organic matter in any environment can produce specific compounds or induce specific stereochemical changes, which allow conclusions to be drawn with regard to the degree of biodegradation of the organic matter (Seifert & Moldowan, 1979). The fate of certain specific classes of compounds that serve as environmental indicators, namely isoprenoids, sterols, and triterpanes, are discussed in this paper.

### Accumulation and preservation of organic matter in Recent sediments

Carbon is cycled through the biosphere by a combination of photosynthesis and oxidation. In simplest terms, plants can be thought of as incorporating carbon from atmospheric carbon dioxide into their cells (Fig. 1). The plants are subsequently consumed by animals, which partly or completely degrade the plant material and give off excess carbon dioxide. On death, decaying plants and organisms are largely oxidised, either microbially or chemically, to carbon dioxide, which is returned to the atmospheric pool of carbon dioxide. However, 99.9 percent of the carbon is recycled to the atmosphere as carbon dioxide, and only 0.1 percent deposited and incorporated into the sedimentary carbon sink. These preserved organic carbon compounds are, in many cases, extremely useful as indicators of the source of organic matter and the environmental conditions of deposition, and have been collectively referred to as biological markers or chemical fossils (Eglinton, 1973). Biological markers are generally defined as compounds whose carbon skeletons remain unaltered or are altered in a predictable manner over a long geolo-

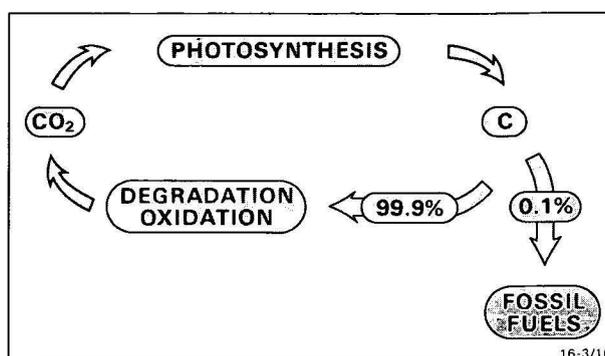


Figure 1. Highly simplified representation of the carbon cycle.

gical time, and can be correlated with a specific input of organic matter to the environment.

Following deposition and accumulation of the organic matter, a variety of maturational changes can occur during diagenesis (Fig. 2). In general, diagenetic effects are considered to occur at temperatures below 50°C at depths where no cracking of the molecules can occur from thermal effects.

The nature of the organic material exposed to these early-stage diagenetic reactions will, to a large extent, be determined by the depositional environment. The two extreme types of environment are non-marine and marine, and various intermediate environments exist: deltaic sediments, for example, contain a predominantly marine contribution that is diluted by terrigenous material from rivers and streams.

Figure 3 is a very simple diagram to show a few of the major factors that can affect the type of organic matter found in the sedimentary environment. In a marine environment, autochthonous material is generated from phytoplankton residing in the uppermost layers of the water column, which are illuminated by sunlight, i.e. the euphotic zone. As this organic matter percolates down through the water column it will be grazed by zooplankton, a proportion of which will in turn be consumed by large invertebrates and fish. A certain amount of phytoplankton and zooplankton debris may reach the sediment/water interface unaltered or may be attacked by bacteria in the water column. In addition, an allochthonous contribution of organic matter in a marine environment can be derived from continental run-off or by various other means such as aeolian transport or, in certain environments, ice-rafting.

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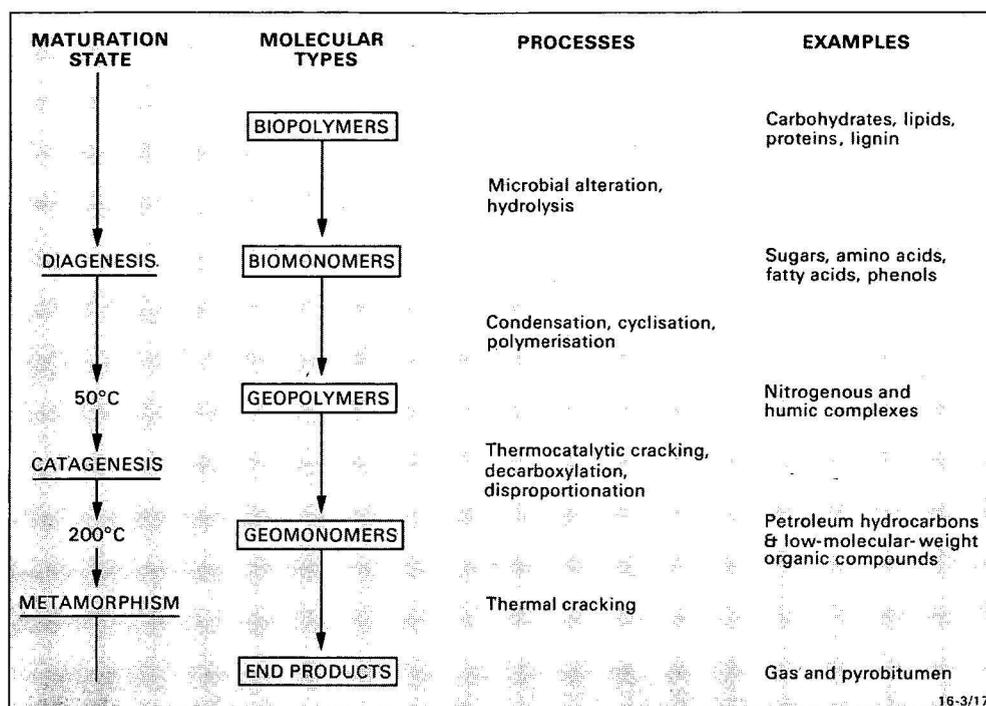


Figure 2. A summary of the major processes that can occur to the main types of organic matter in the geologic record.

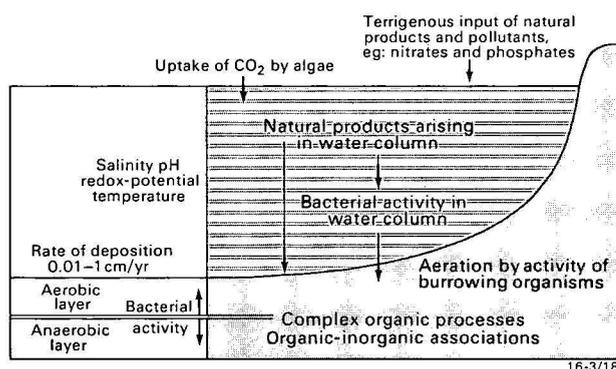


Figure 3. Schematic diagram of the various interdependent chemical and biological factors that affect the ultimate fate of biolipids in Recent sediments. (From Philp & others, 1976).

The organic matter from all sources may be further degraded by microbial attack in the water column, at the sediment/water interface, and in the upper few centimetres of the sediment itself, producing biological markers which cannot immediately be correlated with the source of the organic material.

The major factor controlling the rate of microbial degradation will be the amount of oxygen available either in the sediment or overlying water column. Ultimately, oxygen availability is reflected in the distribution of biological markers in the sedimentary record. For example, a benthic fauna will actively scavenge and rework organic material filtering down through an oxic water column. Below the sediment/water interface, little primary productivity occurs, and the main process is that of consumption of organic matter (Fig. 4). The bottom muds under oxygen-rich water columns are often anoxic, but can be extensively disrupted by invertebrates such as polychaetes, holo-

thurians, and bivalves. On the other hand, in an anoxic environment, oxygen depletion depresses and eventually eliminates benthic metazoan life (Fig. 5). At oxygen concentrations of 0.1 ml/l, and below, suspension feeders disappear, leaving anaerobic bacteria as the only effective reworkers of organic matter. Bacterial activity is slowed down by the lack of bioturbation, which limits the diffusion of oxidants into the sediment. The sediments formed under these conditions are generally laminated and very rich in organic matter.

The environments which appear to be best suited to the preservation, as distinct from accumulation, of organic matter can be divided into four categories.

**Large anoxic lakes.** Permanent stratification of such lakes promotes development of anoxic bottom waters. These lakes are formed under warm equable climatic conditions that favour lacustrine anoxia and, ultimately, deposition of source material that gives rise to non-marine oil; e.g. Lake Tanganyika.

**Anoxic silled basins.** These are landlocked silled basins with positive water balance, such as the Baltic and Black Seas.

**Anoxic layers.** These are caused by upwelling where there is high surface biological productivity and, hence, the oxygen supply in deep water cannot match demand; e.g. Benguela current and Peru coastal upwelling.

**Open ocean anoxic layers.** These are formed in oxygen minimum layers of the northeast Pacific and northern Indian oceans, far from the polar regions (Demaison & Moore, 1980).

Accordingly, it is clear that the distribution of biological markers in Recent sediments will be influenced both by the source material and the depositional environment. In the following section it is proposed to examine some of the changes that can occur to specific biological markers, the significance of these changes, and how they can be used as environmental indicators.

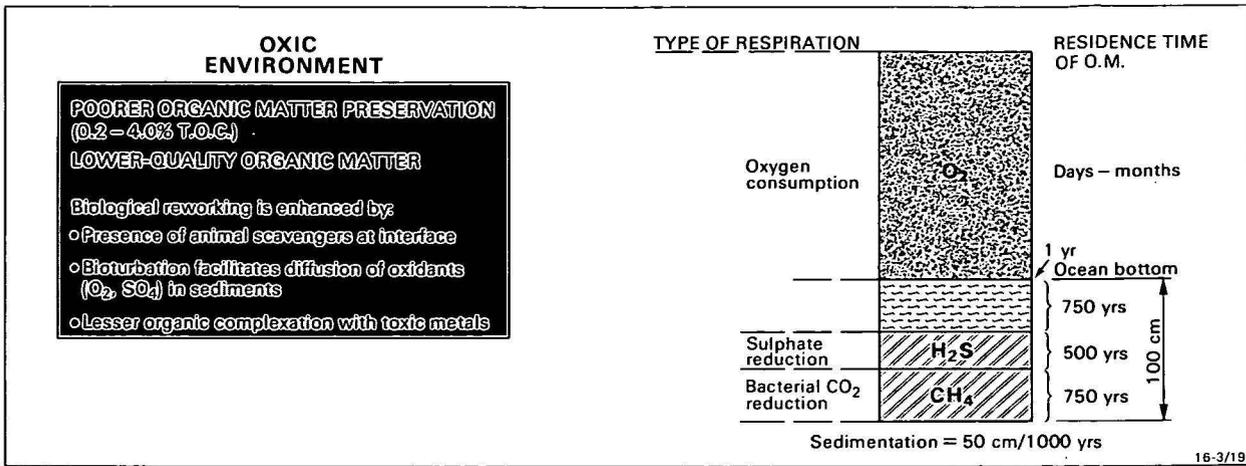


Figure 4. Degradation of organic matter in an oxic environment. (Adapted from Demaison & Moore, 1980). Diagonally shaded area is anoxic.

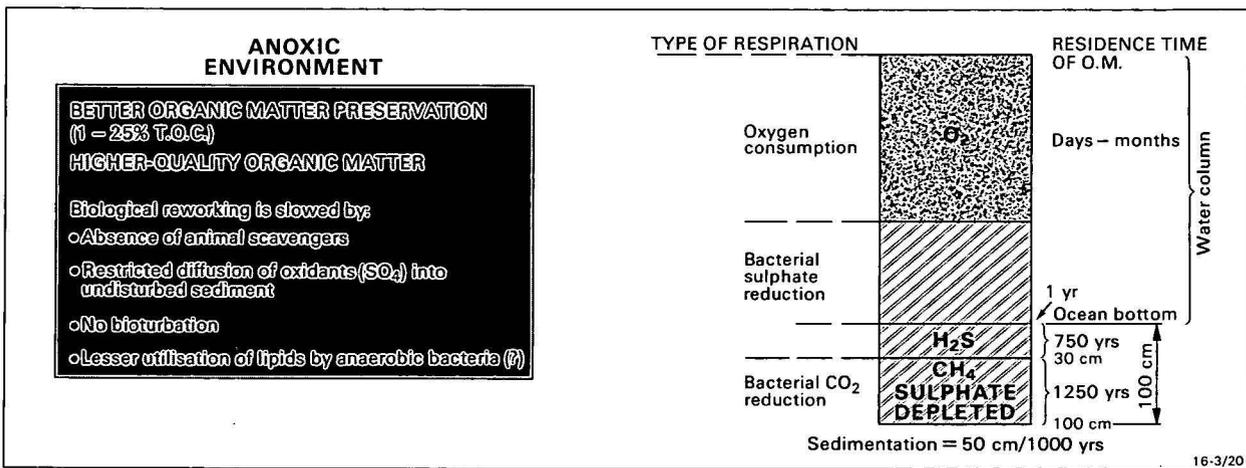


Figure 5. Degradation of organic matter in an anoxic environment. (Adapted from Demaison & Moore, 1980). Diagonally shaded area is anoxic.

Diagenetic alteration of biological markers

Pristane and phytane

One of the most widely studied diagenetic reactions in Recent sediments is the fate of the phytyl side-chain of chlorophyll. Brooks & others (1969) initially suggested that variations in pristane and phytane ratios reflect differences in oxidation conditions during the early stages of chlorophyll decomposition. Johns & others (1980) recently produced evidence of a two-step degradation process for chlorophyll. The first step is destruction of the chlorin ring system and the second, conversion of the phytyl ester to soluble degradation products and non-solvent-extractable or bound phytol. The second step is definitely the more complex part of the degradation process. Didyk & others (1978) summarised various microbial and geochemical paths that have been demonstrated or postulated for the degradation of phytol under various environmental conditions.

The pristane/phytane ratio has been widely used to obtain information on palaeoenvironments of deposition (Powell & McKirdy, 1973). Preservation of the phytane skeleton is facilitated by a reducing environment, whereas the formation of pristane via decarboxylation

of phytanic acid occurs under oxidising conditions (Fig. 6). In Recent sediments, a low pristane/phytane ratio (< 1), together with high chlorin and sulphur contents, indicates an anoxic environment (i.e. path shown on left hand side of Fig. 6). Conversely, high pristane/phytane values (> 1) and low chlorin and sulphur contents may indicate an oxic environment.

Stereochemical studies of acyclic isoprenoid compounds can also provide information on their origin and paths of formation. Naturally-occurring phytol has been shown to have the relative stereochemical configuration of 7R, 11R. The stereochemistry of pristane in Recent sediments and naturally occurring marine zooplankton is compatible with an origin from phytol with retention of configuration, and is thus compatible with catabolism of phytoplankton phytol. Likewise, the major isoprenoid acids in the Green River oil shale have stereochemical configurations directly comparable with that of phytol. Pristane in the Green River shale comprises 80 percent of the 6R, 10S isomer, compatible with an origin from phytol and retention of configuration, and 20 percent of the 6R, 10R and/or 6S, 10S isomers. The presence of the latter isomers was interpreted as indicating derivation from either an acyclic isoprenoid other than phytol or phytol via reactions

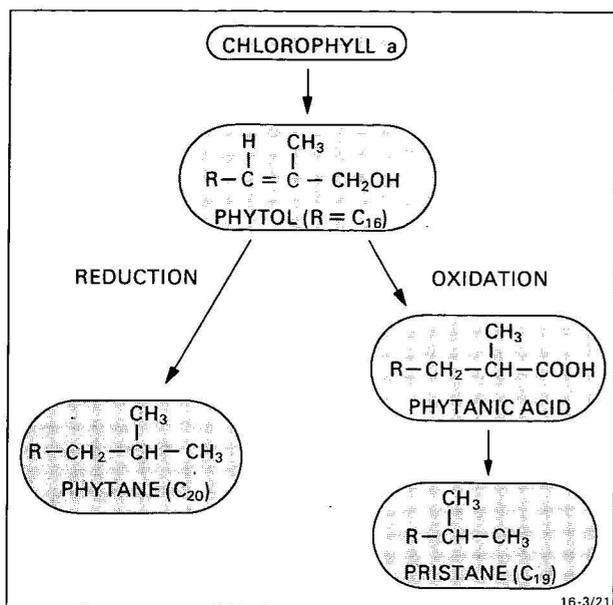


Figure 6. The major paths postulated for the formation of pristane and phytane in aquatic environments.

leading to epimerisation of the methyl branched positions (Patience & others, 1978).

#### Sterols

The steroid hydrocarbon structure is a relatively stable nucleus, which can incorporate functional groups such as alcohols, ketones, and olefinic linkages either in the nucleus or the C-17 side-chain (Fig. 7). Several species of plants and animals produce only specific sterols or have unique sterol fingerprints, which permit their use as tracers of supply from such sources. The sterols (1) (Fig. 7) can be subsequently converted into stenones (2), stanones (3), stanols (4), sterenes (5) and steranes (6) by a complex series of microbiological and chemical reactions.

Diagenetic alteration of sterols by geochemical and biochemical processes can lead to the accumulation of more stable transformation products in sea water and sediments. Several studies have been made of the structure and concentration of these products in marine and lacustrine environments to determine various paths and rates of steroid degradation.

In early studies, Gaskell & Eglinton (1975) showed that hydrogenation of unsaturated sterols occurs rapidly in contemporary aquatic sediments to give  $5\alpha$ - and  $5\beta$ -stanols in a ratio dependent on the microbial population of the sediments. More recently, Gagosian & others (1981) examined the content of sterols and their transformation products in surface sediments and the overlying water column from three different marine environments. These included two anoxic sediments from the Black Sea and the South West African shelf, and a sample from a North Atlantic sediment, which was taken to represent a site of low productivity and oxic surface sediment.

Although the distribution of sterols in surface sediments is primarily controlled by the source of supply, their distribution in the sediments can be quite different from that in the overlying water column. Such differences are caused by the distribution of benthic macroorganisms, and the size, composition, and

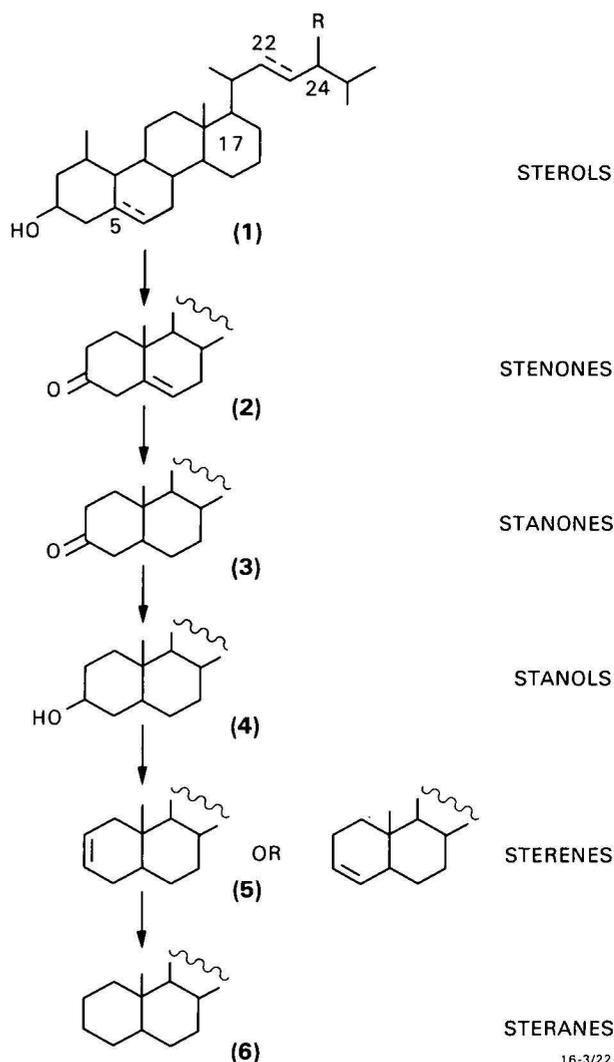
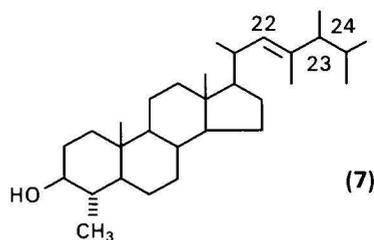


Figure 7. Structures and inter-relation of various sterols found in contemporary environments.

density of particulate material. The major sterol found by Gagosian & others (1981) in the Black Sea and Walvis Bay sediments was a 4-methyl dinosterol (7)



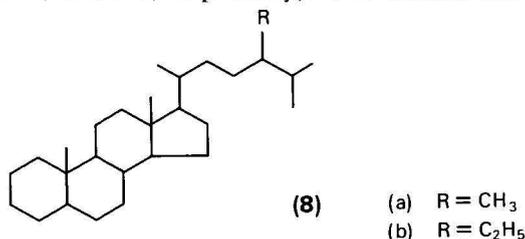
which had previously been identified in the Black Sea sapropel by Boon & others (1979). The same sterol has been encountered as a major sterol in some dinoflagellates and is thus a good example of the possibility of a direct correlation between a source organism and a specific biological marker compound.

