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Geological significance of sulphur oxidoreduction by bacteria

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In the natural environment, sulphur is continually recycled between reservoirs of oxidized and reduced sulphur, notably the oceans, evaporites and shales. In the short term the cycle approximates a steady state but throughout geological time there have been episodic shifts from steady state that have led, for example, to large-scale deposition of mineral sulphides and elemental sulphur and to fluctuations in oceanic sulphur chemistry.

Current evidence suggests that dissimilatory sulphate reduction played a major role in the geochemical sulphur cycle for the last 2–2.8 Ga. It can also be assumed that sulphur-oxidizing bacteria participated in the oxidative phase of the cycle, although their contribution cannot be evaluated quantitatively.

Biogeochemical cycles are interdependent and the activities of sulphur bacteria have important implications with respect to the geochemistry of other elements such as carbon, iron, alkaline earths and oxygen.

1. INTRODUCTION

Like most other elements, sulphur in the terrestrial environment is continually transferred between a number of reservoirs, a process that is termed geochemical cycling. The main reservoirs of oxidized sulphur (sulphate) are the seas and evaporites, and those of reduced sulphur (sulphide) are the sediments (and sedimentary rocks, mainly shales) and metamorphic and igneous rocks (table 1). Sulphur fluxes to and from the smaller reservoirs such as the atmosphere and biosphere are rapid in geological terms but it is the transfer of sulphur between the major reservoirs that is of particular geological significance. Metamorphic and igneous rocks are relatively immobile, their rate of turnover being about 6% that of the sedimentary shale reservoir (Holser & Kaplan 1966). For the present discussion, therefore, the geochemical cycle of sulphur may be viewed in terms of the interchange between oceans, evaporites and sediments with rivers acting as the conduit by which sulphur from continental deposits is returned to the seas (figure 1).

In the short term, and on a global scale, this cycle approximates a steady state with only minor fluctuations in the magnitudes of the reservoirs. Over geological time, however, there have been episodic shifts in steady state that led to major redistributions of sulphur between reservoirs on both a regional and global scale, and which were related to changes in the reservoirs of several other elements. It is the purpose of this paper to examine to what extent the sulphur bacteria, by virtue of their abilities to change the oxidation state of sulphur, have contributed to these geochemical events. There is, of course, no direct way of approaching this question. We must instead attempt to interpret evidence recorded in rocks in the light of our knowledge of the activities of these bacteria in the modern environment.

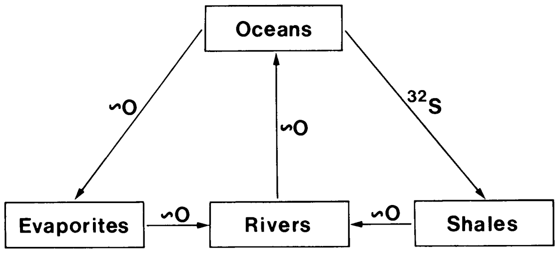

FIGURE 1. A simplified geochemical cycle showing the transfers of sulphur between oceans, evaporites and shales. Also shown are the associated sulphur isotopic trends (see §5).

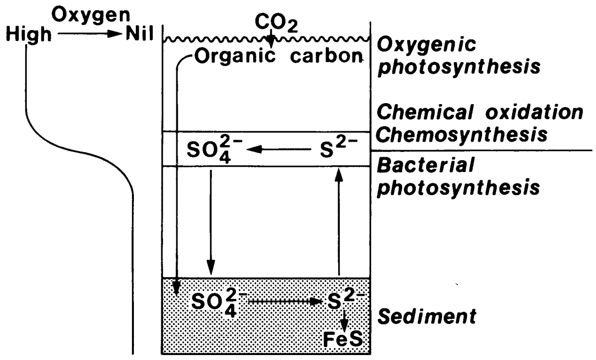

FIGURE 2. Sulphur transformations in an idealized closed aqueous basin, showing the link with organic carbon production and relations to oxygen content.

TABLE 1. TERRESTRIAL RESERVOIRS OF SULPHUR

(Data for biosphere from Ericksson (1963); others from Holser & Kaplan (1966).)

reservoir	S/Tg
oxidized	
oceans	1.3×10^9
evaporites	5×10^9
fresh water	3×10^3
atmosphere	3.6
reduced	
sediments (mainly shales)	2.7×10^9
metamorphic and igneous rocks	7×10^9
biosphere†	5.6×10^3

† Includes dead organic matter.

2. MICROORGANISMS AND THE MODERN GEOCHEMICAL SULPHUR CYCLE

In the modern environment, sulphur bacteria have clearly defined roles in sulphur cycling. This is illustrated in figure 2 which describes, schematically, sulphur transformations in an idealized closed aqueous basin. Organic matter is synthesized by algae and cyanobacteria in the near-surface oxic zone of the water column and may be supplemented by detrital matter from terrestrial sources. Lower in the water column most of the readily metabolizable organic matter is degraded by aerobic microorganisms, oxygen is consumed, and eventually at some depth a boundary between oxygenated and oxygen-free waters is established, termed the oxycline by Burton (1980). Below the oxycline, fermentations create reducing conditions that allow the development of bacterial sulphate reduction. Generally this is most intense at or just below the sediment–water interface where particulate carbon that has escaped degradation within the water column accumulates.

Depending on the supply of reactable iron, some or all of the sulphide may be fixed in the form of iron sulphides in sediments which, after consolidation and lithification, become pyritic shales. The remaining sulphide diffuses towards the oxycline where it is reoxidized either chemically or by chemosynthetic sulphur bacteria and other aerobic sulphur-oxidizing organisms, or both. If the oxycline is within the photic zone, photosynthetic sulphur bacteria may develop in the upper layers of the anoxic zone. A second zone of sulphate reduction may also develop, supported by readily metabolizable organic matter produced by the chemo- and photoautotrophs.

Table 2. Sulphur cycling in Lake Belovod

(From Sorokin (1970).)

		sulphate reduction	sulphide oxidation†/{(µmol/l)/28 h}		
water depth/m		(µmol/l)/24 h	chemical	chemosynthetic	photosynthetic
9	base of oxycline	—	8.1	1.3	0.2
10		—	5.8	3.7	1.2
11		—	4.9	3.3	3.1
12		—	2.8	1.8	1.5
13		0	2.8	1.2	0.8
14		0.9	0.8	0.6	0.6
17		0	—	—	—
23	Sediment–water interface	4.5	—	—	—

† Oxidation to S^{VI}: includes SO_4^{2-} and $S_2O_3^{2-}$.

The above scenario has been described for a number of basins including the Black Sea (Sorokin 1962, 1964) and fresh water lakes in the U.S.S.R. (Sorokin 1970). An example is Lake Belovod, in the Vladimirskaya region of the U.S.S.R., that was the subject of a detailed study by Sorokin (1970). Lake Belovod is a meromictic water body with a maximum depth of 23 m and a well defined oxycline between about 7 and 10 m. Radioactive tracer techniques were used to estimate rates of sulphate reduction and sulphide oxidation at various levels of the water column: chemosynthetic, photosynthetic and chemical contributions to the latter process were differentiated by comparing activities under dark and day–night régimes and in the presence and absence of a growth inhibitor (chloroform or thymol). An underlying assumption was that the rates of chemical and chemosynthetic oxidation remained constant under the two régimes. While this is not necessarily true, the data (table 2) reveal, at least qualitatively, the stratification of reductive and oxidative activities outlined in figure 2. It was further shown that the zones of chemosynthetic and photosynthetic sulphide oxidation corresponded to those of chemosynthetic and bacterial photosynthetic carbon dioxide fixation, respectively, while the major algal photosynthetic zone occupied the upper 3–4 m of the water column.