Stanols in surface sediments can either be derived from organisms and incorporated unaltered into the sediments or produced by microbial reduction of sterols at the sediment/water interface or in the anoxic water column. Gagosian & others (1981) found that the

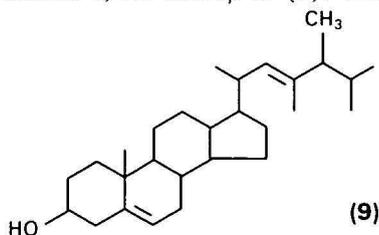
lowest stanol/sterol ratios were in oxic sediments (North Atlantic) and the highest in anoxic sediments (Black Sea and Walvis Bay). Microbial hydrogenation of sterols has been postulated as a major source of stanols in anoxic lacustrine sediments (Gaskell & Eglinton, 1975). Dehydration of stenols and stanols leads to the formation of steranes and rearranged steranes, or diasteranes, via intermediate sterenes. Gagosian & others (1981) found that, in surface sediments from Walvis Bay, concentrations of individual steradienes corresponded to the concentrations of related sterols, and the levels of the monosterene concentrations corresponded to the levels of their respective stanols. In oxic sediments from the North Atlantic, sterenes were virtually absent. This was postulated to be due either to the low levels of sterol precursors or alternative faster paths for sterol degradation in oxic sediments. Stanones in sediments are derived from planktic or benthic organisms and from microbial or chemical oxidation of sterols and stanols.

In summary, Gagosian & others (1981) found that in areas where there is low productivity in the surface waters and oxic sediments, sterol and stanol concentrations in the sediments are low, sterene concentrations are extremely low, and stanones are absent. In areas of high productivity and anoxic sediments, there are high sterol and stanol concentrations, and the distributions of 4-desmethyl steroids and steradienes correlate with stenols and monosterenes with stanols.

In addition to the relative distribution of sterols in the sediments, the stereochemical assignment of the alkyl group at the C<sub>24</sub> position has important biosynthetic, taxonomic, and geochemical implications. Routine separation of the C<sub>24</sub> sterane isomers in sediment extracts has the potential to provide information on the nature of contributing organisms and also the isomerisation reactions thought to occur in steranes with increasing depth of burial and associated temperature rise. Maxwell & others (1980) recently reported a method for the complete separation of the 24R and 24S isomers of the 24-methyl and 24-ethyl-5 $\alpha$ -cholesta-8a and b, respectively). This method was used



to study the C<sub>24</sub> configuration in steranes from a sedimentary rock and a crude oil, and those obtained from the reduction of sterols in a marine coccolithophorid. Maxwell & others (1980) found that the major free sterol from the marine alga *Emiliania huxleyi* was 24-methylcholesta-5,22E-dien-3 $\beta$ -ol (9). Conversion to

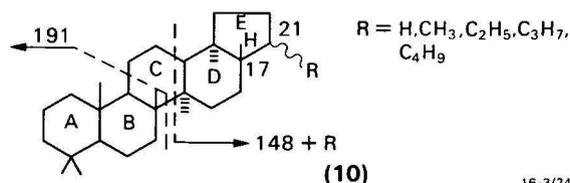


the corresponding sterane and analysis by high-resolution gas chromatography showed that the 24R and 24S

isomers were present in the ratio 4.3:1. It could, therefore, be concluded that the major free sterol of *E. huxleyi* is (24S)-24-methylcholesta-5,22-dien-3 $\beta$ -ol. The same configuration is produced by the diatoms *Phaeodactylum tricornutum* and *Nitzschia closterium*. However, the phytoflagellate *Ochromonas* spp. (Chryso-phyceae) produced sterols with the opposite C-24 configuration to *E. huxleyi*. Such specific stereochemical differences may be useful in the classification of many such microscopic algae (which can be difficult by other techniques) and in determining the contribution of specific organisms to a sediment.

#### Triterpanes

Hopane-type triterpanes (10) have been shown to be ubiquitous biological markers in sedimentary organic matter (Ourisson & others, 1979). The mass spectrum



of hopane derivatives is extremely useful, since it produces two major fragments that facilitate monitoring of these compounds in complex mixtures by gas chromatography-mass spectrometry (GC-MS).

In addition, the relative intensities of the fragments due to rings A and B (m/z 191) and rings D and E (m/z 148 + R) can be directly correlated with the *cis*- or *trans*-nature of the D/E ring junction. The stereochemistry of naturally occurring hopanes is 17 $\beta$ H,21 $\beta$ H. However, in more mature samples, the isomer that is thermally more stable is formed, i.e. 17 $\alpha$ H,21 $\beta$ H. In addition, C<sub>31</sub>-hopanes and above have an asymmetric carbon atom at the C<sub>22</sub> position and, hence, it is also possible for R and S isomers to be formed at this position as the sample matures. In Recent sediments the profile of the hopanes consists only of 17 $\beta$ H,21 $\beta$ H isomers, but as the sediment is subjected to increasing

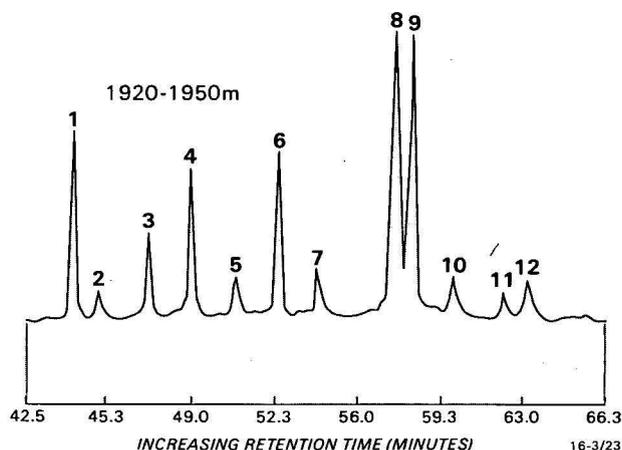


Figure 8. Single ion chromatogram of m/z 191 used to illustrate typical hopane distribution in sediment extract.

Peaks numbered 2, 5, 7, and 10 correspond to the C<sub>27</sub>, C<sub>29</sub>, C<sub>30</sub>, C<sub>31</sub>, 17 $\beta$ H, 21 $\beta$ H-hopanes. Peaks 1, 4, 6, 8, 9, 11, and 12 correspond to the 17 $\alpha$ H, 21 $\beta$ H isomers with 8 and 9, and 11 and 12 being diastereomeric pairs. Peak 3 is a C<sub>28</sub>-triterpane.

thermal stress, the 17 $\alpha$ H,21 $\beta$ H isomers appear along with the 22R and S diastereomers. Figure 8 shows an example of the hopane distribution in a sample that has undergone limited diagenesis. The presence of both isomers at each carbon number is clearly indicated in this chromatogram, which has been obtained by GC-MS using the technique of single ion monitoring. Thus, although hopanes can be used as source indicators, these compounds also have the potential to be extremely useful as a maturation parameter.

### Conclusions

The main aim of this paper has been to summarise some of the major factors affecting the preservation of organic matter in sediments. In addition it has illustrated the use of pristane/phytane ratios as indicators of the oxic/anoxic nature of the environments of deposition, and shown that sterols can be used as source indicators of organic matter in sediments, and that hopane-type triterpanes can be used as a maturation parameter.

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# Geobiological role of cyanobacterial mats in sedimentary environments: production and preservation of organic matter

John Bauld<sup>1</sup>

Cyanobacterial mats are among the most productive of aquatic photosynthetic systems. They were prevalent during the Precambrian, but now occupy limited, albeit widespread, ecological niches. Organic carbon produced by cyanobacterial mats is, potentially, a source material for kerogen and, later, hydrocarbon formation, a carbon and energy source for biogenic H<sub>2</sub>S production and metal sulphide deposition, and a reductant for abiogenic sulphide formation. The paper considers the microbiological and environmental constraints on the occurrence, primary productivity, decomposition, and preservation potential of modern cyanobacterial mats. It appears that bacterial decomposition to CO<sub>2</sub> and CH<sub>4</sub> will proceed at salinities up to halite saturation, even under anoxic conditions, and that substantial preservation will not take place except at salinities beyond this. Anoxic conditions alone will not prevent decomposition of cyanobacterial mat organic carbon. Mat-constructing cyanobacteria appear well-adapted to environments of fluctuating salinity and periodic desiccation. A model that accommodates the environmental limits imposed by the physiology of cyanobacterial primary producers and bacterial decomposers is consistent with the shallow fluctuating saline lake palaeoenvironment invoked to explain some oil shale occurrences.

## Introduction

Cyanobacterial mats are organosedimentary structures, often laminated, that grow at sediment/water interfaces. These carpet-like structures (e.g. Fig. 1) are constructed by benthic microbial communities, usually dominated by filamentous cyanobacteria. The cyanobacteria are photosynthetic prokaryotes and all members of the group utilise light energy to synthesise organic carbon from CO<sub>2</sub> whilst evolving O<sub>2</sub> (Stanier,

1977). Some members of the group also carry out facultative anoxygenic photosynthesis, in which H<sub>2</sub>S, rather than H<sub>2</sub>O, is used as an electron donor, and S<sup>0</sup> replaces O<sub>2</sub> as the oxidised product (Padan, 1979). Cyanobacteria are also referred to by a plethora of other names including cyanophycophyta, cyanochloronta, cyanophyta, myxophyta, blue-green bacteria and blue-green algae. The terms 'cyanobacterial mat', 'blue-green algal mat', and 'algal mat' are often used interchangeably. However, the last term should be restricted to those mats constructed or dominated by eucaryotic photosynthetic microorganisms, such as diatoms.

Mats may be constructed by a single cyanobacterial species. For instance, *Entophysalis* sp. builds pustular (mammillate) mats in Shark Bay, Western Australia (Figs. 2, 3, 4). In other mats there may be a dominant species associated with one or more subdominant species. In Spencer Gulf, South Australia, *Lyngbya* sp. (Fig. 5) dominates tufted mat, where *Microcoleus* sp. (Figs. 6, 7) and *Schizothrix* (*Phormidium?*) sp. are subdominant. Whilst one or more cyanobacterial species construct the mat and are responsible for the biological component of morphogenetic control, the structure often also contains a variety of photosynthetic and heterotrophic bacteria, and eucaryotic algae, of various cellular morphologies and biochemical functions. Analogous fossil structures, known as stromatolites (Walter, 1976), which preserve a record of such mats and their activities, may also contain recognisable microfossils which bear a close morphological similarity to living cyanobacteria. The great antiquity of mat-constructing microorganisms is attested to by recent reports of 3500 m.y.-old Archaean stromatolites from the Warrawoona Group of the eastern Pilbara Block (Walter & others, 1980).

This paper briefly discusses the geobiological significance of cyanobacterial mats with particular emphasis on the consequences of their photosynthetic activities. The production of organic carbon by cyanobacterial mats is particularly relevant to resource geologists, since organic carbon is potentially a source material for hydrocarbon formation, a carbon and



Figure 1. Smooth mat in the high intertidal zone of north-eastern Spencer Gulf, South Australia.

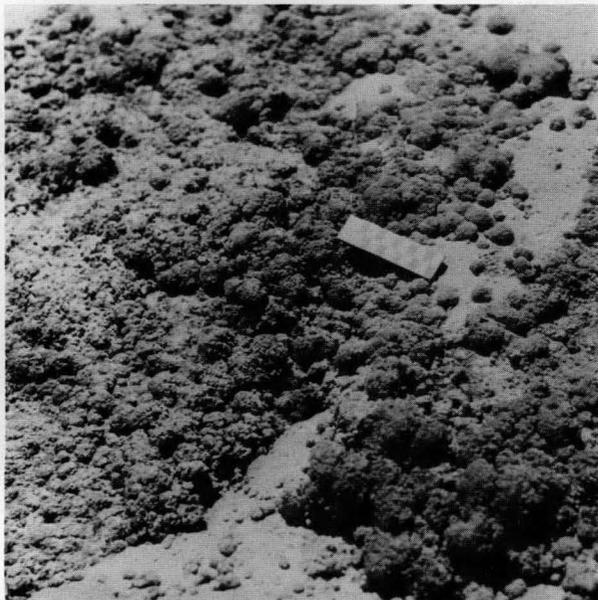
A thin layer of photosynthetically active filamentous cyanobacteria (1-2 mm thick) covers black, FeS-rich, reducing sediments. This figure, which shows water-logged mat, illustrates the mechanical strength of the cohesive fabric produced by the entangled trichomes of *Microcoleus* sp., their enveloping mucilaginous sheaths, and trapped and bound sediment (see Figs. 6 and 7).

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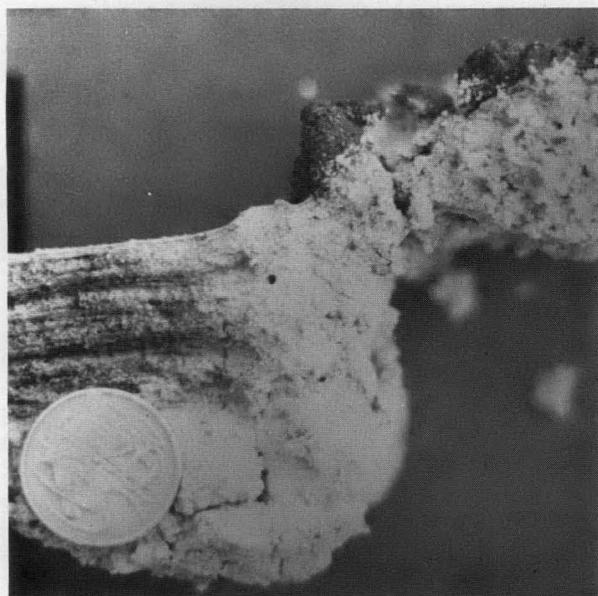
energy source for biogenic H<sub>2</sub>S production and subsequent metal sulphide deposition, and a source of reductant for the formation of abiogenic sulphides.

### Occurrence of cyanobacterial mats in modern environments

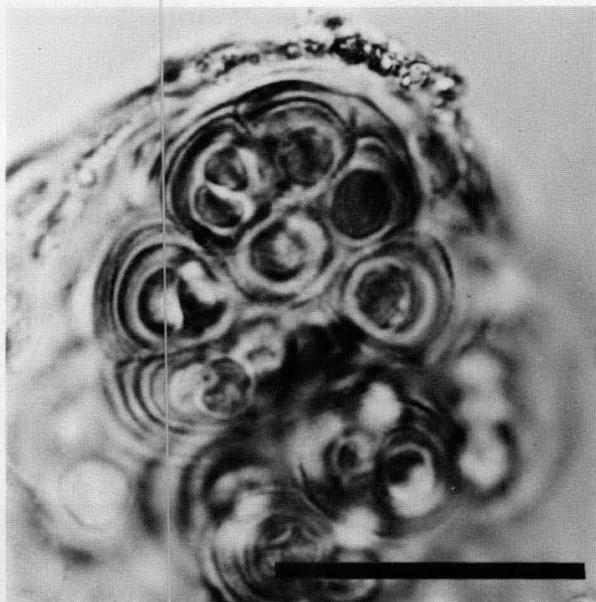
Cyanobacteria occur in a wide range of modern environments (Whitton & Sinclair, 1975), but cyanobacterial mats are generally restricted to more severe or extreme environments. Extant cyanobacterial mats



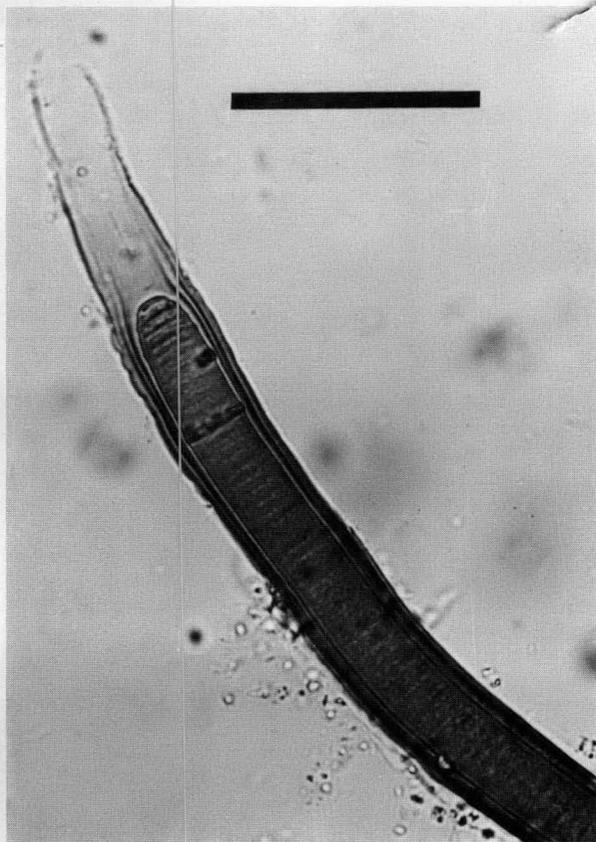
**Figure 2.** Pustular (mammillate) mat in the intertidal zone at Hutchison Embayment, Hamelin Pool, Shark Bay, Western Australia. The mat is constructed by *Entophysalis* (Fig. 4). (Scale 10 cm).



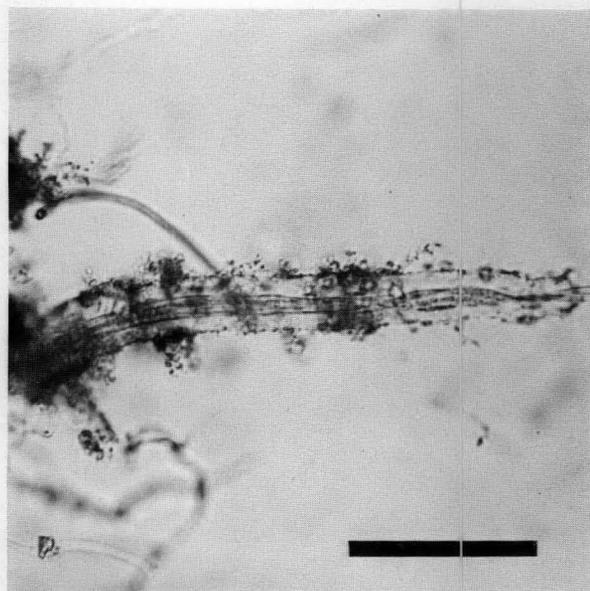
**Figure 3.** Vertical section through adjacent smooth (left) and pustular (right) mats from near Flagpole Landing, Hamelin Pool. Smooth mat covers laminated, reducing sediments while pustular mat sediments appear neither laminated nor reducing. (Coin is 28 mm in diameter.)



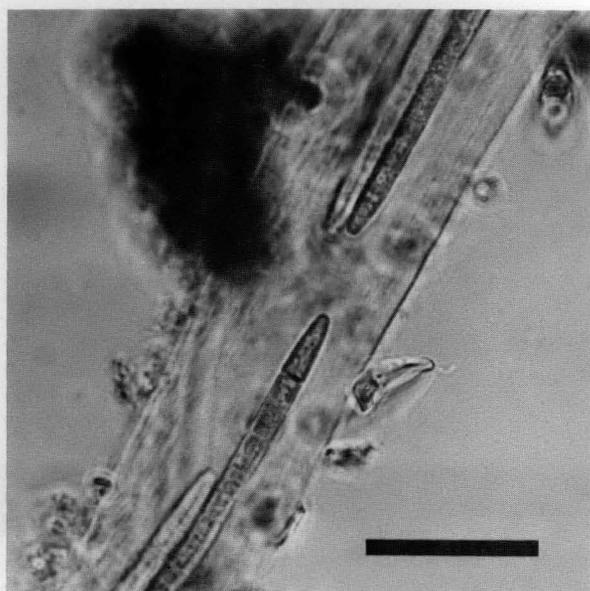
**Figure 4.** *Entophysalis* sp., a coccoid, colonial cyanobacterium that constructs pustular mat (Figs. 2 and 3). The gelatinous sheaths, which contain a brown pigment, are a series of concentric layered envelopes, and encase individual cells and colonies. Sediment particles can be seen adhering to the outermost sheath (scale bar = 25 μm).



**Figure 5.** *Lyngbya* sp., the dominant cyanobacterium in tufted mat. This example is from mats in Fisherman Bay, Spencer Gulf. The thick lamellated sheath, deeply stained by brown pigment, is a tube encasing a single trichome. (Scale bar = 50 μm).



**Figure 6.** *Microcoleus* sp. from smooth mat, Spencer Gulf. Several trichomes are contained within a thin, loosely fitting tubular sheath. The sticky mucilaginous sheath binds and traps sediment particles (seen here clearly outlining the external surface of the sheath) and promotes cohesion and mechanical strength (see Fig. 1). (Scale bar = 50  $\mu\text{m}$ ).



**Figure 7.** *Microcoleus* sp., showing the thin tubular nature of the sheath, which contains several trichomes with conical apical cells. Sediment and detritus, and diatom frustules, adhere to the outer surface of the sheath. (Scale bar = 25  $\mu\text{m}$ .)

Habitat location	Environmental regime of mat	Mat characteristics	Dominant genera	Reference
<b>LACUSTRINE</b>				
St. George Bay, Signy Is., Antarctica	Freshwater. Permanently submerged.	Flat, felt-like. Extends to water depth of $\geq 1$ m.	<i>Phormidium</i> spp.	Fogg & Horne (1970)
Lake Bonney, South Victoria Land, Antarctica.	Permanently submerged. Saline; 1.4‰ (5 m) 310.7‰ (20 m).	Thick, smooth mat. 3-5 cm thick, to ca 10 m.	<i>Phormidium</i> sp. <i>Schizothrix</i> spp.	Parker & others (1977)
Green Lake, New York, U.S.A.	Saline, meromictic. Active calcite precipitation. Submerged, partial exposure late summer.	Mat $\leq 1$ cm thick, coating stromatolitic bioherms.	<i>Schizothrix calcicola</i> <i>Entophysalis rivularis</i> <i>Calothrix parietana</i>	Eggleston & Dean (1976)
Solar Lake, Gulf of Aqaba, Israel.	Saline, submerged growth with marginal exposure late summer.	Four distinct mat types, ranging from flat (marginal) to flocculent (bottom of lake).	<i>Microcoleus</i> sp. <i>Oscillatoria limnetica</i> <i>Oscillatoria salina</i>	Krumbein & others (1977)
<b>GEOHERMAL</b>				
Alkaline hot springs, Yellowstone National Park, Wyoming.	Pools and outflow channels, temp. range 32-59° C.	Mats with conical columns to 10 cm relief. <i>Conophyton</i> stromatolites.	<i>Phormidium tenue</i>	Walter & others (1976)
<b>MARGINAL MARINE: SUBTIDAL</b>				
Outer reef flats, Great Barrier Reef.	Essentially permanently subtidal—exposure ca. 1 day/month during lowest tide.	Small, brownish gelatinous domes, 2-4 cm diam.	<i>Phormidium hendersonii</i>	Monty (1979)
Trucial Coast, near Abu Dhabi.	Subtidal to depths of 3 m	Gelatinous domes, 18 cm diam., 6 cm high.	<i>Phormidium hendersonii</i>	Kinsman & Park (1976)
<b>MARGINAL MARINE: INTERTIDAL</b>				
Spencer Gulf, S.A.	High intertidal zone, salinity ca 45‰ and up.	Flat, smooth mat, 2-5 cm thick.	<i>Microcoleus</i> sp. <i>Schizothrix</i> sp. (?)	Bauld & others (1980)
Laguna Madre, Texas.	Intertidal zone, 10‰-200‰.	Tufted (reticulate) mat, $\leq 2$ cm thick.	<i>Lyngbya confervoides</i>	Sorensen & Conover (1962)
Hamelin Pool, Shark Bay, W.A.	Low to mid intertidal zone, 50-70‰ and up.	Pustular (mammillate) mat ca 2 cm thick.	<i>Entophysalis major</i>	Logan & others (1974)

**Table 1.** Examples of cyanobacterial mats from modern environments.

inhabit aquatic environments (Table 1), where they may be either permanently submerged or intermittently exposed. They are commonly found in marginal marine environments of tropical (e.g. Bahamas; Black, 1933), semi-arid (e.g. Spencer Gulf; Bauld & others, 1980) and arid (e.g. Persian Gulf; Kendall & Skipwith, 1968) climates. Cyanobacterial mats are cosmopolitan in geothermal springs (Castenholz, 1969), and widespread in permanent and ephemeral saline lakes (Bauld, 1981).

The greatest areal and temporal accumulations of mat biomass are generally associated with environments which are, in biological terms, either permanently or transiently 'extreme'. Physical parameters of importance include temperature, hydrological regime, salinity, and water activity. Extremes of these favour cyanobacterial mat development indirectly by relieving grazing pressure. In contrast to microorganisms, including cyanobacteria, grazing animals are unable to survive and reproduce at the extremes of the environmental ranges encountered in or around aquatic habitats. For example, while mat-forming cyanobacteria in alkaline hot springs have an upper temperature limit of  $\sim 73\text{--}74^\circ\text{C}$ , grazing metazoans are unable to grow at temperatures greater than  $\sim 45\text{--}50^\circ\text{C}$  (Brock, 1967).

A selection of cyanobacterial mats from representative habitats is documented in Table 1. As with many planktic cyanobacteria, benthic mat-constructing species often exhibit a cosmopolitan distribution. Thus, mats of the same morphology, constructed by the same cyanobacterial species, have been found in widely separated locations. Pustular mat, constructed by *Entophysalis*, occurs in the low intertidal zones of Shark Bay, (Logan & others, 1974), Laguna Mormona, Baja California (Horodyski & Vonder Haar, 1975), and the Persian Gulf (Kinsman & Park, 1976). Similarly, *Phormidium hendersonii* constructs laminated gelatinous domes in subtidal environments at Bermuda (Golubic & Focke, 1978), the Great Barrier Reef (Monty, 1979), and the Trucial Coast of the Persian Gulf (Kinsman & Park, 1976).

In both pustular and domal mats a single cyanobacterial species completely dominates the microflora of the structure (Golubic, 1976; Golubic & Focke, 1978). This is not always the case. Some mats develop a distinctive stratification, usually controlled by gradients of dissolved oxygen, dissolved  $\text{H}_2\text{S}$ , and light intensity. The mat ecosystem then comprises a vertical succession of microbial communities, photosynthetic pigments, and photosynthetic capacity, with associated heterotrophic processes such as bacterial sulphate reduction (Golubic, 1976; Cardoso & others, 1978; Jørgensen & others, 1979; Margulis & others, 1980).

Cyanobacteria can compete successfully with other photosynthetic microorganisms for space and nutrients (Whitton & Sinclair, 1975) and it is likely, therefore, that, in the absence of grazing, mats would be widespread in shallow subtidal or lacustrine environments. The stromatolite record demonstrates that cyanobacterial mats (or functionally analogous structures) were widespread in the Precambrian, but declined thereafter (Fischer, 1965), coincidentally with the advent of grazing and burrowing animals (Garrett, 1970). Prior to grazing, the accumulation of organic carbon in unlithified sediments would have been

governed solely by relative rates of cyanobacterial production and heterotrophic microbial decomposition.

### Source of organic carbon

Cyanobacterial mats are but one of many present-day sources of photosynthetically generated organic matter. However, the presence of microfossils and stromatolites in early Precambrian sedimentary rocks suggests that these or analogous microbial ecosystems were widespread during early Earth history and, together with phytoplankton, probably constituted the major source of photosynthetically derived organic matter at that time.

Recent investigations of cyanobacterial mat colonisation associated with a prograding shoreline in northeastern Spencer Gulf (Bauld & others, 1980) have examined the rates of primary productivity (photosynthesis of organic carbon from  $\text{CO}_2$ ) by intertidal cyanobacterial mats and the rates of bacterial sulphate reduction in mat-associated sediments. These mats are reasonable analogues of Precambrian benthic microbial ecosystems, since they develop in the high intertidal plain of an exposed coastline, where metazoan grazing pressure appears to be minimal (Garrett, 1970), and they appear to be the only significant source of organic carbon for bacterial sulphate reduction. Although diatoms are present on the sand grains that are transported over or trapped in the mats, their contribution to the supply of organic carbon seems to be minimal, since germanium inhibition of diatoms (Thomas & Dodson, 1974) has no detectable effect on primary productivity (Bauld, unpublished). The dependence of bacterial sulphate reduction on cyanobacterial primary productivity has been demonstrated by Bauld & others (1980) and G. W. Skyring, L. A. Chambers & J. Bauld (unpublished results).

Cyanobacterial mats generally show primary productivities towards the higher end of the range for aquatic ecosystems (Table 2). The rates for Solar Lake and Drakesbad Hot Springs mats are exceedingly high. The lowest rates shown in Table 2 (Hamelin Pool and the low end of the range for Spencer Gulf) are ascribable to environmental factors, in particular the effects of prolonged and severe desiccation. Oceanic primary production by phytoplankton is often in the range  $0.1\text{--}0.2\text{ g C m}^{-2}\text{ d}^{-1}$  (Steemann Nielsen, 1975). A notable exception to this generality was observed in the upwelling area of the Peru Current, where primary production was reported to be  $\sim 10\text{ g C m}^{-2}\text{ d}^{-1}$  (Ryther & others, 1971). Other epibenthic microalgal systems appear generally less productive than cyanobacterial mats: for example, the following rates ( $\text{g C m}^{-2}\text{ d}^{-1}$ ) have been reported;  $\sim 0.6$  in Georgia salt marshes (Pomeroy, 1959);  $\sim 0.01\text{--}0.02$  in littoral Lake Tahoe (Flint & others, 1977);  $\sim 0.1\text{--}1.0$  for Niva Bay, Øresund (Gargas, 1970); and  $0.05\text{--}0.34$  for Port Phillip Bay (Axelrad & others, 1979).

Other photoautotrophic and chemoautotrophic microorganisms may be present in most cyanobacterial mats, but are particularly evident in stratified mats (Cardoso & others, 1978; Jørgensen & others, 1979; Margulis & others, 1980). Although little is known of their quantitative significance to organic carbon production in such mats, data from other stratified environments suggest that this aspect merits investigation. For instance, primary production by red and purple

Location	Rate g C m <sup>-2</sup> d <sup>-1</sup>	Cyanobacteria	Reference
LACUSTRINE			
Algal Lake, Ross Is., Antarctica	1.91-3.63	<i>Oscillatoria</i> spp. <i>Phormidium</i> sp. <i>Nostoc</i> sp.	Goldman & others (1972)
Solar Lake, Gulf of Aqaba	8.4-12.0	<i>Oscillatoria</i> spp. <i>Phormidium</i> sp. <i>Microcoleus</i> sp.	Cohen & others (1980)
GEOTHERMAL			
Ohanapecosh Hot Springs, Washington	2.2-4.2	<i>Schizothrix</i> sp. <i>Phormidium</i> sp.	Stockner (1968)
Drakesbad Hot Springs, California	7-12	<i>Synechococcus</i> sp.	Lenn (1966)
MARGINAL MARINE: INTERTIDAL			
Hamelin Pool, Shark Bay, W.A.	0.09-0.48	<i>Microcoleus</i> sp. <i>Schizothrix</i> sp. <i>Lyngbya</i> sp.	Bauld & others (1979)
Long Island Sound, Connecticut	4.45-8.10	<i>Oscillatoria</i> sp. <i>Lyngbya</i> sp. <i>Merismopedia</i> sp.	Burkholder & others (1965)
Spencer Gulf, S.A.	0.2-3.1	<i>Microcoleus</i> sp. <i>Schizothrix</i> sp. <i>Lyngbya</i> sp.	Bauld & others (1980)

**Table 2. Primary productivity of cyanobacterial mats.**

Location	Cyanobacteria	% TOC (DW)*	Reference
Solar Lake, Gulf of Aqaba	<i>Microcoleus</i> <i>Phormidium</i> <i>Oscillatoria</i>	8-15 (0-5 cm)	Krumbein & others (1977)
Harbor Is., Texas	<i>Lyngbya</i>	32	Parker & Leo (1965)
Laguna Lejia, Antofagasta	Not reported	3.1 (0-1 cm) 1.2 (2-5 cm)	Simoneit & others (1980)
Laguna Guerrero Negro, Baja California	<i>Microcoleus</i> <i>Lyngbya</i>	29.6 (0-1.3 cm) 9.7 (1.3-2.0 cm) 9.1 (2.0-9.5 cm)	Philp & others (1978)
Coast Lake, Ross Is., McMurdo Sound	<i>Oscillatoria</i> <i>Phormidium</i> <i>Calothrix</i>	24	Matsumoto & others (1979)
Kleberg Point Lagoon, Baffin Bay, Texas	Not reported	2.2-5 (0-60 cm)	Behrens & Frishman (1971)
Languna Mormona, Baja California	Not reported	5.4 (0-12 cm)	Peters & others (1981)
Various stromatolites (Precambrian, Cambrian, Devonian)	—	0.01-1.1	McKirdy (1976, Table 2)

\*Total Organic Carbon (Dry Weight)

**Table 3. Organic carbon content of modern cyanobacterial mats and ancient analogues.**

(photosynthetic) bacteria may contribute 20-85 percent of the total production in a number of meromictic lakes (see Pfennig, 1978). Chemoautotrophic (non-photosynthetic) primary production has been demonstrated at the H<sub>2</sub>S/O<sub>2</sub> interface in nearshore sediments (Kepkay & others, 1979), in the water column of the Black Sea and Cariaco Trench (Tuttle & Jannasch, 1979), and the Galápagos Rift hydrothermal vents (Karl & others, 1980), but its quantitative significance is not yet established.

### Preservation or decomposition?

High rates of organic carbon production are a necessary, but insufficient, condition for large-scale kerogen formation. The degree of subsequent preservation of the organic carbon is controlled by a complex sequence

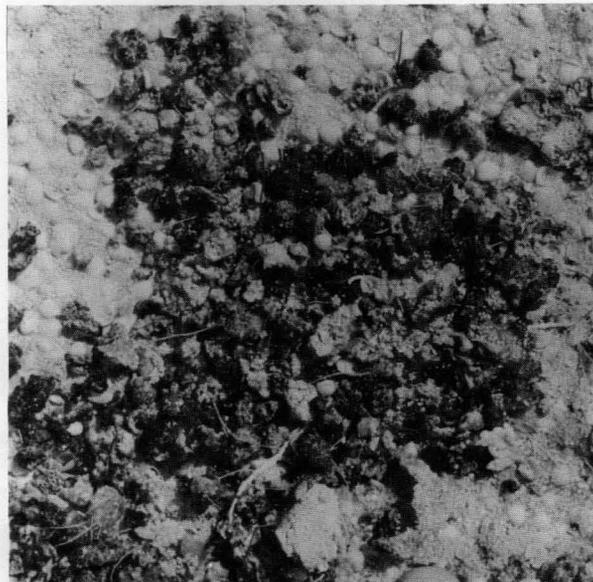
of biological and physico-chemical processes, which may promote or inhibit eventual decomposition to CH<sub>4</sub> and CO<sub>2</sub>, the terminal products of aerobic (CO<sub>2</sub>) and anaerobic (CO<sub>2</sub>, CH<sub>4</sub>) microbial respiration. Sulphate reduction and methanogenesis are the terminal processes in the anaerobic decomposition of organic matter.

The organic carbon contents of modern cyanobacterial mats and mat-associated sediments (Table 3) are high relative to other, non-mat sediments. Tissot & Welte (1978) regarded sediments containing ≥0.5 percent Total Organic Carbon (TOC) to be rich in organic matter. Oceanic sediments are generally in the range 0.1-0.6 percent TOC (Hunt, 1979, table 4.8). Larger concentrations of organic carbon accumulate in sediments of anoxic silled basins and stratified lakes,

e.g. Black Sea, 1-15 percent; Cariaco Trench, 0.6-5 percent; Lake Tanganyika, 7-11 percent (Hunt, 1979; Demaison & Moore, 1980). Mat sediments are reported to contain more than 2-3 percent TOC and frequently up to 15-30 percent TOC (Table 3), whereas non-mat sediments from adjacent areas of shallow, well-mixed waters contain significantly less organic carbon, e.g. 0.4 percent TOC in the Laguna Madre (Philippi, 1965). The concentrations of organic carbon preserved in a range of lithified stromatolites are less than those in modern mats by up to 2-3 orders of magnitude (Table 3).

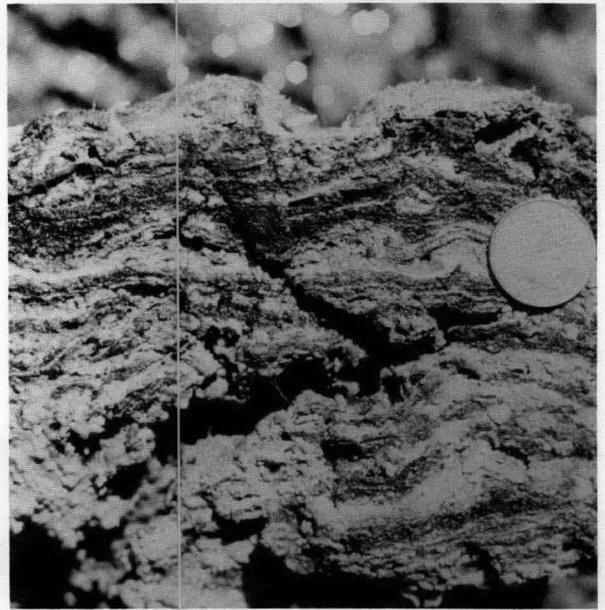
While many modern cyanobacterial mats are not well preserved, being subject to desiccation and subsequent deflation, metazoan grazing, and heterotrophic microbial decomposition, there are examples of well-preserved mats. For instance, the mats in Baffin Bay examined by Behrens & Frishman (1971) have accumulated to a depth of ~60 cm during the last ~1000 years, while the finely laminated mats in Solar Lake represent ~2500 years of deposition and are up to ~1.5 m thick (Cohen & others, 1980). Trucial Coast mats have accumulated to a thickness of ~1 m over the past ~4500 years (Park, 1976).

The preservation potential of cyanobacterial mats is governed by mat structure and fabric and by the physico-chemical environment. The former is largely controlled by the morphologies of the constructing cyanobacteria, while the latter is a product of topography, hydrology, and sedimentary regime (e.g. Park, 1977). For instance, although the pustular (mammillate) mat constructed by *Entophysalis major* (Fig. 4) is found preserved as the analogous *Eoentophysalis belcherensis* in comparable Precambrian stromatolites (Golubic & Hofmann, 1976), this mat type appears generally to lack preservation potential. Intact pustular mats do not support in situ bacterial sulphate reduction: sulphide is undetectable (Bauld & others, 1979).



**Figure 8. Fragments of pustular mat (Hamelin Pool) which have been eroded by wave action and removed from their environment of growth.**

Pustular mat lacks the mechanical strength of those (e.g. smooth) mats constructed by filamentous cyanobacteria and is more susceptible to erosion (Toe is ~2 cm across).



**Figure 9. Tufted mat from Lharidon Bight, Hamelin Pool.** *Lyngbya* sp. (see Fig. 5) is the major constructing organism, but *Microcoleus* and photosynthetic bacteria are also present. The mat shows accumulation of growth laminations. Coin is 28 mm in diameter.

and the associated sediments do not appear to be reducing (Fig. 3). It is only when *Entophysalis* colonies and mat fragments are eroded by wave action and transported to a depositional environment (Fig. 8) that they are likely to support the development of anoxic conditions and, hence, higher preservation. This phenomenon is analogous to the anaerobic decomposition of phytoplankton after their sedimentation out of the oxic water column, and is in contrast to the more characteristic in situ anaerobic decomposition of mats constructed by filamentous cyanobacteria (Figs. 3, 9).

The cohesive filamentous matrix of many mats promotes considerable micro-environmental modification, which possibly enhances preservation potential. The mat acts as an 'ecological membrane' (Armstrong & Odum, 1964), which modifies the sediment/water interface, substantially decreasing permeability (Bubela, 1980) and thus presenting a barrier to both gas and liquid transfer across the mat/water interface. Environmental parameters, such as dissolved oxygen, Eh, H<sub>2</sub>S, and light intensity, undergo abrupt changes at the interface and exhibit steep gradients beneath the mat surface (Jørgensen & others, 1979).

Virtually all species of benthic cyanobacteria involved in mat construction possess sheaths of various thicknesses and consistencies (see Figs. 4, 7, 8, 9). The gelatinous or mucilaginous sheaths appear to have a higher preservation potential than cellular contents (e.g. Knoll & others, 1975; Golubic & Hofmann, 1976; McKirdy, 1976; J. H. Oehler, 1976; Park, 1977). Golubic & Hoffmann (1976), who studied *Entophysalis* (and its Precambrian analogue *Eoentophysalis*), speculated that metal accumulation in the sheath, by chelation with the sheath pigment, scytonemine, might inhibit decomposition. Similarly, Degens & Mopper (1976) suggested that bound metals inhibited microbial degradation. In mats constructed by filamentous oscillatorecean cyanobacteria, upward gliding, as a consequence of positive phototaxis, causes (some) trichomes

to glide out of their tubular sheaths. The latter remain behind, together with dead or inactive trichomes, in the encroaching anoxic sediment. Trichomes buried beyond the light penetration zone are unable to obtain their obligate requirement for light energy and will die. It is not clear whether the apparent preferential preservation of sheath material is a behavioural phenomenon, i.e. most trichomes glide out of their sheaths leaving them behind, or whether it is due to differential susceptibility to decomposition of sheaths and trichomes. There appears to be no obvious reason why sheath material should be markedly better preserved, since the constituent mucopolysaccharides (Lang, 1968) should not be particularly recalcitrant molecules. Cell walls may also be preserved to some extent, either as organic residues (D. Z. Oehler, 1976) or as mineral replacements e.g. hematite (Licari & Cloud, 1972).