Variations of the cycle described in figure 2 apply in other environmental situations. As discussed later, elemental sulphur is sometimes a major by-product of the oxidative phase. Under the high-energy conditions that characterize most marine environments and shallow water bodies, the oxycline develops within the sediments, provided that sufficient organic material is available. One variation that has especial significance in the formation of elemental sulphur is where the oxycline is created at depth within rock, by the merging of sulphuretted and oxic ground waters. All these situations, however, involve successions of biochemical and chemical processes that are essentially equivalent. Indeed they represent in microcosm the global biogeochemical sulphur cycle.

Because of low temperatures and remoteness from hydrothermal or volcanic activity we can conclude that, in the majority of modern terrestrial environments, sulphide arises by bacterial sulphate reduction. This conclusion is supported by results of direct measurements of the rates of sulphate reduction in a variety of groundwaters and saline and freshwater sediments (see summaries by Trudinger 1979, 1981). Generally, the most intense reduction is observed in shallow water saline environments where both sulphate and organic matter are in abundant supply. The annual flux of biogenic sulphide into the world ocean sediments, mainly in those of the continental shelf, slope and rise, has been recently estimated at close to 100 Tg (Volkov & Rosanov 1982).

Relatively few studies have been made on sulphide oxidation *in situ* but, in view of the general lack of sulphide accumulation in the modern environment, it can be assumed that the overall rates of oxidation are of the same order as those of sulphate reduction. As Jørgensen (this symposium) has reported, oxidation may range from mainly chemical to mainly biological depending on the characteristics of the oxic–anoxic interface. Lake Belovod appears to be intermediate between these two extremes. If the rates of sulphide oxidation cited in table 2 are quantitatively realistic then between 50 and 60 % of the overall sulphide oxidation is chemical.

Of more relevance in a geological context are the oxidative reactions involved in weathering of pyritic rocks and, to a lesser extent, elemental sulphur and base metal deposits. Sulphur-oxidizing organisms are commonly detected in association with sulphur and sulphide deposits (see, for example, Kuznetsov *et al.* 1963; Sokolova & Karavailo 1968) but direct evidence for their quantitative importance in oxidative weathering is lacking. Their *potential* importance in sulphide oxidation, however, has been amply demonstrated by studies on the utilization of microorganisms in hydrometallurgical processes (Torma 1977; Kelly *et al.* 1979; Ralph 1979). Sulphur-oxidizing bacteria, particularly those with the additional ability to oxidize ferrous iron, are effective catalysts for the oxidative degradation of pyrite and other sulphide minerals and extraction of economically important metals such as copper.

Nevertheless, the conditions employed in hydrometallurgical operations are designed to optimize mineral degradation and are far removed from those that apply to the natural environment. The relative effectiveness of microbial over chemical sulphide oxidation is not necessarily equivalent in both situations. For the present, then, we may presume that microbial sulphide oxidation contributes significantly to the weathering phase of the geochemical sulphur cycle but we can place no realistic value on the extent of this contribution.

3. The problem of diagnosis

How can we recognize the past activities of sulphur bacteria? The main manifestations of sulphur transformations in the geological record are chemical precipitates: metal sulphides, elemental sulphur, anhydrite and gypsum (or sometimes dolomite pseudomorphs of anhydrite and gypsum). Except where particular mineral assemblages are strongly indicative of high-temperature formation, mineralogies and textures provide no compelling clues as to the sources of reactive sulphur. Pyritic framboids – assemblages of microcrystalline pyrite with a raspberry-like surface texture – are common in pyritic rocks and modern anoxic sediments and had often been considered to be products of biological activity (see discussions by Trudinger (1976) and Krouse & McCready (1979)). Similar structures have now been synthesized in the laboratory by purely inorganic mechanisms and the presence of framboids in sediments is probably related to the prevailing physico-chemical conditions rather than specifically to biological activity.