Anoxic reducing conditions and/or high salinity are usually advanced as prerequisites for organic carbon preservation. Presented without qualification, such statements should be regarded with some caution. Microorganisms, the primary agents of decomposition, obtain their nutrients from solution and can only grow in direct contact with water. Increasing salinity lowers water activity ( $a_w$ ) until a point is reached when thermodynamic problems are insurmountable and the microbes can no longer grow (Brown, 1976). Gypsum is saturated when normal sea water (3.5%;  $a_w = 0.98$ ) is concentrated about 3-fold ( $a_w = 0.93$ ) and halite crystallisation occurs after 10-fold concentration ( $a_w = 0.74$ ) (Bernier, 1971). Extremely halophilic bacteria (aerobic heterotrophs) are ubiquitous in salt lakes and can grow at salinities approximating saturated NaCl (~350 g NaCl per litre of solution; 35%;  $a_w = 0.75$ ), but all microbial activity will cease at higher salinities (lower  $a_w$ ) (Brown, 1976) and prevent further decomposition.

The high concentrations of dissolved organic carbon reported in Great Salt Lake (Post, 1977) and the Dead Sea (Nissenbaum, 1975) are consistent with the enhanced preservation attributed to saline waters. The rate and extent of decomposition processes at salinities approaching halite saturation are poorly documented. Post (1977) noted that  $H_2S$  and  $CH_4$  were evolved from Great Salt Lake sediments. This is consistent with the occurrence of the terminal anaerobic decomposition processes, bacterial sulphate reduction and methanogenesis. J. G. Zeikus (personal communication) has found that, while sulphate reduction rates in Great Salt Lake sediments are comparable to those in active marine sediments, methanogenesis occurs at low rates. The presence of  $H_2S$  in sediments of the Dead Sea (Nissenbaum, 1975) and the Wadi Natrun Lakes (Imhoff & others, 1979) is consistent with the presence of extremely halophilic sulphate-reducing bacteria. The occurrence of high concentrations of dissolved organic carbon in highly saline environments (referred to above) suggests that, at very high salinities, organic carbon production may outstrip decomposition. Notwithstanding the lack of available data on decomposition rates under moderate to high salinities, it seems unlikely that bacterial decomposition would be prevented, even under anoxic, reducing conditions, until salinities exceeded NaCl saturation and microbial activity ceased.

Grazing is a surface process which pre-empts mat accretion and initiates microbial decomposition of pre-

viously photosynthetically active cyanobacteria. Burrowing animals, on the other hand, interrupt the ordered laminations of buried mat, and accelerate microbial decomposition of the organic carbon by introducing oxygenated waters and nutrients. Gebelein (1974), citing Shark Bay as an example, pointed out that invertebrate grazers are nearly absent from the subtidal and intertidal zone of Hamelin Pool, where salinities may reach 9 percent (Logan & others, 1974), compared to the less saline areas of Shark Bay. On the other hand, examples of grazing metazoans are known from salt lakes and commercial salt fields. For example, an ostracod species from a salt lake of fluctuating salinity will grow at salinities up to 19 percent (P. De Deckker, personal communication), and anostracan crustaceans will grow at salinities as high as 33 percent (Mitchell & Geddes, 1977). The brine shrimp *Parartemia zietziana*, which grows at salinities up to 28.5 percent (Mitchell & Geddes, 1977), is an extensive bottom feeder (Marchant, 1976) and has been observed to graze and ingest cyanobacteria from stromatolitic mats (Lea, 1978). In normal marine environments, cyanobacterial mats in the subtidal and low intertidal zones are reported to be grazed by gastropods (Garrett, 1970; Pace & others, 1979) and by amphipods (Brenner & others, 1976). It is probable that sub-aerial exposure, rather than salinity, is the critical factor which limits grazing in these latter environments.

Another indirect effect of increasing salinity is the concomitant decrease in oxygen solubility (e.g. Nixon, 1974). Aerobic microbial respiration will exhaust the available dissolved oxygen quicker than in less saline conditions, promoting the anoxic conditions that are considered to enhance preservation. In modern environments, decreased oxygen availability will diminish the activities of benthic metazoans which, in turn, will decrease sediment reworking and irrigation by oxygenated water (e.g. Demaison & Moore, 1980).

However, anoxic conditions alone will not necessarily inhibit decomposition (Foree & McCarty, 1970; Jewell & McCarty, 1971). Doemel & Brock (1977), who investigated microbial mats in geothermal environments, provided the first clear evidence of the complete decomposition of organic matter under anoxic conditions. Methanogenesis occurs in these mats (Ward, 1978), and the immediate precursors of the  $CH_4$  formed have been identified (Zeikus & others, 1980). In addition, recently isolated species of sulphate-reducing bacteria are known to oxidise a wide range of organic substrates to  $CO_2$  (Widdel & Pfennig, 1977; Widdel, 1980). Of interest with respect to saline environments is the finding by Ward & Olson (1980) that methanogenesis is insignificant relative to decomposition to  $CO_2$  by sulphate-reducing bacteria in high-sulphate geothermal mats. This is consistent with the work of G. W. Skyring & others (unpublished results), which shows that sulphate-reducing bacteria in Spencer Gulf intertidal cyanobacterial mats would have to use most of the measured cyanobacterial primary production to sustain the measured rates of sulphate reduction.  $H_2S$  evolved during anaerobic decomposition of cyanobacterial mats may subsequently form polysulphides (Cohen & others, 1980) or perhaps react with lipids and fatty acids to produce thiols, which would be recalcitrant to normal degradation mechanisms (J. G. Zeikus, personal communication).

## Geochemical consequences of cyanobacterial activity

Cyanobacterial mats, as a source of organic carbon through geologic time from the Precambrian to the present, should be of interest to students of both sulphide mineralisation and hydrocarbon generation. Bacterial sulphate reduction, using organic carbon derived from cyanobacterial mats, has been implicated in recent models for the genesis of stratiform sulphide mineral deposits (Renfro, 1974; Ferguson & Burne, 1981). Organic matter has also been invoked as the reductant for abiological sulphate reduction (Barton, 1967; Williams, 1978). A wide range of hydrocarbons occurs in cyanobacterial mats and mat-associated sediments (e.g. Philp, 1980), protokerogens are present in modern mats (Cohen & others, 1980; Peters & others, 1981), and kerogens occur in Precambrian stromatolites (McKirby, 1976). Experimental investigations of organic carbon production and decomposition in modern cyanobacterial mats, and the biological and environmental factors controlling these processes, will assist in predicting the palaeoenvironments in which organic carbon was produced, accumulated, and preserved.

Cyanobacterial mats are among the most productive of aquatic photosynthetic systems (Table 2) and, thus, can provide a substantial flow of organic carbon, which may be viewed as facing two mutually antagonistic fates—preservation or decomposition. However, there may be a subtle interdependence between these two opposing processes, in that some decomposition may be a prerequisite for eventual preservation. For instance, aerobic decomposition to CO<sub>2</sub> is a rapid and efficient process which soon depletes available oxygen in organic-rich sedimentary environments, and thence ceases. Aerobic decomposition is subsequently replaced by anaerobic decomposition processes, which are potentially capable of completely degrading organic carbon to CO<sub>2</sub> and CH<sub>4</sub>, but which may also produce inhibitory compounds that enhance preservation.

Generally, decomposition is promoted by biological agents, while environmental factors may mitigate or prevent this fate. As we have seen, the major agents of cyanobacterial mat decomposition are grazing and burrowing metazoans (absent in the Precambrian) and the spectrum of aerobic and anaerobic heterotrophic bacteria that develop within the mat. While high temperatures, high salinities, and anoxic conditions may inhibit or preclude metazoans, microbial decomposition of organic carbon can take place under anoxic and highly reducing conditions, at all temperatures (~0–100°C) in the presence of liquid water, and at salinities up to halite saturation. There is, thus, an impressive array of degradation agents present in aquatic environments. Organic carbon will not be safely preserved until salinities exceed that at which halite has precipitated, since it is only beyond this that a<sub>w</sub> becomes sufficiently low to prevent microbial activity. Desiccation, even in the absence of high salinity, will also prevent microbial decomposition, but will make the mat vulnerable to deflation.

An environmental model that accommodates these requirements and leads to the accumulation of large quantities of organic matter would be, for instance, a shallow saline lake of fluctuating salinity in a large arid to semi-arid basin. The lake periodically undergoes total evaporation followed later by flash flooding, which

brings with it (clayey) sediments to cap the organic carbon-evaporite lining the lake floor. Such a model accommodates the requirement of low to moderately high salinities required for cyanobacterial mat growth. Cyanobacterial mats are well adapted to fluctuating salinities and the changes in water levels and marginal inundation associated with evaporation and wind-driven internal tides. Production of organic carbon by cyanobacterial mats will occur at close to maximum rates over a wide salinity range (Bauld & others, 1980), and full recovery from desiccation would be very rapid (J. Bauld, unpublished data). The evidence discussed earlier in this paper suggests that maximum preservation will be achieved if such productive periods are followed by rapid increases in salinity beyond halite saturation, accompanied or followed by burial under flood-borne sediment load. This would enable the mat, and associated evaporites, to be buried rapidly and prevent substantial flushing of hypersaline interstitial waters. Moderate to highly saline environments are likely to favour preservation, as a result of cementation and lithification of organic carbon by carbonates and evaporites.

Both Friedman (1980) and Kirkland & Evans (1981) have emphasised the importance of saline, evaporitic environments as potential hydrocarbon sources. Kirkland & Evans (1981) restricted their examination primarily to planktic sources of organic carbon, but Friedman (1980) emphasised benthic systems, and was of the opinion that 'algal mats are among the best of the source rocks and provided the greatest return of liquid hydrocarbon' (Friedman, 1980, p. 607). Cyanobacterial mats accumulating in environments such as saline lakes (e.g. Solar Lake) and marginal marine environments (e.g. Trucial Coast) must be considered to be excellent contenders for diagenetic conversion to kerogen. Protokerogen constituted 5 percent of the organic carbon present in the top 12 cm of laminated mat from Laguna Mormona (Peters & others, 1981). Cohen & others (1980) observed that protokerogen in Solar Lake mats increased with depth, from 3 percent of TOC in the upper layers, to 22 percent 80 cm below the mat surface. The presence of pheophytane, phycocyanin and  $\alpha$ - and  $\beta$ -carotene in Solar Lake mats suggested that the mats were in a very early stage of diagenesis (Cohen & others, 1980).

The possibility that the enormous oil shale reserves hosted by the Green River Formation accumulated from benthic cyanobacteria has been advanced by Eugster & Hardie (1975). They suggested that the two oil shale facies present were formed in a shallow saline lacustrine environment. A fluctuating hydrological regime of periodic desiccation-flooding-desiccation cycles, common to such environments (Bauld, 1981), caused polygonal cracking of marginal mats, dried fragments of which were transported to depressions during subsequent flooding, where they produced lenses of oil shale breccias. Eugster & Hardie (1975) postulated that the organic-rich dolomitic laminites were produced by the accumulation of flocculent mats of gelatinous cyanobacteria. Similar mats are seen today in the saline lakes, Lake Lenore and Soap Lake (Washington), where crumbly gelatinous mats of *Anacystis marina* and *Plectonema nostocorum* cover much of the bottom sediments (Castenholz, 1960a, 1960b). Highly productive (5 g C m<sup>-2</sup> d<sup>-1</sup>) flocculent benthic mats also form in the bottom of Solar Lake (Krumbein & others,

1977) under high H<sub>2</sub>S concentrations and low light intensities.

The properties of kerogens preserved in carbonates and cherts of Proterozoic and Palaeozoic stromatolites are consistent with their derivation from the mucopolysaccharide cyanobacterial sheaths (McKirby, 1976). Finely lamellar material of benthic origin constitutes the bulk of material in many oil shales (Hutton & others, 1980). This material, which Hutton & others (1980) referred to as alginite B (also 'lamellar alginite' or 'lamosite'), consists of thin elongate lipid-rich anastomosing films derived from (presumptive) cyanobacterial mats or benthic microbial blooms. Kerogen from the Green River Formation oil shale is predominantly alginite B, and includes pristane and phytane (McKirby & others, 1980), and the major component of kerogen in the oil-prone Observatory Hill Beds of the Officer Basin is also lamellar alginite B (McKirby & Kantsler, 1980). Alginite B is present in the Cambrian Beetle Creek Formation of the Georgina Basin (McKirby & others, 1980).

Tissot & Welte (1978, p. 22) stated that primary production by 'phytobenthos may be of local importance but on a world-wide scale it can be practically ignored' and they did not further consider the potential of such systems for hydrocarbon generation. However, cyanobacterial mats are highly productive systems (Table 2) and the physicochemical properties of these environments confer a high preservation potential. Furthermore, cyanobacterial mats (or analogous structures) were considerably more widespread in the past, as evidenced by the abundance of stromatolites in Precambrian sequences. While not yet proven, the properties of alginite B, its association with mineral material to form lamosite, and the association of lamosites with authigenic evaporites and saline environments are all consistent with a cyanobacterial origin. The occurrence of oil shows in Cambrian and Precambrian stromatolitic dolomites (White & Youngs, 1980; Muir & others, 1980) is also consistent with a cyanobacterial mat origin. The information thus far available suggests that palaeoenvironments likely to have hosted cyanobacterial mats could well have produced petroleum source rocks.

### Acknowledgements

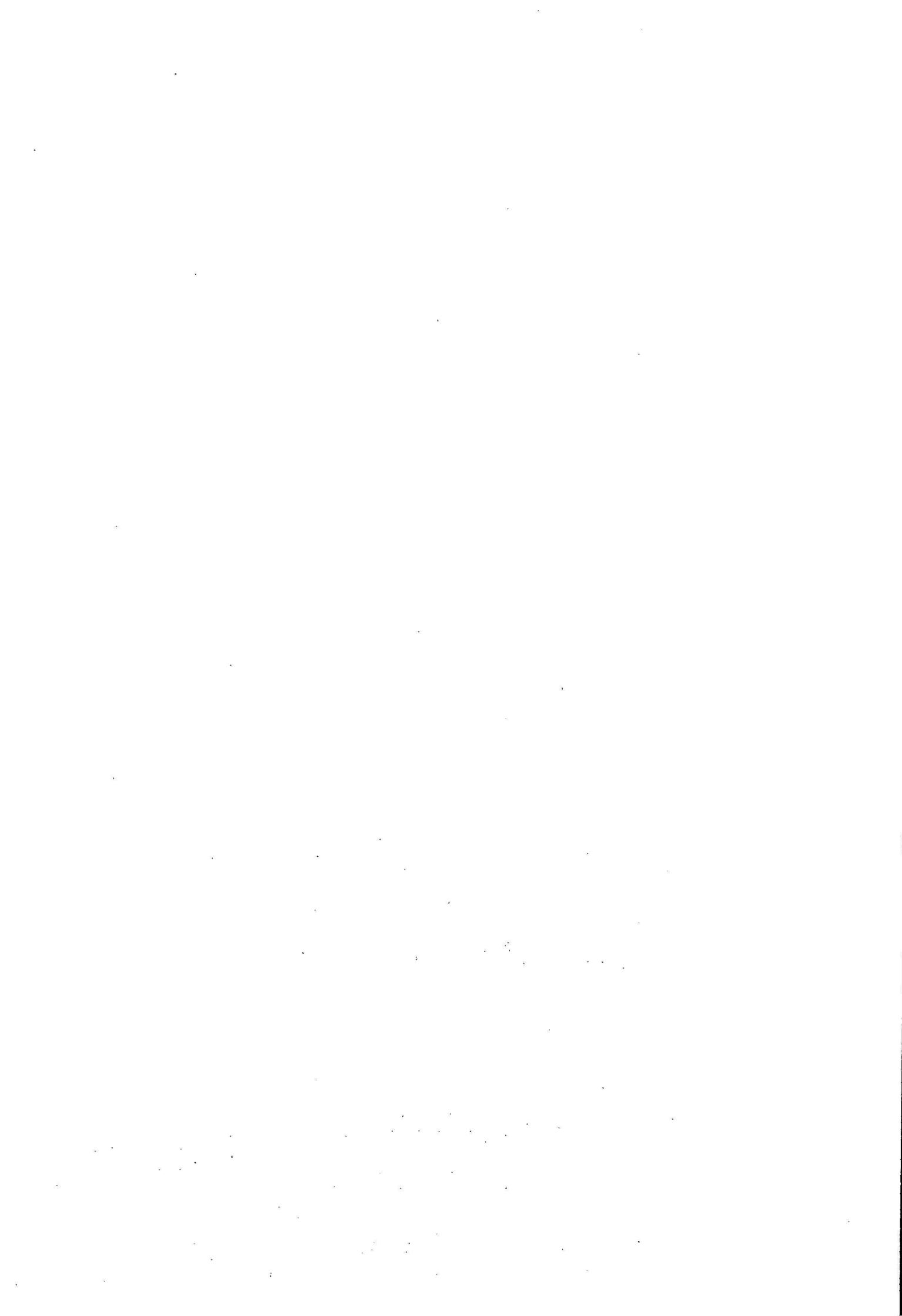
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# Interactions between saline redbed groundwaters and peritidal carbonates, Spencer Gulf, South Australia: significance for models of stratiform copper ore genesis

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A commonly cited model for the genesis of stratiform Cu deposits that lack either igneous or hydrothermal associations has been tested in modern environments, on the northeastern shore of Spencer Gulf, South Australia. In this area, saline continental redbed groundwaters mobilise Fe and Mn from the aquifer sediments and transport these metals to coastal Holocene carbonate complexes. There they may precipitate in sediments in ephemeral lakes or around springs formed by the emerging groundwaters. The continental groundwaters are generally acidic and oxidising, and they discharge mainly in the supratidal zone, remote from the major areas of bacterial sulphate reduction in the intertidal zones of the sedimentary complexes. Conversion of Fe in the groundwaters to sulphides is not widespread, but occurs if the influence of the groundwaters is attenuated by seasonal decrease in flow rate or by interaction with the alkaline, reducing marine carbonate environment of the peritidal zones.

The Spencer Gulf investigations strongly support the contention that terrestrial groundwaters of suitable pH, Eh, and salinity for the transport of high concentrations of Cu, Pb, and Zn may be generated in semi-arid climates, and that these groundwaters are capable of mobilising large quantities of metals held in Fe-oxide grain coatings. The formation of a stratiform metal deposit zoned in accordance with metal sulphide solubilities is more difficult to envisage. The absence from the supratidal sequence of a thick deposit of organic matter capable of sustaining bacterial sulphate reduction means that the metals are more likely to be removed from solution by adsorption onto the marine carbonates, or by oxidation and precipitation as oxides or hydroxides.

## Introduction

Stratiform deposits that lack evidence of either igneous or hydrothermal influence are important and globally widespread sources of copper. They presumably accumulated as a result of sedimentary and diagenetic processes operating at low temperatures, but the precise nature of these processes remains obscure. Commonly proposed genetic models actually contradict some characteristics of these deposits. Renfro (1974), and Rose (1976) put forward theories to account for various aspects of this type of ore genesis. In this paper we attempt to test these theories by examining the relevant geological, hydrological, geochemical, sedimentological, and biological aspects of an appropriate modern environment, the northeastern shore of Spencer Gulf, South Australia (Fig. 1).

## Characteristics of stratiform copper deposits

Guilloy & Pelissonnier (1974) found that 'copper shale' and copper-bearing argillaceous limestones occurred in transgressive deposits, localised around palaeoreliefs, and set in a reducing facies at the first major boundary between silt and carbonate sedimentation.

Renfro (1974) indicated that copper shales are: (1) contained within strata that accumulated along the shoreward fringe of a shallow, semi-restricted marine lagoon or inland sea; (2) hosted by reduced, grey to black sandstone that is generally stromatolitic; (3) underlain by redbeds or otherwise oxidised continental clastic sediment; (4) overlain by strata that contain dolomite, gypsum, anhydrite and/or halite; and (5)

laterally or vertically zoned with respect to metal content.

Rose (1976) noted that redbed copper deposits occur within or immediately marginal to thick sequences of red, brown, purple, or yellow mudstone or shale deposited in fluvial-deltaic or other terrestrial or marginal-marine environments. The mineralised zone itself is in greenish sediments that contain evidence of organic material and reducing conditions.

## Genetic theories

No analogous present-day environment of copper concentration has been described. Rickard (1974) concluded that there are three potential environments where the geochemical behaviour of copper at low temperatures might lead to the formation of a stratified copper sulphide ore: (1) the sediments of active ocean ridges; (2) partly connate subsurface water systems and (3) near-shore organic-rich sediments supplied by runoff from adjacent mineralised continental areas. The third of these environments is compatible with many of the characteristics of stratiform copper deposits summarised above. Renfro (1974) proposed a model for copper ore formation that depends upon processes operating in certain environments of this type, i.e. those analogous to coastal sabkhas of the Persian Gulf or the Gulf of California. This model requires the mobilisation and transport of trace amounts of copper, silver, lead, and zinc from continental redbeds by low-salinity terrestrial formation waters of low pH and high Eh. On reaching the coastal zone these waters interact with organic-rich intertidal sediments that were deposited during a marine transgression from deposits of algal mats and then buried by supratidal evaporites after subsequent marine regression. The metal-bearing waters react with dissolved sulphide formed by microbial sulphate reduction in the organic-rich layers, and

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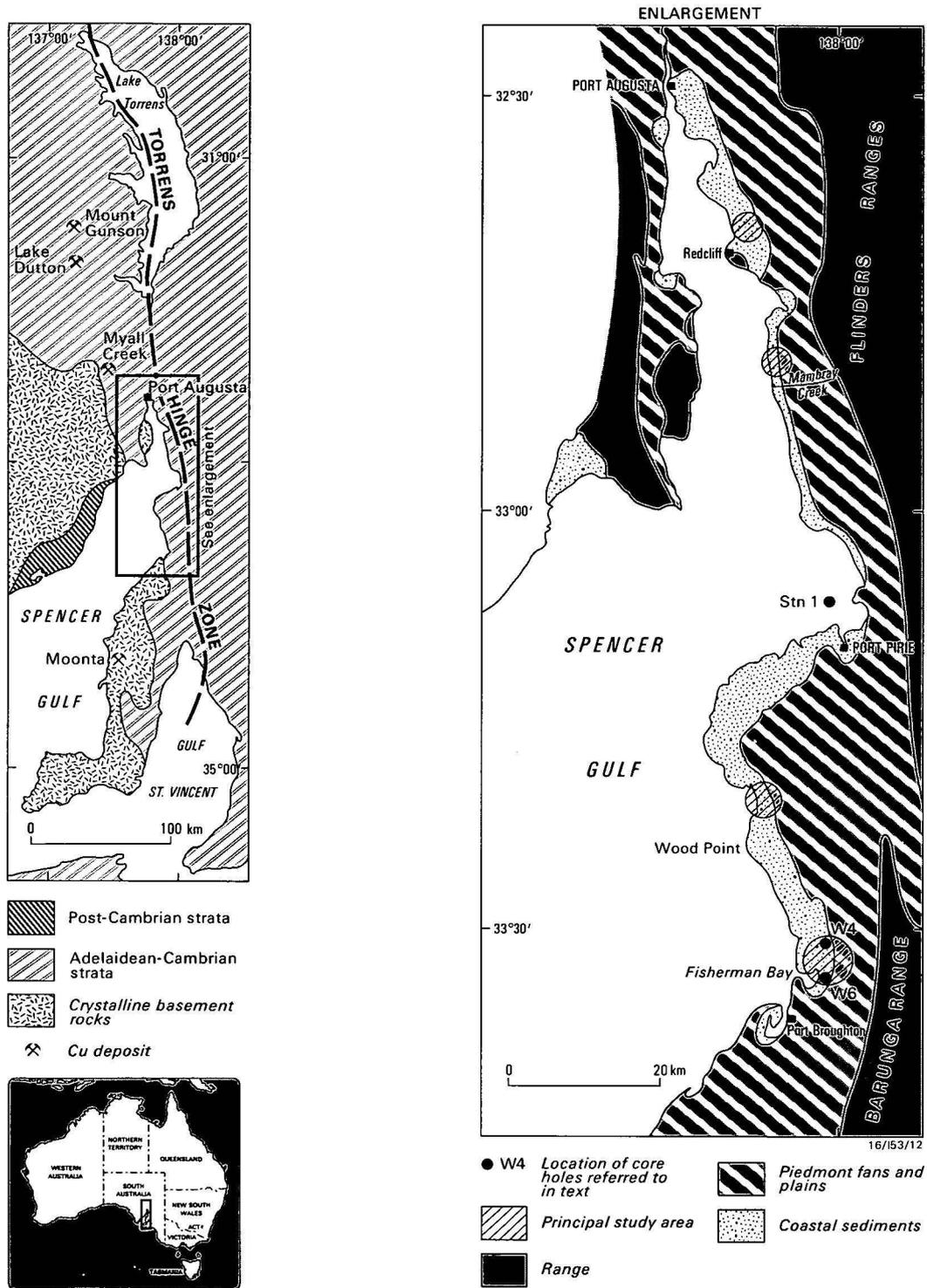


Figure 1. Location of study areas in Spencer Gulf, showing major structural provinces and copper prospects.

metal sulphides are formed, which are zoned seawards according to their relative solubilities. This model explains the internal zoning of stratiform deposits and their setting between underlying oxidised strata and overlying evaporites.

Rose (1976) has shown that low-salinity waters are relatively ineffective in transporting dissolved copper, as the solubility of copper at near-neutral pH values is less than 1 ppm. Much higher solubilities are possible in chloride-rich brines because the cuprous ion is able to form the complex ions,  $CuCl_2^-$  and  $CuCl_3^{2-}$ . Rose

concluded that, unless the terrestrial formation waters of Renfro's model were saline, copper would not be sufficiently soluble in them to give rise to appreciable deposits.

### Setting of Spencer Gulf

We consider the northeastern coast of Spencer Gulf to be an appropriate place to test the feasibility of these models. The coastal sediments of the area have a depositional setting similar to that of sediments associated with many stratiform copper deposits (Fig. 2). The

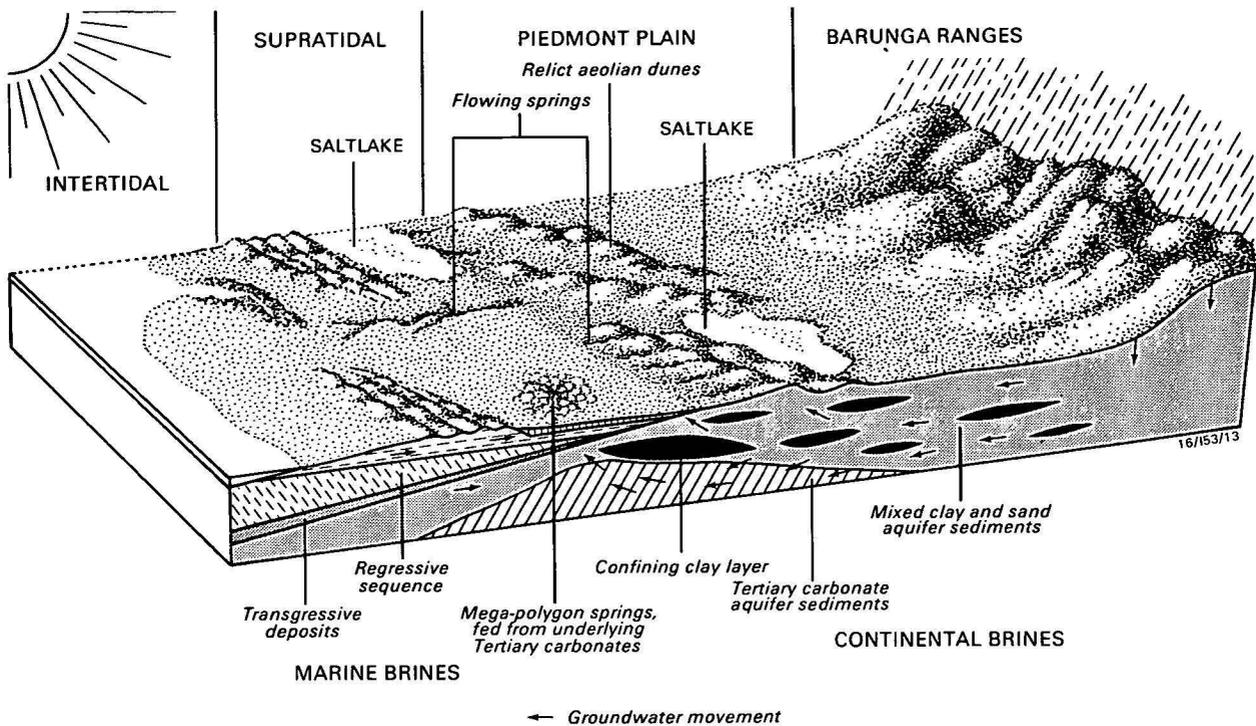


Figure 2. Composite diagram showing aquifer characteristics and varieties of groundwater discharge in the vicinity of Wood Point and Fisherman Bay.

Gulf occupies part of a compound rift valley system (Fig. 1) known as the Torrens sunklands (Fenner, 1930). The area is a rich copper province, but the Proterozoic sediments adjacent to the northeastern shore of the Gulf are not extensively mineralised, and are composed dominantly of quartzites. The Gulf is flanked by a piedmont plain constructed by alluvial fans north of Port Pirie, and by alluvial plains and Pleistocene aeolian dunes south of Port Pirie. The sediments of these plains are Quaternary redbeds, which, at the shoreward margin, consist of yellow-brown or red-brown, quartz-rich clayey sands and sandy clays containing secondary carbonate (Firman, 1965; Hiern & others, 1973; Colwell & Burne, 1978).

The area experiences a semi-arid climate, and surface drainage is limited. However, there is active groundwater movement through aquifers of the piedmont plain from areas of recharge in the higher rainfall areas of the hills to areas of groundwater discharge in the coastal zone. There they interact with sediments that have been deposited during the Holocene transgressive and more recent regressive phases. The sediments include carbonates, evaporites, and organic matter derived from intertidal cyanobacterial mats (Burne & Colwell, in press). A preliminary account of the distribution, structure, and primary productivity of these mats, the rates at which sulphate is reduced in sediments below the mats, and the sulphur isotope composition of both the sulphides and porewater sulphate within the mat sediments is given in Bauld & others (1980).

### Hydrology and lithology of the aquifer systems

Most of the groundwater entering the coastal areas at Spencer Gulf is transported through a near-surface aquifer system in surface Pleistocene aeolian sands and underlying alluvial sediments (Fig. 2). The Pleistocene

aquifer system is heterogeneous and comprises areas of quartz sand interfingered with calccrete-containing clay lenses of much lower permeability. Where these clay sediments are extensive they may act as an aquiclude, confining the groundwaters to deeper parts of the Pleistocene sediments or to underlying Tertiary carbonates before they emerge as groundwater springs.

The alluvial sediments have as their provenance the quartzites of the southern Flinders Ranges, but the surface aeolian sands may have a more distant north-western provenance. The Pleistocene sediments are mineralogically relatively simple (Table 1). The sands are almost pure quartz, whereas the more clayey sediments also contain calccrete, clay minerals, and, at some locations, the evaporite minerals, gypsum and celestite (Colwell & Burne, 1978). These evaporites may be relics of a playa lake system thought to have developed on the coastal plain during an arid period in the Quaternary (Firman, 1965). The Pleistocene sediments contain up to 5 percent Fe. Although no specific iron oxides were detected, microscopic examination indicated that some of the Fe is in the form of ferric oxides coating sediment grains. The heavy-metal content of the clayey aquifer sediments is considerably higher than that of the sandy quartz layers (Table 1), but in both cases the values are low. The readily extractable metal concentrations may be considerably lower than the totals given in Table 1: Cartwright & others (1976) found that the EDTA-extractable Cu, Pb, and Zn contents of uncontaminated soils in the Port Pirie region are typically less than 2, 10, and 5  $\mu\text{g/g}$ , respectively.

### Chemistry of groundwater

Groundwaters entering the Wood Point and Fisherman Bay coastal areas have variable, but generally high salt contents (Table 2). The semi-arid climate causes

Sediment type	Location (Fig. 1)	Mineralogy	Fe (%)	Cu	Zn (ppm)	Pb
Calcareous, clayey sands & sandy clays	Station 1	Quartz, calcite, plagioclase, K-feldspar, mica, chlorite, ?hematite	2.7	26	26	
	W4; 5.2-12.7 m	n.d.	to	to	to	<5
			4.9	34	78	
"	W6; 5.7-7.5 m	Calcite, quartz, ?tr. feldspar, ?tr. kaolinite	1.3	8	13	
			to	to	to	<5
			6.52	50	35	
Quartz sand	W6; 13-28 m	Quartz	0.47	5	5	
			to	to	to	<5
			1.37	12	31	
			0.06	<1	4	
			to	to	to	<5
			3.28	2	31	

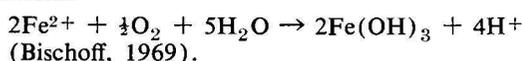
Table 1. Mineralogy and metal contents of Pleistocene sediments from northeastern Spencer Gulf.

	TDS (g/l)	pH	Eh (mV)	Alkalinity (meq/l)	Fe	Mn	Cu Pb Co Ni (ppm)
Unconfined groundwaters from the Pleistocene aquifer system	4 to 13	6.8	+50	3	1	0.5	<0.01
Confined groundwaters from a grey, sandy zone at depths near 20 m in the Pleistocene aquifer system	4	6.0	(?) Reducing	<1	60	5	<0.01
Sea water	3.5	8.1	+250	2.4	0.02	0.01	<0.01

Table 2. Chemical composition of groundwaters from the Pleistocene aquifer system near Wood Point and Fisherman Bay.

a strong seasonal variation in both the flow rate and salinity of the unconfined groundwaters, but much smaller variations in the confined groundwaters.

Within the Pleistocene sediments of the aquifer system, biological activity tends to lower the Eh of the groundwaters, with the result that ferric and manganic ions in the sediments are reduced and taken into solution. The pH of the waters is also lowered by CO<sub>2</sub> generated by the biological processes and, if dissolved Fe(II) is re-oxidised, by H<sup>+</sup> ions produced in the reaction:



The extent to which reactions of this type occur depends on the local hydrological regime. They are least likely to occur in conditions of rapid groundwater flow in the wet season in the highly permeable surface sands. Water movement through the unconfined surface aquifer is slower in the dry season, and these groundwaters may become mildly oxidising and contain traces of Fe and Mn (Table 2). Confined groundwaters associated with deeper, grey and, presumably, reduced zones may, under favourable conditions, develop abnormally high Fe and Mn concentrations (Table 2). However, no groundwaters have been found which contain more than traces of Cu, Pb, or Zn.

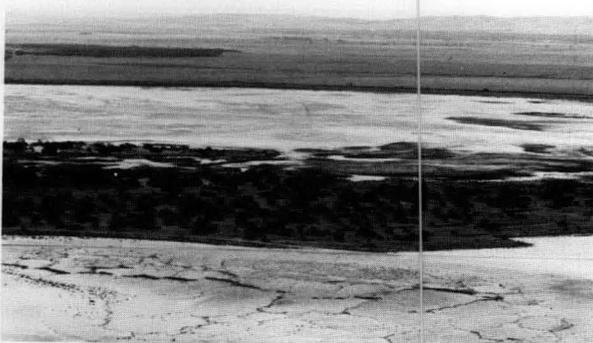
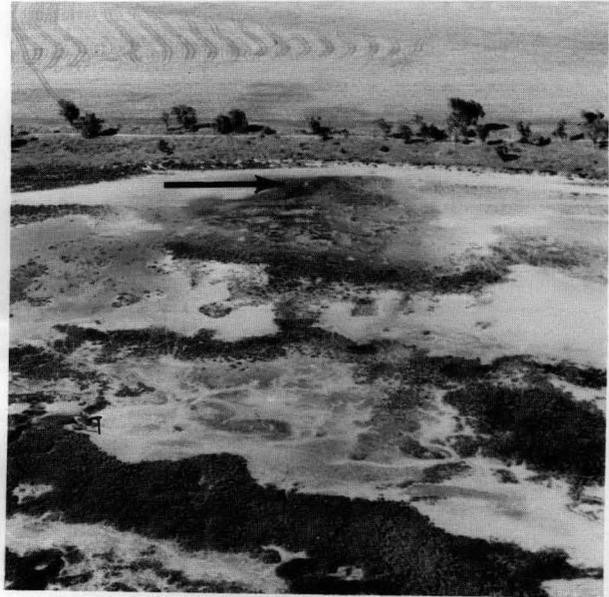
### Environments of groundwater discharge and geochemistry

The continental groundwaters emerge at the surface at the landward margin of the Holocene coastal complexes or within their supratidal zones (Fig. 2). Continental groundwaters underlie the supratidal zones of these complexes and pass seawards into a zone of mixing with interstitial waters of marine origin. The emerging groundwaters may form ephemeral lakes, or springs, some of which discharge onto the intertidal zone (Fig. 3).

Terrestrial groundwaters entering the coastal sedimentary complexes are, to varying degrees, acidic and oxidising, whereas the supratidal and intertidal sediments are usually alkaline and, particularly in the finer-grained sediments, reducing. Accordingly, the geochemical evolution of the incoming groundwaters usually involves: (1) increases in pH, (2) decreases in Eh, and (3) changes in salinity, owing to evaporation and/or mixing with marine brines. Depending on the acidity and Eh of the waters, their flow rate, and the hydrological characteristics of the environment of discharge, either the marine or terrestrial groundwater chemistry may dominate the environment of discharge.

The effect of flow rate is most evident in the terrestrial groundwater-dominated ephemeral lake at Wood Point (Fig. 3a). This groundwater is supplied from unconfined parts of the Pleistocene aquifer system and, in the dry season, it maintains the water table below the sediment surface. Under these conditions, groundwater flow is sufficiently sluggish to allow bacterial sulphate reduction to become established, and sulphide concentrations up to 0.5 percent to be generated in the sediments, presumably as iron sulphides (L. A. Chambers, unpublished results). During the wet season, there is a relatively rapid influx of mildly acidic and oxidising near-surface groundwaters that flood the lake. As result the iron sulphides in the sediments are oxidised. However, the less saline conditions that accompany the oxidising groundwaters also stimulate growth of cyanobacteria and charophytes, which may be sources of organic matter for subsequent bacterial sulphate reduction.

In areas where the groundwater discharge is in the form of springs from the confined parts of the aquifer, seasonal variations in flow rate are relatively small, and the chemistry of the environment may be controlled by the composition of the incoming waters and the local topography. At one location in Fisherman Bay (Fig. 3d), Fe- and Mn-bearing groundwaters enrich the



**Figure 3. Aerial photographs of areas of groundwater discharge;**

- a. Ephemeral gypsum lake, north of Wood Point. (top left)
- b. Spring channel discharging onto a supratidal plain, forming a fan of clay and gypsum, north of Redcliff. (middle left)
- c. Petrifying spring lithifying intertidal carbonate sediments to form a crust with megapolygons (foreground), Fisherman Bay. (bottom left)
- d. Iron precipitating around groundwater spring (arrowed), Fisherman Bay. (above right)

intertidal and supratidal sediments in these metals. However, contrasting groundwater chemistry and environments of discharge between the northern and southern parts of the area have led to Fe precipitation as Fe-sulphides and Fe-oxides, respectively. In the northern areas, the groundwaters emerge near the landward fringe of the intertidal zone and flow seawards into tidal pools that are sites of bacterial sulphate reduction. In these pools, dissolved Fe and finely divided ferric hydroxides in the groundwaters are converted to Fe-sulphides.

In contrast, groundwaters in the southern part of the Fe-rich area surface in the supratidal zone and are sufficiently acidic and oxidising to impose these conditions on the sediments immediately surrounding the spring source. These conditions attenuate with distance from the spring source, with the result that there is a pronounced geochemical gradient from the spring source to the surrounding marine sediments. Initially, the pH of the strongly acidic and mildly oxidising spring waters increases as they encounter the marine carbonates of the supratidal zone. As a result, a lens of goethite is precipitated in the redbeds near the terrestrial/marine sediment interface, and the overlying marine carbonates are dissolved. Because the goethite is precipitated under acidic conditions, Mn and trace metals are retained in solution till the waters enter a zone of excess carbonate at the periphery of the Fe-mineralised area. There, Mn and the remaining Fe are precipitated as manganese and ferromanganese oxides together with coprecipitated traces of Ni and Co under near neutral but oxidising conditions. Bacterial sulphate reduction is strongly inhibited by the oxidising spring waters, but has become established in the top few centimetres of the sediments, particularly at the

landward edge of the area. Both the rates of sulphate reduction and the amounts of fixed sulphide are low (Table 3). It appears, therefore, that sulphidisation of the Fe-lens and of the Mn-rich sediments at the periphery would require modification of the existing groundwater regime.