Much of our understanding of the biogeochemistry of sulphur in palaeoenvironments is based on sulphur isotopic data. Reduced sulphur in meteorites has a fairly uniform isotopic composition similar to that of terrestrial magmatic sulphur. It is thought that this represents the isotopic composition of primordial terrestrial sulphur and that departures from this value are caused by selective utilization of isotopes during transformation from one state to another.

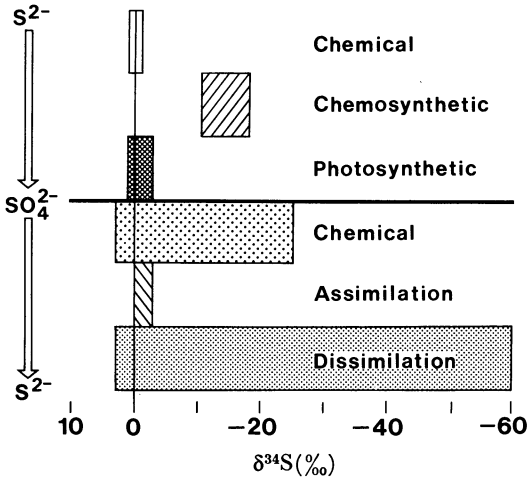

FIGURE 3. Kinetic sulphur isotope effects associated with chemical and biological sulphur oxidoreductions: $\delta^{34}S$ values are expressed relative to the initial substrate.

Isotopic compositions are generally expressed in 'del' notation by which the ratios of the two most abundant isotopes, ^{32}S and ^{34}S, in a sample and standard are compared:

$$\delta^{34}S = \left\{\frac{(^{34}S/^{32}S)_{\text{sample}}}{(^{34}S/^{32}S)_{\text{standard}}} - 1\right\} \times 1000. \tag{1}$$

Troilite from the Cañon Diablo meteorite is the accepted geochemical standard which, by definition, has a $\delta^{34}S$ value of zero.

The potential use of isotopic data as a diagnostic tool in sulphur biogeochemistry became apparent with the discovery that large isotopic fractionations can occur during dissimilatory (but not assimilatory) sulphate reduction (Thode *et al.* 1951), owing to a kinetic isotope effect that favours the reduction of $^{32}SO_4^{2-}$ over $^{34}SO_4^{2-}$. The kinetic isotope effect, however, is not constant (figure 3) but may range from around 0‰ to −46‰ in laboratory experiments with pure cultures (Kaplan & Rittenberg 1964) and to −60‰ in sediments (Chambers & Trudinger 1979). The factors controlling the isotope effect are not well understood. Models have been proposed (see, for example, Rees 1973) in which the overall isotope fractionation is a function of the relative rates of two or more steps in the sulphate reduction pathway, each of which exhibits a kinetic isotope effect. The models predict that there should be an inverse relation between the overall isotope fractionation and the specific rate of sulphate reduction. However, in practice, while the largest isotope effects appear to be related to low rates of reduction per organism, there is no clear correlation between the degree of isotope fractionation and the reduction rate (Chambers & Trudinger 1979).

In open systems, where sulphate is unlimited, the kinetic isotope effect is the sole controlling factor on the isotopic composition of biogenic sulphide. When the sulphate supply is restricted, however, sulphate becomes increasingly enriched in ^{34}S with time, owing to the preferential reduction of $^{32}SO_4^{2-}$. Late-stage sulphides, therefore, contain less ^{32}S than those formed in the early stages of the reaction, and eventually become *depleted* in ^{32}S compared with the initial sulphate. In fully restricted environments the changes in isotope composition with respect to sulphate depletion are formally described by the Rayleigh distillation equations, from which values for the kinetic isotope effect can be derived. This situation would apply to a closed aqueous basin from which sulphide was continually incorporated into sediments, and has been observed in deeper sections of marine sediments where diffusion from the overlying waters is insignificant. Goldhaber & Kaplan (1974), for example, reported that, in a sediment core off the continental shelf in the southwestern Atlantic Ocean, the Rayleigh relation between changes in sulphate concentration and ^{34}S content was obeyed over the depth range 32–249 m below the sediment surface. The calculated kinetic isotope effect was -26‰.

In near-surface sediments, the diffusion of sulphate from the overlying water becomes an important additional factor in determining the isotopic composition of biogenic sulfide (Jørgensen 1979; Goldhaber & Kaplan 1980). Diffusion effects are compounded because, owing to the more extensive utilization of [^{32}S]sulphate in pore waters, the ratio of the diffusion rates of [^{32}S]- and [^{34}S]sulphate are greater than the ^{32}S:^{34}S ratio of sulphate in the overlying water. Thus the sites of bacterial sulphate reduction within the sediment are continually supplied with sulphate that is more enriched in ^{32}S than would be so for a fully closed sediment. Evidence for diffusion effects on isotopic fractionation was obtained by studies on near-surface (0–3 m) sediments in the Gulf of California. By applying a mathematical expression, incorporating differential isotopic diffusion, to data on the sulphate concentration and ^{34}S content in pore waters, Goldhaber & Kaplan (1980) calculated a kinetic isotope effect of *ca.* -60‰. This was similar to the value estimated from the δ^{34}S values of metastable iron sulphides in the upper few centimetres of the sediments where fully open conditions were assumed to apply.

From the above considerations it would be predicted that sulphides derived from the products of dissimilatory sulphate reduction in marine sediments would be highly variable isotopically but with an overall tendency towards enrichment in ^{32}S with respect to seawater sulphate. This is indeed so: δ^{34}S values for sulphides in modern marine sediments range from about $+26$ to -50‰ compared with *ca.* 20‰ for seawater sulphate (Chambers 1982; Lew 1981). These isotopic characteristics of biogenic sulphide provide the main basis for distinguishing between biogenic and abiogenic reduced sulphur in palaeoenvironments.

Interpretation of palaeoisotopic data, however, can be complicated by the fact that sulphur isotopes are fractionated by chemical processes at high temperatures. Isotope exchange between sulphide and sulphate, favouring ^{32}S enrichment in sulphide, occurs at temperatures above *ca.* 200 °C in the presence of elemental sulphur (Robinson 1973). Theoretical studies have shown that the equilibrium of the exchange reaction will depend markedly on pH, temperature and redox conditions (Ohmoto 1972), and that 'biogenic' isotopic patterns could develop in hydrothermal situations where these conditions vary. Moreover, kinetic isotope effects are associated with abiological sulphate reduction (figure 3) by organic matter (Kiyosu 1980) or ferrous iron (Ohmoto *et al.* 1976). These reactions take place above *ca.* 250 °C and there is evidence that they occur during the generation of hydrothermal solutions by circulation of seawater through the crust (Bonatti 1975). Conclusions based solely on the isotope characteristics of minerals in palaeoenvironments are therefore often suspect and must be supported by other information on the environmental conditions prevailing at the time of mineral formation.

Oxidation of sulphide, either chemical or biological, causes relatively little fractionation of sulphur isotopes (figure 3) and we have no other means of distinguishing between biological and chemical processes in the oxidative part of the geochemical cycle. The following sections of this paper therefore deal primarily with the geochemical effects of sulphate reduction.

4. SULPHUR AND SULPHIDE DEPOSITS

A good deal of the current interest in the biogeochemistry of sulphur stems from the possible role that organisms have played in the formation of elemental sulphur and sulphide deposits of economic importance.

Sulphur deposits

There are now good reasons for believing that deposits of elemental sulphur other than those of volcanic or hydrothermal origin were produced by oxidation of hydrogen sulphide generated by bacterial sulphate reduction. Ruckmick *et al.* (1979) classify such biogenic deposits as biosyngenetic or bioepigenetic depending on whether they were produced as sediments or as replacements of anhydrite and gypsum by biogenic sulphur and calcite.