	[S <sup>2-</sup> ] ppm	Sulphate reduction rate $\mu\text{mol m}^{-2}\text{d}^{-1}$
Landward edge:		
Black surface mud	800	187
Middle:		
Black surface mud	<5	350
Seaward edge:		
Blue surface mud	<5	43
Green surface mud	<5	17
Grey mud under Fe-lens	<5	<0.1

Table 3. Sulphide concentrations and sulphate reduction rates in Fe-rich sediments in an area of continental groundwater discharge at Fisherman Bay (unpublished data of G. W. Skyring).

## Discussion

### Availability of metals

The major shortcoming of Spencer Gulf as a potential analogue for ancient copper ore-forming environments is the lack of readily leachable metals in the redbeds of the coastal plain aquifers. This may be due to the absence of rich metal sources in the provenance quartzites of the Flinders and Barunga Ranges. Total Cu concentrations in the finer-grained Quaternary redbed sediments are comparable with the 15 ppm that Rose (1976) suggested was adequate for the generation of an ore deposit (Table 1), but they may occur in relatively inaccessible sites within the sedimentary grains and not associated with the Fe-oxide grain coatings.

### Groundwaters as potential media for the mobilisation and transport of metals

The hydrology of the Spencer Gulf coastal plain is similar to that suggested by Renfro (1974) for his model. The semi-arid climate and significant topographic relief of Spencer Gulf would lead to a considerably greater groundwater flow rate than would be experienced in an arid region of low topography, such as that invoked by Renfro. However, residence times of groundwaters in the confined deeper aquifer systems may be similar to those of Renfro's model coastal plains.

The groundwaters of the Wood Point and Fisherman Bay areas generally have chlorinities greater than the 0.5 M suggested by Rose for the optimum generation of high Cu solubilities. It is unlikely that high Cu concentrations could be generated at the extremes of the wide range of Eh and pH values found in these waters. However, there are groundwaters between these extremes with a combination of chlorinity, Eh, and pH that would permit the solution of Cu in sufficient concentrations for them to be effective ore-forming solutions (Fig. 4).

It has been suggested that groundwaters mobilise metals from the Fe-oxide grain coatings of the aquifer sediments either as a result of originally hydrated Fe-oxide phases such as goethite converting to hematite and expelling metals into solution (Rose, 1976) or as a result of Fe-oxides being dissolved as Fe(III) and

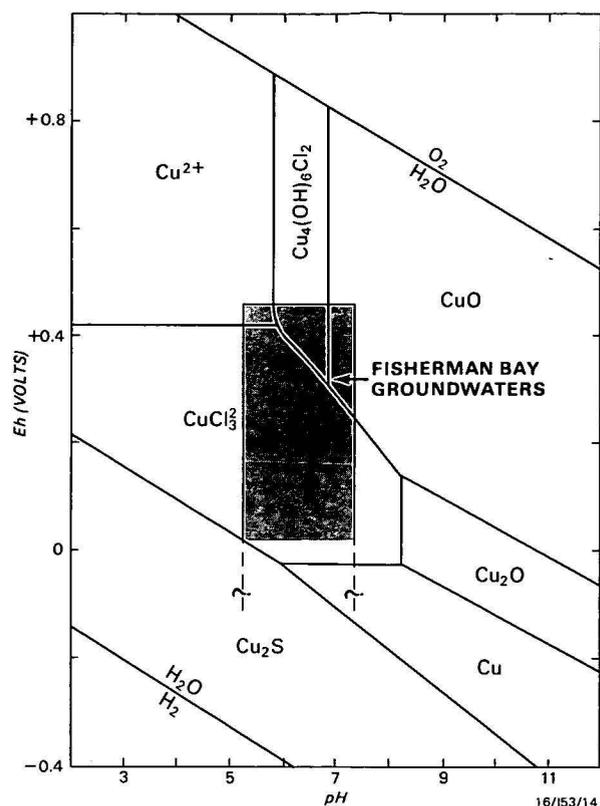


Figure 4. Eh-pH diagram for the system Cu-O-H-S-Cl, 25°C,  $\Sigma S = 10^{-4}$  m, Cl = 0.5 m as NaCl. Boundaries of Cu species at  $10^{-4}$  m. Stability of copper sulphides other than chalcocite is not shown (modified from Rose, 1976). Fisherman Bay groundwaters plot close to the area of high Cu solubility.

then reduced to Fe(II) within the aquifer system (Renfro, 1974). No evidence has been obtained for the former process, but dissolution of Fe is widespread in the aquifer systems of Spencer Gulf and, in the deeper sediments, it is efficient enough to generate groundwater Fe concentrations comparable to those associated with volcanic exhalations.

### The mechanism for precipitation of metals

Although there is evidence that the paragenesis of some stratiform Cu deposits may be complex, with Cu replacing pyrite, and Pb and Zn being introduced later than the Cu (e.g. Jung & Knitzschke, 1976), in a number of deposits the metal sulphides are zoned according to their solubility products. This suggests simultaneous precipitation of metals and sulphide by direct, relatively rapid interaction of metal-bearing saline terrestrial groundwaters and H<sub>2</sub>S-bearing porewaters. Conditions in the coastal areas of Spencer Gulf, unfortunately, do not favour this process. Many of the sites of groundwater discharge do support a population of cyanobacteria that are a source of carbon for subsequent sulphate reduction, but the main areas of sulphate reduction are in the cyanobacterial flats and marshes of the high intertidal zone, which, apart from the area of the Fisherman Bay iron pans, lie some distance from the zones of groundwater discharge.

Unlike the model proposed by Renfro, the landward margin of the Holocene transgressive/regressive sequence does not preserve organic remains of former intertidal cyanobacterial mat, and, therefore, is not an area of widespread bacterial sulphate reduction.

Metal sulphide formation is also limited by the incompatibility of the mildly oxidising groundwaters with the strongly reducing conditions required for bacterial sulphate reduction. Thus sulphate reduction may be completely inhibited locally or seasonally around zones of groundwater discharge; but, with increasing distance away from the spring source or during seasonal decreases in flow rate, bacterial sulphate reduction becomes established.

Interaction of acidic, strongly metalliferous groundwaters with alkaline, reducing, peritidal environments, such as those of Fisherman Bay, should result in metal precipitation in the following order:

1. Oxidation and precipitation of Fe under mildly oxidising and slightly acid conditions near the interface between terrestrial clastics and overlying marine carbonates.
2. Oxidation and precipitation of Mn in the carbonates immediately adjacent to the terrestrial redbeds under mildly oxidising but near-neutral pH conditions.
3. Precipitation and absorption of part of the Pb, Zn, and Cu content of the groundwaters in association with Mn.
4. Complete precipitation of the remaining metals from the groundwaters as metal sulphides by reaction with strongly reducing, slightly alkaline, marine porewaters.

### Conclusions

Our examination of Spencer Gulf coastal environments has demonstrated the feasibility of some aspects of proposed models of ore genesis. Terrestrial chloride-rich groundwaters capable of transporting high concentrations of Cu, Pb, and Zn are generated within continental redbeds of semi-arid climates. Groundwater/sediment interactions within the redbed aquifers are capable of mobilising extensive quantities of metals from Fe-oxide grain coatings. There are no obvious reasons why the hydrochemical conditions of the Spencer Gulf aquifer systems could not occur in areas where Fe-oxides of the redbeds were derived from the weathering of small quantities of sulphides in metalliferous granitic or basaltic rocks and were rich in Pb, Zn, or Cu. The lack of evidence for high concentrations of Cu, Pb, or Zn in the Spencer Gulf groundwaters is ascribed to the absence of a metal-enriched provenance for the redbeds.

The formation of a stratiform metal deposit that is zoned in accordance with metal sulphide solubilities is more difficult to envisage from the evidence of the Spencer Gulf coastal environments. The areas of coastal groundwater discharge are closely analogous to the inferred environment of formation of many stratiform copper deposits. They occur at the junction of continental redbeds and peritidal carbonate complexes that have been deposited during a Holocene transgressive/regressive cycle. These sediments are, in places, overlain by evaporites (mainly gypsum) and, in order to satisfy the requirements of Renfro's model, would require only that the transgressive sequence be the site of preservation of a thick deposit of organic matter capable of supporting sulphate reduction. In the absence of such deposits in the areas of groundwater discharge, it is likely that metals transported by the groundwaters would be removed from solution by ad-

sorption onto carbonates or by oxidation followed by precipitation as oxides/hydroxides or carbonates. These metal species could later be converted to sulphides if the nature of the groundwater discharge changed to one that supported sulphate reduction, but the resulting sulphide deposit would have a zonation that would reflect processes other than sequential sulphide precipitation.

### Acknowledgements

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## Summaries of other papers presented

### Models of sulphide ore formation in sedimentary rocks

*L. B. Gustafson*<sup>1</sup>

No group of ore deposits has stirred more controversy, primarily syngenesists versus epigenesists, than stratiform sulphide deposits in sedimentary rocks. This is partly because they are a very diverse group with probably diverse origins, and partly because discussion of the genesis has seldom been constrained by adequate definition of the mineralising system or of the terms syngenesism, epigenesis, and diagenesis. The approach taken here is to examine characteristics of sediment-hosted stratiform deposits, not as many distinct types based on narrowly defined criteria, but as a broad class of related deposits, in order to search for systematic variations that might constrain diagenetic thinking, and to identify the most critical weaknesses in our present understanding.

Volcanogenic massive sulphide deposits are excluded from consideration here, and are distinguished from sediment-hosted stratiform deposits of copper, lead, and zinc by the latter's lack of directly associated volcanism. Mississippi Valley-type deposits are also excluded, and are distinguished by their late timing of mineralisation relative to deposition of host sediments, by much less conformity with their hosts, and by lower iron sulphide and silver contents. These two types, however, are probably part of a continuum in terms of characteristics and mechanisms of formation. Characteristics of the diverse sediment-hosted stratiform deposit are illustrated by 28 selected examples, which include several of the world's giant deposits. Metal ratios of sediment-hosted stratiform copper and lead-zinc deposits are distinctly separate from one another and unlike the range of ratios in volcanogenic deposits. Most sediment-hosted stratiform lead-zinc deposits contain abundant iron sulphide, in contrast to the copper deposits, which are characterised by low iron sulphide contents. Barite is abundant and massive in several of the lead-zinc deposits, but sparse in stratiform copper deposits.

Sediment-hosted stratiform deposits of both copper and lead-zinc range in age from about 2000 m.y. to Recent, and occur in tectonically active intracratonic settings, commonly in fault-controlled sedimentary basins. They do not appear to be related to orogenic events or events at margins of tectonic plates. Local tectonic settings, relation to basin margins, and faulting are diverse. We interpret their unifying features to be that each provides a situation in which basinal groundwater could be moved to a shallow site of sulphide deposition. Regional stratigraphic settings include (1) first marine transgressions over red terrestrial sections (e.g. Zambian deposits, Kupferschiefer, White Pine, Boleo); (2) within marine (and lacustrine) sections containing redbeds (e.g. Dzhezhazgan, Udokan, McArthur River, Redstone River, Spar Lake, Irish deposits); (3) terrestrial sections containing redbeds (e.g. Corocoro, Nacimiento, Largentiere); and (4) marine sections without redbeds (e.g. Sullivan, Meggen, Rammelsberg). Evaporites (bedded or interstitial gypsum, anhydrite or carbonate after sulphate)

or other evidence of aridity (salt casts, desiccation features) are closely associated with deposits in all settings but the last. Although lacking any close association with volcanism, most deposits occur in basins with some regionally contemporaneous volcanic activity (Pb-Zn) or with a significant quantity of volcanic rocks in underlying stratigraphic sections (Cu). Sedimentary facies are important local controls of sulphide distribution, but host lithology varies widely from district to district and, commonly, within districts, and is among the least definitive features of these deposits.

Most sediment-hosted copper deposits (except in Shaba) are associated with bedded host or footwall units that retained high permeability after early diagenesis. The copper mineralisation is invariably 'disseminated' (including stockwork and breccia matrix). Most of the ore is in reduced sediments, which contain (or can be inferred to have originally contained) abundant organic matter. Ore occurs at a redox interface with footwall, hangingwall, or laterally equivalent units that are hematitic (red now or before metamorphism) and barren of sulphide and organic matter. In contrast, most lead-zinc deposits are in sediment that became rather impermeable during early diagenesis. The ores are mostly either massive or banded (i.e. interbedded with sedimentary rock), although some are 'disseminated'. Many deposits are also associated with evaporites and redbeds, though less directly than the copper deposits, and the ore is not obviously controlled by the interface between oxidised and reduced conditions.

Zonation in copper deposits typically follows the sequence: barren (hematite but no sulphide) -chalcocite-bornite-chalcopyrite-pyrite, expressed both outwards and upwards. In many deposits this zonation does not reflect palaeogeography directly. Zonation is commonly continuous across alternations of depositional environments, and probably reflects post-depositional hydrologic regimes and chemical gradients. In deposits with lead-zinc as well as copper, the general zonal sequence Cu-Pb-Zn-Fe is observed. In several deposits this sequence evidently marks increasing distance along an ore solution path. Sedimentary iron formation, both sulphide and oxide facies, appears to have formed in 'distal' portions of some lead-zinc mineralising systems. Zoning patterns are varied. The timing of metal fixation relative to deposition of host sediments and their diagenetic modification is crucial, but rarely constrained by unambiguous evidence. Concretions and authigenic minerals provide some of the best evidence, indicating fixation of base metal sulphides after early diagenesis at McArthur River and Shaba, but much earlier at Rammelsberg. The lack of definitive detailed documentation of evidence for timing and of subtle non-sulphide zoning patterns in most deposits seriously limits our ability to interpret their origins. The lack of information on temperatures of mineralisation in most deposits is also critical.

Unlike volcanogenic massive sulphide deposits, sulphur isotopes in sediment-hosted stratiform deposits do not reflect secular variations in the isotopic composition of sea water, and appear to be dominated by

processes at the site of ore deposition rather than the source of the sulphur. Narrow clustering of  $\delta^{34}\text{S}$  values in lead-zinc deposits appears to reflect systems dominated by mineralising fluids, in contrast with scattered  $\delta^{34}\text{S}$  values in copper deposits, which reflect sulphate reduction reactions at lower temperature and in systems dominated by the depositional environment. The data are ambiguous as to mechanisms and definition of the ore-forming systems. At McArthur River, carbon and oxygen isotopes support interpretation of mineralisation dominated by a hydrothermal ore-forming fluid.

We speculate that most sediment-hosted stratiform deposits of both copper and lead-zinc formed early in the diagenetic history of their enclosing sediments, from brines derived from the sedimentary basin itself. They are thus diagenetic in the broad sense, even though the metals may have been introduced epigenetically into the system defined by the present physical limits of mineralisation. The wide and gradational range of deposit characteristics derives from more or less independent variation of factors linked in a source-transport-trap chain of coincidence. The stratiform copper deposits probably formed from cool sulphate-rich brines, derived at an early stage of basin evolution and migrating up-dip to chemically reducing sites of deposition. The lead-zinc deposits probably formed from similar but more evolved brines that were heated and probably chemically reduced deeper within the basin. Some of the latter may have been formed by exhalation of dense basinal brines on the sea floor.

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### Metal sources and fixation in some stratiform deposits

*Ian B. Lambert*<sup>1</sup>

The timing of metal fixation in the Middle Proterozoic McArthur deposit (averaging ~ 14% Pb + Zn, 7% Fe, and 14% S) is assessed in the light of textures of pyrite from modern exhalative environments, experiments on production of metal sulphide bands, and the significance of S/C ratios. It is argued that the features of this deposit can all be accounted for by sedimentary-exhalative formation of the bedded sulphides, followed by diagenetic processes within the sulphidic muds. Initial results of a Pb-isotope tracer study of sedimentary strata of the McArthur Group imply U mobility and do not define the source of ore metals. Isotopic data allow precipitation of major proportions of FeS from the ore-forming brines ( $T \leq 150^\circ\text{C}?$ ), and biogenic conversion of FeS to pyrite in the near-surface sediments; there is no evidence for biogenic S in sphalerite and galena. Thus, it is likely that microbial processes played a secondary role in ore formation.

In contrast, textures, sulphur isotope data, and metal zonations indicate that generation of copper mineralisation in the Late Proterozoic Tapley Hill Formation of the Stuart Shelf (averaging <1.5% Cu, <4% Fe and <3% S) involved reaction between biogenic pyrite and low temperature cupriferous solutions. This replacement evidently continued (or began) after com-

mencement of deposition of the unconformably overlying Whyalla Sandstone. Likely sources of Cu are the unconformably underlying Pandurra Formation ('redbeds') and mineralised pre-Adelaidean basement.

There is evidence in both cases that metalliferous brines ascended in major fault systems.

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### Saddle dolomite gangue: an indicator of epigenetic mineralisation in sediments

*B. M. Radke*<sup>1</sup>

Where time and temperature constraints can be applied to sulphide accumulation, more realistic models of formation can be developed and appropriate exploration strategies applied. Saddle dolomite gangue occurs with many lead-zinc sulphide occurrences in carbonate host rocks, and is a potential indicator of such mineralisation because it has a broader distribution, is genetically related, and is easily distinguished from 'normal' dolomite.

Empirical evidence suggests concurrent formation of saddle dolomite and sulphides by abiogenic sulphate reduction at epigenetic temperatures (~50–150°C), in the presence of hydrocarbons and sulphate; the latter being derived from either the host carbonate or warm brines that introduced the metal ions.

Saddle dolomite can be distinguished by curved crystal faces and cleavage, sweeping extinction under crossed polars, length-slow character, and crystal habit varying from rhombohedra with slight facial curvature to saddle-shaped forms. This dolomite is non-stoichiometric, being typically calcium-enriched. It occurs as the primary component in replacement dolostone bodies, as void-filling cement in primary and secondary porosity, including veins and breccia types, or in a combination of these modes. Calcite, fluorite, barite, and anhydrite are commonly associated with it.

<sup>1</sup> Bureau of Mineral Resources.

### Lead isotopic systematics of sediment-hosted Pb-Zn deposits

*Matti Vaasjoki*<sup>1</sup> & *Brian L. Gulson*<sup>1</sup>

Examination of recent high-quality data from eight sediment-hosted deposits suggests that these deposits may be grouped on the basis of their lead isotopic compositions in the following manner: (1) deposits with ordinary homogeneous leads, (2) deposits with homogeneous slightly radiogenic leads, (3) deposits with homogeneous grossly radiogenic leads, and (4) deposits with heterogeneous grossly radiogenic leads.

Examples of the first two groups are situated in geological environments characterised by a thick underlying sedimentary pile, and, where established, the age differences between the underlying basement and the immediate hosts of the mineralisation are small. In groups (3) and (4) the characteristic features are the thinness or virtual absence of underlying sedimentary formations and a large age difference between the base-

ment and the host rock. The homogeneity of the group (3) type is attributed to repeated erosion and sedimentation of the basement rocks.

If these relations are maintained in other deposits, the popular notion that homogeneity of lead isotopic compositions in sediment-hosted lead-zinc ores indicates a volcanogenic origin of the lead will be in considerable doubt. Rather, the present assessment suggests that repeated reworking of the source material by processes such as erosion, sedimentation, and perhaps metamorphism more likely produces homogeneous leads in sedimentary environments.

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### Mechanisms of sulphide deposition in sediment-hosted exhalative lead-zinc deposits

*M. J. Russell<sup>1</sup>, M. Solomon<sup>2</sup> & J. L. Walshe<sup>2, 3</sup>*

Sediment-hosted massive sulphide lead-zinc deposits like Sullivan, Navan, Rammelsberg, and McArthur River appear to have formed at or near the sediment/water interface, and, commonly, in basins related to syn-sedimentary growth faults. Unlike volcanic-hosted deposits, they accumulated intermittently over long periods ( $>10^5$  years?).

The Silvermines deposit in Eire is an important example, as it has yielded data on fluid temperature and salinity (I. Samson, personal communication, 1980) that are likely to be of general significance. At this deposit, the growth fault separating Old Red Sandstone from Carboniferous bioclastic limestones and shales has acted as a feeder zone to two major ore zones that extend from the fault into the limestone sequence. The lower (Lower G and K Zones) is of subsurface replacement origin and consists of galena, sphalerite, and minor pyrite, while the upper and main zone (Upper G and B Zones) is mainly exhalative, and consists of galena, sphalerite, pyrite, chert, dolomite, siderite, and barite. The upper zone ore shows scour and pull-apart structures, syndepositional breccias, colloform textures, and well-defined ponds of very fine-grained sphalerite and siderite. The exhalative Magcobar deposit contains barite, pyrite, and minor hematite, and occurs near the growth fault.