Contemporary examples of biosyngenetic sulphur deposition occur in certain coastal areas of the Bay of Bengal (Iya & Sreenivaasayi 1944, 1945) and in Cyrenaican lakes in the northern sector of the Libyan desert (Butlin & Postgate 1954*a*, *b*). For up to 6 months of the year, clay sediments in the Bay of Bengal are flooded by monsoonal high tides, allowing the development of sulphate-reducing bacteria in the subsurface layers. Hydrogen sulphide then diffuses to the oxygenated layers where it is oxidized to elemental sulphur, which may reach concentrations of 20–30 % on a dry mass basis. The Cyrenaican lakes are fed by warm sulphuretted springs, rich in sulphate, and their sediments contain up to 50 % elemental sulphur that has a $\delta^{34}S$ value of *ca.* -19 ‰ relative to the coexisting sulphate (Ivanov 1968), suggesting that a significant proportion is derived from biogenic sulphide produced by sulphate-reducing bacteria that inhabit the deeper lake waters. The mechanism of sulphide oxidation in the Bay of Bengal sediments was not reported but, in the Cyrenaican lakes, blooms of *Chromatium* and *Chlorobium* occur in the upper water layers and undoubtedly make a significant contribution to elemental sulphur production (Butlin & Postgate 1954*a*, *b*).

A biosyngenetic origin has been ascribed by some to economic sulphur deposits such as those of Sicily (Dessau *et al.* 1962) and Cis-Carpathia (Ivanov 1968). In general, however, it is the bioepigenetic deposits that are of economic importance. In 1977, for example, sulphur from these sources accounted for close to 90 % of the global production of mined elemental sulphur (Ruckmick *et al.* 1979) or about 30 % of the total production from all sources.

Bioepigenetic sulphur deposits are associated with evaporite beds that overlie petroleumbearing strata. They are classified as strata-bound or cap rock deposits depending on whether the evaporites are sedimentary or were transported from depth by salt diapirs (Ruckmick *et al.* 1979). In other respects, however, both types of deposit are similar and elemental sulphur is thought to have formed 'where joints and faults permit water, hydrocarbons, and bacteria to rise into evaporites or cap rocks' (Ruckmick *et al.* 1979, p. 470). It is proposed that hydrogen sulphide produced by reduction of sulphate in the percolating groundwaters was oxidized to elemental sulphur when these groundwaters reached oxygenated zones. The participation of sulphide-oxidizing bacteria in the latter process is suspected (Ivanov 1968) but not proved.

TABLE 3. SULPHUR AND CARBON ISOTOPES IN BIOEPIGENETIC SULPHUR DEPOSITS

(After Davis & Kirkland (1977).)

	δ^{34}S† (‰)		δ^{13}C‡ (‰)	
deposit	anhydrite	sulphur	calcite	oil
cap rock				
Challenger Knoll (Gulf of Mexico)	+30	+14.2	−21.7 to −25.3	−26.6 to −26.7
Boling (Gulf Coast)	+12.2 to +39.2	0 to +4.0	−23.8 to −51.1	−24.9 to −27.1
Moss Bluff (Gulf Coast)	+14.0 to +52.7	−10.8 to −5.2		
Spindletop (Gulf Coast)	+17.6 to +61.7	+0.9 to +15.3		
stratabound				
Castile (Texas)	+26.6	+6.7	−24.1 to −38.0	−26.1

† Relative to meteoritic sulphur.

‡ δ^{13}C is analogous to δ^{34}S: the reference standard (PDB) is belemnite from the fossil cephalopod, *Belemnitella americana*, from the Peedee Formation, South Carolina.

It is further proposed that hydrocarbons were the source of organic matter for sulphate reduction and that biogenic carbon dioxide reacted with calcium ions released from calcium sulphate. The net result was a replacement of gypsum or anhydrite by calcite as depicted by the following generalized scheme (Davis & Kirkland 1979; see also below):

$$\begin{tikzcd} \underset{\text{(gypsum)}}{\mathrm{CaSO_4}} + \underset{\text{(petroleum)}}{(\mathrm{C}+4\mathrm{H})} \arrow[r] & \mathrm{H_2S} \arrow[d, "\frac{1}{2}\mathrm{O_2}"] + \underset{\text{(calcite)}}{\mathrm{CaCO_3}} + \mathrm{H_2O} \\ & \mathrm{S^0} + \mathrm{H_2O}. \end{tikzcd}$$

Sulphur and carbon isotope data (table 3) from individual deposits strongly suggest that the above mechanism of bioepigenetic sulphur formation is valid. Sulphur is enriched in ^{32}S with respect to sulphate, and calcite associated with sulphur is, in general, isotopically similar to hydrocarbons from the same environment.

One major problem with the above proposal is that there are no authenticated cases of hydrocarbon utilization by sulphate-reducing bacteria (see, for example, Postgate 1979). However, there is increasing evidence for anaerobic methane oxidation in anoxic sediments and waters where sulphate appears to be the only plausible terminal electron acceptor (Reeburgh 1976, 1980; Kosiur & Warford 1979; Panganiban *et al.* 1979). It is possible that microbial consortia involving sulphate-reducing bacteria are involved.

Sulphide deposits

Participation of sulphur bacteria in the formation of economic sulphide deposits is problematic. The rates of dissimilatory sulphate reduction in many modern marine sediments are commensurate with those of large-scale sedimentary ore deposition (Trudinger *et al.* 1972; Rickard 1973), but *fixation* of sulphide is limited, mainly by lack of reactable metals. The mean sulphide contents of marine sediments are generally less than 2% S, which, at best, could lead to the formation of relatively low-grade ore (Trudinger 1981).

Today, high-grade sulphide mineralization is associated with oceanic spreading centres and rift zones where hot, metalliferous brines are exhaled onto the ocean floor or into rift-related basins (Bonatti 1975). Two locations that have been extensively studied are the Atlantis II Deep of the Red Sea (Degens & Ross 1969) and the East Pacific Rise (E.P.R.) near 21° N (see, for example, Franchetau *et al.* 1979; Haymon & Kastner 1981; Styrt *et al.* 1981), where high concentrations of pyrite, chalcopyrite, sphalerite and other minerals are deposited from brines. In neither case, however, is it likely that sulphate-reducing bacteria are involved in sulphide mineralization: the Atlantis II brines appear to be sterile while the E.P.R. deposits are forming in an oxic environment. Indeed, at the Galapagos spreading centre of the East Pacific, thermal exhalations support dense populations of chemolithotrophic sulphur-oxidizing bacteria that appear to provide a primary food source for a large, and unusual, invertebrate community (Karl *et al.* 1980; Ruby *et al.* 1981). Isotopic and other evidence suggests that both the Atlantis II and E.P.R. sulphides are mainly produced by high-temperature inorganic reduction of sulphate during the formation of the thermal brines (Styrt *et al.* 1981).

The best indications of a biological component in sulphide ore genesis are found in sediment-hosted copper deposits such as White Pine in the U.S.A. and the Kupferschiefer of Europe (Gustafson & Williams 1981; Trudinger & Williams 1982). Typically, sulphides in such deposits are at low concentration (not more than 3% in the Kupferschiefer) and are isotopically variable (δ^{34}S range usually over 30‰). Pyrite is generally framboidal and there are positive correlations between sulphide and organic carbon contents. These properties closely resemble those characteristic of modern anoxic sediments and, taken together, suggest that the sulphide of the copper deposits was fixed under conditions similar to those pertaining today. Even so, a biogenic origin for the sulphide is not universally accepted and it is considered by some that the economic minerals, as distinct from those of iron, were not initial precipitates but were introduced at a later stage by the replacement of pyrite (see discussion by Gustafson & Williams 1981).