Fluid inclusions in the lower ore have homogenisation temperatures up to 265°C, salinities of 13-24 weight percent NaCl equivalent, and include vapour-dominated types. Fluids at this temperature with say, a salinity of 2.5 mol NaCl, on reaching sea water of similar salinity to modern sea water would be positively buoyant initially, but would then reverse buoyancy. The high salinity contrast probably precludes ideal mixing, and leads to double-diffusive effects. The reversing plume probably splits into a buoyant phase that stagnates and spreads laterally at the sea-water surface (giving rise to widespread chemical anomalies at the ore horizon) and a dense phase that collapses onto the sea-floor. The negative  $\delta^{34}\text{S}$  values in the exhalative ore (Coomer & Robinson, 1976) may be derived by (a) incorporation into the plume of biogenic aqueous sulphide species formed in a reducing basin or (b) loss of  $\text{H}_2\text{S}$  from the ore fluid by boiling, followed by sulphide precipitation

in a basin from sulphur derived by biogenic reduction of sea-water sulphate.

The Magcobar deposit is thought to be derived from a plume mixing largely with normal sea water outside the reducing basin.

Reversing plumes are likely to pulsate (Turner, 1966), and Silvermines-type plumes, reaching 100 m above the sea-floor, would have a periodicity of about 5 minutes. This process may be important in producing the microbanding observed locally in the Silvermines ore, but developed strongly in deposits such as McArthur River and Rammelsberg.

In cases like Dugald River, where sea or lake water was probably shallow and hypersaline (M. D. Muir, personal communication), buoyant plumes probably stagnated at the water surface, and shed sulphides from the laterally moving plume.

The vapour-phase inclusions from Silvermines indicate boiling and consequent cooling, which may have led to subsurface nucleation of sulphides in the fluid. Though evidence of this is limited at Silvermines, it is abundant at Bula, where sphalerite 'mud' fills limestone cavities. Hydrothermal fluid at 250°C and with velocity  $10^{-1}$  cm  $\text{s}^{-1}$  could transport spherical sphalerite particles of several microns diameter, and thus effectively limit particle grain size in the emerging fluid. Such a process may partly explain the very fine grain size of parts of the Silvermines ore and also of other relatively unmetamorphosed deposits (e.g. McArthur River).

Earlier workers have pointed to the likelihood of boiling during the formation of this group of deposits. The phenomenon has been examined numerically (in conjunction with A. Bush) using mass transfer calculations to predict the change in composition of a saline liquid and the phases precipitated from the liquid as it rises along the liquid-vapor curve. The model assumes the liquid and vapour rise together and remain in equilibrium as they ascend. Boiling would cease immediately the fluids were quenched by mixing with ambient water.

The liquid was initially assumed to be at 250°C, to have a pH of 4.65, and to be in equilibrium with quartz, sericite, and pyrite. After 9 percent boiling, the temperature had dropped to 200°C and the pH of the liquid had increased to above 5.2, as a result of the loss of  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{S}$  to the vapour phase. The  $f_{\text{O}_2}$  had decreased by 5 log units, mostly as a result of the temperature decrease, though the ratio of oxidised to reduced sulphur species in the liquid had increased as a result of the loss of  $\text{H}_2\text{S}$ . These changes led to sequential precipitation of pyrite, K-feldspar, chalcopyrite, bornite, sphalerite, and gold. No sericite precipitated, even though it was initially assumed to be saturated. Carbonate was not precipitated during this reaction, but, given suitable initial concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , it could be expected to precipitate over at least part of the reaction path. Carbonate precipitation is favoured by the pH increase and initial temperature decrease, and inhibited by the decreasing concentration of  $\text{H}_2\text{CO}_3$  in solution.

The calculations suggest that boiling systems may precipitate bornite together with pyrite and chalcopyrite. The bornite is likely to have replaced earlier-formed pyrite and chalcopyrite, and this reaction sequence is observed in the discordant Cooley and Ridge deposits at McArthur River. K-feldspar (adularia) may be

expected, rather than sericite, chlorite, or smectite, and the presence of adularia in and near the McArthur River stratiform sulphides and of adularia and bornite at Tynagh may result from boiling.

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### The Coxco deposit: lead-zinc mineralisation in a Precambrian karst cavern system

R. N. Walker<sup>1</sup>

The Coxco deposit is a small Mississippi Valley-type deposit within the Carpentarian McArthur Group. The host sequence to the mineralisation is the Reward Dolomite, a shallow-water stromatolitic dolomite with evidence of the former presence of sulphate evaporites. The sequence shows evidence of extensive karsting below a silicified zone that represents a palaeo-weathering surface. Above the unconformity, dolomitic siltstones of the Lynott Formation were deposited, and these also filled the remaining open spaces in the underlying karst cavern system.

Within the phreatic zone of the karst system, fine detrital sediments, dolomite breccias, and chemical cements were deposited. The fine sediments are organic-rich, and the dolomite content is commonly phosphatised. The ore minerals, sphalerite, galena, pyrite, and marcasite, occur within the karst cavities in three forms:

1. colloform crusts on the edges of cavities or overgrowing detrital accumulations within the cavities;
2. fragments of colloform sulphides or fine-bedded sulphide accumulations, which are considered to be disaggregated sulphide crusts; and
3. small sulphide lenses intimately associated with organic matter.

The sulphide mineralisation took place during the active erosional stage of the karst system, probably as a result of bacterial sulphate reduction.

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### Stratiform copper mineralisation—settings & environments

Nigel Rowlands<sup>1</sup>

The Callanna, Burra, and Umberatana lithostratigraphic units of the Proterozoic Adelaidean Supergroup of South Australia are used to illustrate three variations on the copper-in-sediments theme, and show how copper fixation shifted with time across a spectrum of host depositional environments. Anomalous stratiform copper in the Callanna Beds is hosted by either sabkhas or deltas. In the overlying Burra Group, the

copper anomaly is contained in blanket-like cyclic sediments with lacustrine affinities. The stratiform occurrences of copper in the Umberatana Group are associated with deltas. A facies association approach is suggested as a new way of assessing how the syngenetic theory applied to sulphides in sediments may hold for these three stratiform copper occurrences.

Investigation of the host facies associations showed:

- A Callanna stratiform copper model controlled by a clastic/evaporitic interface, representing the change from still-stand sands and/or labile wedge arkoses to sabkhas. The host depositional association is usually a strike-vec-tored one supplied by post-orogenic peneplains, and the facies geometry can be both blanket-like and lentiform (for the rarer occurrences of copper in Callanna palaeodeltas). The host association is characterised by stacked products of arid and humid palaeosabkha phases.
- A Burra stratiform copper model controlled by a clastic/chemical interface, representing the change from wave-dominated sand-blankets to cyclic (non-saline) lacustrine highstands and lowstands (each exhibit confusing paralic overtones). The host depositional association in the Burra Group is a strike-vec-tored one, albeit a different strike system to that of the Callanna Beds. The stratiform copper occurrences are fixed at a regional clastic/chemical interface, interpreted as representing cessation of siliciclastic input from a hinterland in a decelerating uplift phase. The host association is typified by series of blanket-like, shallowing-up cycles.
- An Umberatana stratiform copper model occurring at a coarse clastic/laminite interface, representing the change from river-dominated deltas to prodelta and shelf muds. This stratigraphic level reflects the surge of fluvio-deltaic activity that followed the first great Adelaidean ice age. The host depositional association is a dip-vec-tored one, supplied by a hinterland in an accelerating uplift phase. It is typified by a facies geometry of straight, non-entrenched, multistoried and multilateral sands and gravels with a siliciclastic overbank suite.

Traditionally, stratiform copper deposits in the strict sense have been divided into ore-in-arenite and ore-in-shale sub-types. In this contribution, two criteria are used to reclassify stratiform copper deposits: (1) the facies association 'lap' geometry, which allows subdivision of host systems into 'uplap' and 'oblique lap' domains; and (2) the host sediment transport vector domain, which is either dip-vec-tored or strike-vec-tored.

These two criteria permit classification of stratiform copper deposits as follows:

- Strike-vec-tored, uplap domain—ore-shale deposits of evaporite association, e.g. Kupferschiefer and Callanna Beds.
- Strike-vec-tored, oblique lap domain—ore-shale deposits of paralic (possibly lacustrine) affinity e.g. Roan Antelope, White Pine, and Burra Group.
- Dip-vec-tored, uplap domain—peneconcordant deposits of fluvialite paragenesis, e.g. Nacimiento.
- Dip-vec-tored, oblique lap domain—ore-arenite deposits of deltaic paragenesis, e.g. Mufulira, Udo-kan, and Umberatana Groups, plus some Callanna Beds occurrences.

The copper-in-arenite stratiform deposits are associated with dip-vec-tored systems that are associated with sediment storage. The copper-in-shale deposits are

hosted by strike-vectored systems, which involve sediment dispersal. It appears that the spectrum of host associations for stratiform copper in the Adelaidean of South Australia reflects a change from sediment storage to sediment dispersal. The move of copper across this spectrum with time in the Adelaidean suggests that sedimentary processes did have some control on metal fixing.

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### Mount Isa copper orebodies—evidence against a sedimentary origin

*W. G. Perkins<sup>1</sup>*

The spatial association between stratiform Ag-Pb-Zn orebodies and the 'silica-dolomite' host to the copper orebodies has been explained as an original facies relation. Support for the alternative introduction of copper into a structurally evolved environment is presented.

Textural changes in the 'silica-dolomite' began with bedding-controlled porphyroblastic dolomite replacement, which can affect all microfacies. A complex dolomitic pseudobreccia then formed, dominantly by fracture-controlled metasomatic replacement. Pervasive volume-for-volume silicification arrested the pseudobreccias at all stages in their evolution. Chalcopyrite is also replacive, its distribution controlled largely by crystalline dolomite, occasionally by carbonaceous laminae and phyllosilicates, and, rarely, by bedded fine-grained pyrite.

A model is presented to explain the evolution of these textures. During the main slaty cleavage folding episode, silicic hydrothermal fluids entered a fractured zone resulting from a ductility contrast with the underlying greenschist. Complex dolomite replacement fronts moved upwards and outwards from a series of silicification foci. Towards the close of this folding, copper, cobalt, and probably most of the sulphur for chalcopyrite were introduced along with the silica. The distribution and form of the 'silica-dolomite' is thus explained as a late-stage hydrothermal alteration zone, rather than the result of facies control.

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### Relationship of copper to lead-zinc ore bodies and source of copper at Mount Isa, Queensland

*B. L. Gulson<sup>1</sup>, W. G. Perkins<sup>2</sup> & K. J. Mizon<sup>3</sup>*

A comprehensive trace lead isotope project, involving more than 170 analyses of sulphides and rocks, has recently been completed in an attempt to define the relation between the lead-zinc and copper orebodies and the source of the copper mineralisation at Mount Isa.

Consistent with other massive sulphide deposits, the isotopic data for the lead-zinc ores are uniform and the same as most unmineralised pyritic or pyrrhotitic

dolomite shales, the hosts to the lead-zinc mineralisation.

Two main generations of iron sulphide can be distinguished in hand-specimen and isotopically in the copper orebodies. One (pyrite I/pyrrhotite I) is extremely fine-grained pyrite and/or pyrrhotite in the highly-silicified bedded shales, which resemble those associated with lead-zinc mineralisation. These sulphides contain high lead concentrations (>500 ppm) and have isotopic ratios similar to those in the lead-zinc ores. The other (pyrite II/pyrrhotite II) is usually coarse-grained and often granular; iron sulphide appears to have been introduced with the chalcopyrite, typically has low lead concentrations, and is isotopically consistent with the chalcopyrite.

In those samples, particularly from the 1900 and 3000 orebodies, that contain partly replaced pyritic shale fragments or in which only relict fine-grained bedded pyritic material is visible, the chalcopyrite also has high lead concentrations and the isotopic data are the same as, or converge to, those of the lead-zinc ores.

Sulphides from the copper mineralisation lie on a number of arrays with various thorium/uranium ratios, when plotted on  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$  diagrams. Chalcopyrite and pyrite (II) or pyrrhotite (II) from the major 1100 and 3000 (and minor 200) orebodies lie on the same well-defined array (correlation coefficient 0.997) with a low thorium/uranium ratio of approximately 0.9. The data for the smaller 1900, 650, and 500 orebodies exhibit a greater scatter (correlation coefficient about 0.95) and have an apparent thorium/uranium ratio between 2 and 4. The Q250 mineralisation, known from a single drill hole, also exhibits a large scatter (correlation coefficient 0.95) and high thorium/uranium.

The regularity of the arrays, variable thorium/uranium ratios, chalcopyrite trace-element chemistry (particularly tin), and stratigraphic position are interpreted as indicating different pulses of copper mineralisation. All the arrays for copper mineralisation intersect the average lead-zinc ore value.

Four samples from a fault zone in the 1900 orebody are of very recent origin, and are interpreted, from isotopic and trace-element data, to be remobilised 1900 material. All other samples of chalcopyrite and more radiogenic samples from unmineralised pyritic shales lie on an array that has an apparent age of about  $1865 \pm 50$  m.y. ( $1\sigma$ ) when plotted on a  $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  diagram. This line also intersects the average isotopic value for lead-zinc ore.

The data for the postulated source rocks for the copper orebodies, the Eastern Creek Volcanics, define a well-fitted isochron with an age of  $1710 \pm 25$  m.y. ( $1\sigma$ ); this line also intersects the average isotopic value for lead-zinc ore. Two samples of chalcopyrite from the volcanics fit on the isochron. The Eastern Creek Volcanics have variable thorium/uranium ratios from 2.5 to 3.6. Greenstones from the basement underlying the copper orebodies exhibit a scatter on isotopic plots, and this is interpreted as due to post-crystallisation movement of uranium.

In order to explain the isotopic data and various other features, such as brecciation and replacements related to the mineralisation at Mount Isa, we propose the following model: deposition of the Mount Isa

Group, including Pb-Zn-Ag mineralisation perhaps in a sabkha-type environment; onset of major regional metamorphism at about 1670-1625 m.y. ago (Page, 1978), leading to folding of the Mount Isa Group. Dehydration of the rocks during metamorphism generated pore fluids that not only facilitated slaty cleavage development, but were forerunners of brine solutions that penetrated to the metamorphic basement complexes, such as the 1865 m.y. Cu-rich Leichhardt Metamorphics. Hydrothermal activity at temperatures  $>300^{\circ}\text{C}$  over long periods allowed substantial extraction of Cu, Fe, and Si from the metamorphics, and this activity is reflected in the disturbed Rb-Sr systems in whole rocks and micas (Page, 1978). Movement along the basement fault(s) initiated upward migration of the solutions in pulses, perhaps by a seismic pumping mechanism outlined by Sibson & others (1975). Solutions were constrained by lithostatic pressure of the overlying Mount Isa Group, but on their reaching the Urquhart Shale, hydraulic fracturing (Phillips, 1972) of the dolomitic siltstones and pyritic shales was initiated. Alternatively, the ductility contrast between the Urquhart Shale and underlying greenstones permitted the development of a fracture zone (Perkins, this volume). The Si and Cu were deposited either in response to the pressure drop and boiling, resulting from brecciation, or changes in Eh and pH due to interaction with the carbonates.

The first orebodies introduced may have been the major 1100 and 3000 orebodies; volume problems arise if these orebodies are introduced later. With time, the hydrothermal cell decreased in size, and interacted substantially with the Eastern Creek Volcanics; pulses of solutions gave rise to the 1900, 650, and 500 orebodies. This would provide an explanation for the isotopic data of higher Th/U ratios and less well-correlated arrays. Alternatively, two cycles of mineralisation may have given rise to the 3000-1900 orebodies and later to the 1100-650-500 ores (C. Robertson, personal communication, 1980).

Our model, which is consistent with most geological, textural, and isotopic data, is incompatible with a proposed genetic relation between the Cu and Pb-Zn-Ag mineralisation.

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### Chemical and mineralogical constraints on the genesis of mineralisation in the Mount Gunson region, South Australia

J. Knutson<sup>1</sup>

The Mount Gunson copper deposits occur in Adelaidean (Late Proterozoic) rocks on the Stuart

Shelf, South Australia. Four major cycles of shallow-water sedimentation are recognised in the Adelaidean: namely, the Callanna Beds, and the Burra (absent on the Stuart Shelf), Umberatana, and Wilpena Groups; and there is widespread anomalous Cu-enrichment throughout these sequences.

On the Stuart Shelf, these rocks consist mainly of unmetamorphosed sandstones, mudstones, and dolostones, basic and intermediate volcanics and shallow intrusives. Sedimentary structures such as fine laminations, stromatolites, edgewise breccias, scour and fill structures, and desiccation cracks, and possible pseudomorphs after evaporite minerals indicate a sedimentary regime that included lagoonal, mudflat-supratidal and deeper basinal environments fringing an arid shoreline.

There are two major styles of base-metal sulphide mineralisation in the Mount Gunson area. Firstly, discordant stratabound mineralisation in the Pandurra Formation (Callanna Beds) and, secondly, mainly concordant stratiform mineralisation in the overlying Tapley Hill Formation (Umberatana Group).

The main structural feature in the Mount Gunson area is the Pernatty Culmination, a structural high caused by upwarping of early Adelaidean (Pandurra Formation) and pre-Adelaidean rocks. It consists of a number of north-northwest-trending blocks offset by east-northeast-trending fractures. In places, the Tapley Hill Formation wedges out completely against the Pernatty Culmination, and it is in these areas, where the Pandurra Formation is overlain directly by the Whyalla Sandstone, that base-metal mineralisation is concentrated. Similarly, significant base-metal mineralisation in the Tapley Hill Formation is concentrated on the flanks of the Pernatty Culmination adjacent to mineralised Pandurra Formation.

Cu mineralisation in the Pandurra Formation Cattle Grid deposit (mainly chalcocite, bornite, and chalcopyrite) fills fractures and vugs in the brecciated and sili-cified palaeosurface. It replaces epigenetic pyrite, which formed after at least one episode of subaerial exposure. The isotopic compositions indicate that the sulphide ions for pyrite formation most likely formed biogenically under conditions of unlimited sulphate supply; but lack of organic nutrients indicates that this could not have occurred at the sites of mineralisation.

The Tapley Hill Formation typically consists of finely laminated mudstones and dolostones; the bending of sedimentary bedding around concentrations of framboidal pyrite indicates this pyrite formed before lithification. Cu-Fe sulphide mineralisation, mineralogically and geochemically similar to that in the Pandurra Formation (i.e. enriched in As, Co, Cu, Ni, Pb and Zn) has replaced early pyrite, and is mainly concentrated within the more permeable clastic mudstone layers, occurring as disseminated grains, conformable lenses, and lithologically constrained veinlets and fracture coatings. A wide range of positive S isotope values implies there was a prolonged episode of bacterial sulphate reduction without replenishment of sulphate. Chemical data indicate that, in contrast to the mineralised zone in the Pandurra Formation, there has been no significant addition of Fe and S since the time of sedimentation.

There is both vertical and lateral zonation of Cu, Pb, and Zn mineralisation in the Tapley Hill Formation. Generally, Cu is concentrated next to discontinuities at both the base and top, with Pb and, in

particular, Zn persisting further into the formation. There is a decrease in Cu relative to Pb and Zn outwards from Mount Gunson. There is also vertical and lateral zonation in the Cu-Fe sulphide assemblage, from chalcocite and bornite to bornite and chalcopyrite, chalcopyrite and pyrite, and, finally, pyrite.

In summary, the distribution of Cu-Pb-Zn mineralisation in the vicinity of Mount Gunson, and its apparent control by major structural features, such as lineaments, faults, and palaeohighs, support the hypothesis that mineralising fluids flowed up through these zones of crustal weakness and precipitated as Cu-Pb-Zn sulphides in chemically and structurally favourable beds. The similarity of Cu-Pb-Zn mineralogy and minor-element trends in both the Pandurra and Tapley Hill Formations suggest the same mineralising event caused both styles of mineralisation, although it may have occurred over a long period and, possibly, was intermittent. The source of base metals could have been basement mineralisation as well as Adelaidean sedimentary and igneous rocks.

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### Diagenetic mineralisation in the Wollgorang Formation McArthur Basin, Northern Territory

*Michael J. Jackson*<sup>1</sup>

The Wollgorang Formation is a predominantly dolomitic siltstone and shale unit, about 100 m thick, in the lower part of the McArthur Basin sequence. It has a uniform lithological character over a large area (some 60 000 sq. km) in the northeastern part of the Northern Territory, and contains evidence of both shallow-water deposition (ripples, desiccation cracks, stromatolites) and possible deeper-water deposition (black laminated pyritic shales and slump breccia beds).

Field research and initial geochemical and petrological studies of drill core have shown anomalous (but uneconomic) base-metal values consistently at three stratigraphic levels: near the base of the unit, in a redbed sequence; near the middle, in black carbonaceous shales with prominent dolomite nodules; and near the top, in crystalline dolostone or sandstone. The mineralisation is stratabound, either in the form of disseminated small euhedral crystals (few  $\mu\text{m}$  in size) or as coarser euhedral to subhedral grains or aggregates; none of the crystals or grains shows any evidence of a clastic origin and they are, therefore, interpreted as diagenetic.

The mineralisation in the middle of the formation is similar to that in the McArthur River Pb-Zn-Ag deposit, situated some 3200 m higher in the sequence.

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### Studies of modern sedimentary environments as an exploration aid

*Chris von der Borch*<sup>1</sup>

Spectacular advances have been made over the past two decades in multi-disciplinary studies of modern depositional systems. Environments studied include, on

the one hand, oceanic and, on the other, subaerial, lacustrine, and shallow marine areas. Significant syngenetic concentrations of base-metal sulphides have been discovered only in specific oceanic environments, for example the Red Sea median basins and the East Pacific Rise hot springs, all of which are in rift-related settings. Modern shallow-marine and subaerial facies sediments have not been found to contain metal sulphide concentrations significantly above background. This is despite the observation that many modern facies closely resemble ancient counterparts that host stratabound and stratiform ores. In these ancient examples, isotopic and petrographic evidence favors epigenetic introduction of the metals into the sediment pile relatively early during diagenesis. However, a consistent association with present or past rifting and high heat flow exists in both syngenetic and epigenetic metal concentrations. Depending on the 'maturity' of the rift at a particular period of its development and the related evolution of the sedimentary environments during rift filling, genetically associated hydrothermal fluids may develop one of the following types of ore concentrations.

1. Mineralised seafloor hydrothermal-spring vents (e.g. East Pacific Rise, which is an ocean-floor spreading centre with negligible sediment cover, situated in a fully developed ocean basin).
2. Precipitated syngenetic metal sulphides (e.g. median brine basins of the Red Sea, a region of restricted oceanic crust development and evaporites, in a rift that has only recently evolved to the ocean-floor spreading phase).
3. Epigenetic, diagenetically emplaced metal sulphides (e.g. McArthur River H.Y.C. black pyritic shale orebody, situated in a palaeorift with a thick largely non-marine sedimentary sequence).

Modern sedimentological and structural studies in oceanic regions, therefore, can provide useful genetic information on metal-enriched hydrothermal fluids and syngenetic deposition of metal sulphides, in settings which may be analogous to some major ancient deposits. Studies of modern depositional environments associated with subaerial, lacustrine, and shallow-marine situations provide useful geometrical, lithological, hydrological, and geochemical data, which enhance our understanding of orebody formation and geometry, and ore localisation in terms of solution paths and receptor beds. As ore deposits become increasingly difficult to locate, better understanding of control by sedimentary environments will be required. This will have to be combined with a better understanding of the structural and 'palaeogeothermal' regimes that pertained during emplacement. Future techniques for exploration, particularly for low-grade concealed stratabound orebodies, will approach the complexity of those used in the subsurface for petroleum exploration, and will involve increasingly sophisticated sedimentological and structural criteria.

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### Distribution of metals in sediments

*L. J. Warren*<sup>1</sup>

Sediments were collected from relatively 'clean' areas of Spencer Gulf, South Australia, outside the

influence of the lead-zinc smelter at Port Pirie. Each sample was separated into a series of size fractions and density sub-fractions, which were analysed for their heavy-metal contents. The metal distributions were compared with those from contaminated sediments nearer the smelter, where the concentrations of lead and zinc were about 30 times higher. The increase in metal concentrations was not spread uniformly over all components. The shell fragments, for example, had a large capacity for heavy metals and were the main metal reservoir in many of the sediment samples.

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### Determination of dissolved sulphide in marine sediments

*J. Hauser*<sup>1</sup>

The concentration of dissolved sulphide in interstitial water is a factor controlling the Eh, pH, and chemical constituents of anoxic marine sediments and it affects the nature and extent of biological and chemical processes occurring therein. Thus, a knowledge of dissolved sulphide levels is of primary importance in chemical, biological, and geological studies of bacterial sulphate reduction and its consequences in sedimentary environments.

A number of procedures for the determination of dissolved sulphide in marine sediments have been reported, but few workers have attempted to rationalise their technique or assess its reliability. Three previously reported procedures were investigated to assess their suitability for the determination of dissolved sulphide in recent coastal sediments.

1. Direct insertion of a sulphide ion selective electrode (SISE) into the sediment. Since the SISE response depends on the pH and chemical composition of the sample, as well as the age of the electrode, this method is only suitable for obtaining semi-quantitative data on the relative levels of dissolved sulphide down a sediment core sample.
2. Pressure filtration using nitrogen. This procedure was time consuming and was found to be unsuitable for coarse sandy sediments. The levels of dissolved sulphide were much lower than expected ( $< 1 \mu\text{g S}^{2-} \text{ ml}^{-1}$  pore water), which indicates that oxidation of samples probably occurred during the filtration process.
3. Suspension of sediment in a phosphate buffer system and subsequent determination of  $\text{H}_2\text{S}$  evolved in a nitrogen stream. This method allowed minimum exposure of the sediment to air, and only 2-5 g of sample was required for analysis.  $\text{H}_2\text{S}$  was trapped in an alkaline reagent and determined using the SISE with a standard additions procedure for quantification.  $5 \mu\text{g}$  of sulphide- $\text{S}^{2-}$  was required for the determination. Careful control of the nitrogen flow rate, pH of the buffer solution, and evolution times was necessary for reliable results.

Only method 3 gave consistent results for all types of sediment analysed. In the analysis of sediment core samples the maximum levels of dissolved sulphide obtained were  $4 \mu\text{g S}^{2-} \text{ g}^{-1}$  sediment for a sandy sedi-

ment, and  $40 \mu\text{g S}^{2-} \text{ g}^{-1}$  sediment for a fine silty sediment.

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### Sulphate reduction in coastal marine sediments: magnitude and controls

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In recent years, rates of sulphate reduction have been measured in sediments of a variety of coastal marine environments, including salt marshes, bays, coral reefs, intertidal zones, and the Baltic Sea. The amount of sulphide produced has been estimated to account for a few to 100 percent of the net primary production. Thus, this process can represent a major route for the flow of organic matter in coastal zones. The sulphide can exist as free sulphide (volatile), bound sulphide (acid volatile), or pyrite. The form is important in assessing the potential chemical reactions that can occur, and the biological effects that the process can exert.

The published rates of sulphate reduction in coastal marine sediments range from  $< 1$  to  $> 200 \text{ mmol S m}^{-2} \text{ day}^{-1}$ . If a C:S ratio of 2:1 is assumed, the carbon equivalents become  $0.2\text{-}2.4 \text{ g C m}^{-2} \text{ day}^{-1}$  or about  $70\text{-}700 \text{ g C m}^{-2} \text{ yr}^{-1}$ . This covers the range for most estimates of planktic and benthic primary production, except those for temperate salt marshes and some intertidal mats. While this type of information cannot be used rigorously, it is obvious that sulphate reduction can account for the dissimilation of a significant portion of the fixed carbon in many coastal ecosystems.

A number of factors can affect sulphate reduction rates. These deserve consideration, because, most often, data on in situ sulphate reduction rates are available for only a limited number of samples spatially and temporally. The factors include ambient temperature, the amount of oxidisable organic matter, the rate of sediment accumulation, biological and abiotic turbation of the sediment, the rate of interstitial water movement, and the cycle of wetting and drying in interstitial sediments. In each field study, it is necessary to identify the factors that control sulphate reduction rates, if one is to define the dynamics of the process, and, certainly, if even semi-realistic yearly rates of production are to be calculated.

While it is recognised that the production of sulphide can affect the physical and biological nature of systems, and that much of the primary production in coastal ecosystems can be cycled through the process, there have been relatively few attempts to measure rates of sulphate reduction in the field, and but two or three studies in which seasonal rates have been measured. In large part, this is caused by the limitations of the techniques for measurement. Although a variety of techniques have been employed, all are laborious; thus, one measures a few rates for a great effort. There is a great need for development of a rapid and direct technique.

The techniques which have been most commonly employed are:

- (1) sulphide accumulation with time in a sealed vessel;

- (2) model system calculations based on the amount of sulphide present in a sediment and the diffusion rate, aerobic use etc. or by estimating the rate of sedimentation;
- (3) counts of viable sulphate-reducing bacteria;
- (4) electrical impedance (Oremland & Silverman, 1979) and,
- (5) addition of  $^{35}\text{SO}_4^{2-}$  to a sediment slurry or an undisturbed sediment core.

The first three techniques are of limited use, and the electrical impedance procedure has not yet been used in enough different situations to be evaluated. Thus,  $^{35}\text{SO}_4^{2-}$  addition technique is the most commonly used now. Slurry techniques have been largely replaced by direct injection procedures. However, they have the potential advantage of reducing local core to core variation, and if they can be shown to yield equivalent results to the direct injection technique, as demonstrated by Jorgensen (1978) for Danish coastal sediments, they may regain popularity with investigators.

Two methods have been proposed for directly labelling sediment, that of Jorgensen (1978), where fluid label is injected horizontally into the core at precise depths, using a syringe and needle, and that of Skyring & others (1979), where the isotope is spotted on a glass rod, dried, and then inserted vertically through the entire length of the core. While each technique has advantages, the method of Skyring & others (1979) seems preferable, since all zones of sulphate reduction are labelled down the core. It is possible that both techniques can give an overestimate of the true rate of sulphate reduction, if significant sulphate depletion occurs in microzones of active sulphate reduction. This overestimate would result from use of the 'average' sulphate concentration of a core to calculate isotopic specific activity. This possibility needs to be evaluated for each sediment type examined.

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### Sulphate reduction rates in modern sediments and implications for ore formation

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Rates of biological reduction of sulphate to sulphide have been measured in a wide variety of sedimentary environments. In general, sulphate reduction rates in marine sediments are from 4 to 200 mmol m<sup>-2</sup> day<sup>-1</sup>, and are 10 to 100 times greater than rates measured in non-marine sediments. The highest sulphate reduction rates occur in sediments colonised by cyanobacteria. In some natural environments, biological sulphate reduction could result in the precipitation of heavy-metal sulphides at concentrations commensurate with those of ore deposits.

In ore deposits, metal sulphides often occur in microbands of almost pure mineral. It is sometimes difficult to envisage how biogenic sulphide, apparently produced in large volumes of sediment, is concentrated into much smaller volumes of heavy-metal sulphides. In basin and intertidal sediments, the most active sulphate reduction zone is at the sediment/water interface. A basin sediment covered by a 21 m column of 0.2 mM (e.g. Zn, 13.0 ppm) metal solution and supporting a sulphate reduction rate of 20 mmol m<sup>-2</sup> day<sup>-1</sup> could be covered by a 100 μm thick layer of ZnS in 212 days. In an intertidal sediment or carbonate host rock 1 m<sup>2</sup> × 1 cm, in which sulphate was reduced at 20 mmol m<sup>-2</sup> day<sup>-1</sup>, 21 000 l of a 0.2 mM metal solution would be required to permit the precipitation of an equivalent quantity of ZnS. At a flow rate of 1.0 cm day<sup>-1</sup> this would take 5.8 years. Extensions of these simple models have been made to evaluate constraints, such as sulphate reduction rates and the properties and composition of ore-forming brines, for metal sulphide precipitation and preservation in basins, intertidal sediments, and subterranean carbonate rocks.

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### Early diagenesis in some deep sea sediments, northeast Indian Ocean

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Geochemical studies have been undertaken on a number of deep sea cores from the northeast Indian Ocean. Most of the cores from the abyssal and bathyal zones show little or no evidence of bacterial sulphate reduction; alkalinity and sulphate content of the pore waters and reduced sulphur content of the sediments being used as a measure of this. However, two sites, one in the Timor Trough, the other in the Bali Trough, showed abundant evidence of bacterial sulphate reduction and were studied in more detail.

Sediment from the Timor Trough was obtained from DSDP Site 262. Some of the highest levels of pore-water alkalinity measured in marine sediments are found at this site and, together with abundant framboidal pyrite and the extremely low concentrations of pore-water sulphate, they indicate vigorous sulphate reduction. The maximum alkalinity values occur at a depth of about 50 m below the sediment/water interface, which is much deeper than normal. It is uncertain at this stage whether this is a reflection of present-day bacterial activity or is essentially a 'fossil' peak frozen into the sediments by methane hydrates.  $\delta^{34}\text{S}$  values determined on pyrite are consistent with a biogenic origin; however they vary down the drill hole, and there appears to be no consistent pattern of variation.

The Bali Trough investigations were undertaken on a gravity core. Abundant framboidal pyrite, depletion of sulphate, and increases in ammonia and total alkalinity again indicate abundant sulphate reduction.  $\delta^{34}\text{S}$  values for pyrite-sulphur are again consistent with a biogenic origin for the pyrite, but, unlike in the Timor Trough, there is a strong correlation between increasing enrichment in  $^{32}\text{S}$  and depth. This is an unusual trend for modern sediments. The only other sites where

it has been noted are in the Santa Catalina Basin, in Spencer Gulf, South Australia, and in one site in the Gulf of California. The same trend has been noted in cores from the McArthur and Kupferschiefer deposits. In both these cases the trend is ascribed to bacterial sulphate reduction in a closed system, but it is difficult to apply the same explanation to the Bali Trough.

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### Sulphur isotope distributions and the depositional environment

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The interpretation of sulphur isotope distributions in sedimentary sulphides has been refined with increasing awareness of the mechanisms and environmental controls of sulphur isotope fractionation. The major distinction is between hydrothermal environments and those in which bacterial sulphate reduction occurs at low temperature. The effects of temperature and substrate concentrations on the bacterial reduction rate and the associated isotope fractionation have been studied in laboratory cultures, and the results integrated with those of studies of sulphur diagenesis in modern marine environments. The following mathematical relation has been derived for relative frequencies ( $Y_1/Y_2$ ) of  $\delta^{34}\text{S}$  values ( $X_1$  and  $X_2$ ) of the instantaneously produced sulphide, in a system closed with respect to sulphate:

$$Y_1/Y_2 = [10^{-3}X_1 + \alpha/10^{-3}X_2 + \alpha] \frac{2\alpha-1}{1-\alpha} \quad (1)$$

where  $\alpha$  is the fractionation factor.

Comparison of frequency plots of  $\delta^{34}\text{S}$  (sulphide) values from intertidal and subtidal environments shows no clear distinction in either isotope pattern or extent of fractionation. Extensive data from the intertidal zone at Spencer Gulf, South Australia show a normal distribution indicative of an open system, but a similar pattern is seen for a subtidal environment in the Baltic Sea. Other subtidal environments for which there are sufficient data show broad flat distributions with a spread towards heavier values, as expected for closed systems. These patterns are associated with more rapid sedimentation rates than in the Baltic Sea. Increasing  $^{34}\text{S}$  with depth is a common variation in vertical profile, but there are examples of the reverse trend in the Bali Trough, Santa Catalina Basin and Spencer Gulf. Sediments of the last two areas exhibit depositional discontinuities.

In ancient sediments, the same types of patterns are seen for sulphides that, on independent criteria, are considered biogenic. However, the position of the pattern relative to the value considered possible for coeval sea-water sulphate is often quite different from modern analogues. An extreme example is the distribution from the Kapunda deposit in the Tapley Hill Formation of the Adelaide Geosyncline, which includes  $\delta^{34}\text{S}$  values as high as +46‰.

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### Precambrian sulphur isotopes: implications for the global sulphur cycle

*T. H. Donnelly*<sup>1</sup>

The strictly anaerobic dissimilatory sulphate-reducing bacteria are important in the global cycling of sulphur, and a major question is when did dissimilatory sulphate reduction evolve? Modern sulphate-reducing bacteria produce sulphide that is generally enriched in  $^{32}\text{S}$  compared to the starting sulphate. This phenomenon provides the basis for assessing the origin of sulphide in both modern and ancient environments. The isotopic compositions of Precambrian sulphide and sulphate minerals suggest that, prior to ~2000 m.y. ago, sulphide was the major sulphur component in sediments and the hydrosphere, and was derived mainly from mantle sources. After ~2000 m.y. ago, when free oxygen was present, sulphate became the major sulphur component of the seas, and was the main sulphur source for both biological and abiological sulphide formation. Dissimilatory sulphate reduction then became widespread.

Archaean sulphates have  $\delta^{34}\text{S}$  values of  $+2 \pm 2\%$ . A minor proportion of Archaean and Lower Proterozoic volcanogenic sulphides, however, exhibit  $\delta^{34}\text{S}$  values greater than this, indicating that they were formed by reduction of an oxidised sulphur source other than sulphate. The source of this  $^{34}\text{S}$ -enriched sulphide was probably  $\text{SO}_2$  ( $\text{SO}_3^{2-}$  or  $\text{HSO}_3^-$ ) introduced into the hydrosphere in exhalations containing a large excess of  $\text{H}_2\text{S}$  over  $\text{SO}_2$ . Under these conditions, isotopic equilibria favour  $^{34}\text{S}$ -enrichment in  $\text{SO}_2$ . It is suggested that: 1. in the anoxic environments of the primitive Earth, sulphite was the most readily available and persistent sulphur source for evolving procaryotes; 2. biological sulphite reduction evolved early among procaryotes and was the initial event leading to the eventual evolution of dissimilatory sulphate reduction; and 3. the ability of organisms to reduce sulphate evolved only when sulphate became the predominant sulphur compound in the hydrosphere.

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### Diagenesis of organic matter in shallow marine sediments: an experimental study

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An experimental system has been designed to study the early diagenesis of organic matter in shallow marine sediments, under laboratory conditions. The system has facilities for operating at a range of temperatures and pressures. Organic matter was supplied in the form of cyanobacterial mats from Spencer Gulf, South Australia, and Shark Bay, Western Australia, and changes in the distribution of aliphatic and aromatic hydrocarbons, fatty acids, heterocycles, and fulvic and humic acids were recorded over three years. Initially, the patterns of fatty acids and hydrocarbons were indicative of material derived from cyanobacteria. Within two years, however, these patterns diminished and were replaced by those characteristic of bacterially derived material. The results indicate

that primary organic matter is rapidly degraded by bacteria and replaced by organic material of bacterial origin.

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## Sources of organic matter in Precambrian sediments

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Reduced carbon (kerogen and solvent-extractable compounds) or graphite occurs in sediments of all ages, including the oldest known, those at Isua in Greenland (3800 m.y. old). Its distribution among sedimentary facies is poorly known in Precambrian sequences, but seems not to have changed markedly with time. This uniformity must mask much evidence of radical evolutionary innovations that occurred during the Precambrian, from the very origin of life, through the origin of autotrophy (use of CO<sub>2</sub> as the major source of carbon for growth), photoautotrophy (where light is used as the energy source for growth), oxygen-releasing photoautotrophy (an innovation which would have fundamentally changed the surface chemistry of the Earth), the origin of eucaryotes (i.e., of sexual reproduction) and, finally, sometime late in the Precambrian, the origin of metazoans, and, subsequently, the beginning of grazing, burrowing, and bioturbation, which would have had significant effects on the preservation and distribution of organic matter.

Techniques that can be used to search for signs of these evolutionary innovations are the interpretation of microfossils and stromatolites (the oldest are 3500 m.y. old), kerogen composition (particularly its car-

bon isotopic composition) and, indirectly, interpretation of the chemistry of sediments (e.g. interpreting uraninite-bearing conglomerates, banded iron formations, and palaeosols in terms of the oxygen content of the atmosphere). Evidence from any one of these approaches is rarely unequivocal, but, taken together, it leads to a consistent interpretation (that none the less is tentative).

Meteorites known as carbonaceous chondrites may have been a significant extraterrestrial source of organic matter early in Earth history (during the Hadean, particularly during the period of 'late heavy bombardment' that ended about 3900 m.y. years ago). However, no carbon from this source has yet been recognised. The first clear evidence of life is 3500 m.y. old, and it is apparent that by then autotrophy had already evolved. Oxygen-releasing photoautotrophy probably evolved during the late Archaean. Controversy surrounds this interpretation and also the dating of the origin of eucaryotes, but here it is suggested that the oldest eucaryotes are about 1400 m.y. old. The oldest undoubted metazoan fossils are about 650 m.y. old, though tenuous evidence suggests a considerably earlier origin. Bioturbation began on a large scale early in the Cambrian (about 570 m.y. ago).

Combined palaeontological, sedimentological, and geochemical studies are rapidly giving us a much clearer view of Precambrian evolutionary events than we had only a decade ago. We are approaching an understanding of evolutionary changes in the cycles of the major elements, C,N,O,P,S (Fe and Mn, U and others) that are controlled by the biosphere. Such an understanding is fundamental to interpreting all sediments and the mineral deposits and petroleum accumulations they contain.

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