Much research has been undertaken on the genesis of shale- and carbonate-hosted lead–zinc deposits, which are among the world's major sources of these important metals. Many such deposits appear to have been formed in sedimentary environments that supported vigorous microbial communities. They are frequently closely associated with stromatolites (Mendelsohn 1976) – organosedimentary structures formed by accretion of sediment by microorganisms – and in at least one case (the shale-hosted McArthur deposit of the Northern Territory, Australia), structures interpreted as bacterial microfossils have been described from within the ore zone (Oehler & Logan 1977).

It is now widely considered that the sulphide in sediment-hosted lead–zinc deposits arose by the reduction of seawater sulphate or marine sulphate evaporites. The δ^{34}S values of sulphide, however, tend to be much less variable than those of the aforementioned copper deposits, and opinions differ as to whether the reduction was biological (see, for example, Sangster 1976) or chemical (Gustafson & Williams 1981). In some situations, such as the McArthur deposit, there appears to be clear evidence for a dual sulphur source (Smith & Croxford 1973) or, at least, for two distinct processes (Williams & Rye 1974) associated with pyrite and lead–zinc mineralization, respectively. Only pyrite exhibits a sulphur isotopic pattern consistent with a biogenic source of sulphide: $\delta^{34}S$ values increase systematically from the base to the top of the mineralized zone, a trend that could be accounted for by bacterial sulphate reduction in a closed basin. Sphalerite and galena show no such systematic isotopic trends.

In most sulphide deposits the initial depositional and early diagenetic features have been at least partly obscured by the metamorphic effects of pressure and temperature. The significance of the McArthur deposit is that it is relatively unmetamorphosed and its mineralogical, structural and geochemical characteristics may more closely reflect the original depositional conditions.

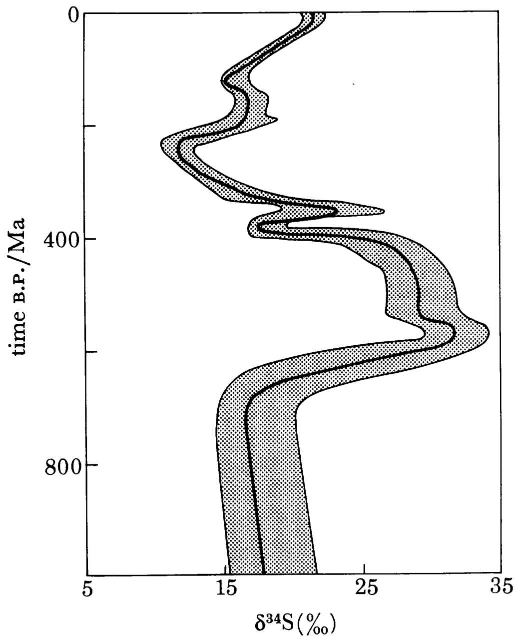

FIGURE 4. The sulphur isotopic age curve for marine sulphate evaporites from the late Proterozoic to the present. The heavy line represents the best estimate for the $\delta^{34}S$ of sulphate minerals in equilibrium with world ocean sulphate at specific dates. The shaded area is an estimate of the uncertainty of the curve. (Adapted from Claypool *et al.* (1980).)

The general conclusion is that bacterial sulphate reduction has made, at best, an indirect contribution to the genesis of economic sulphide minerals, such as those of copper, lead and zinc. On the other hand, as discussed in the following section, biogenic sulphide is probably the main precursor of pyrite – by far the most abundant mineral in sedimentary rocks.

5. HISTORY OF OCEANIC SULPHATE SINCE THE LATE PROTEROZOIC

The present oceans contain about 28 mM sulphate with a uniform $\delta^{34}S$ value of *ca.* +20‰, values that represent the balance between the inputs and outputs of sulphur depicted in figure 1. Extensive studies on material of worldwide distribution, from the late Proterozoic onwards, however, have shown that $\delta^{34}S$ values of sulphate evaporites have not remained constant with time, but have undergone episodic shifts over a range of about +10 to +30‰ (figure 4) (Claypool *et al.* 1980). The isotope effect associated with the crystallization of gypsum is small (1–2‰) (Thode & Monster 1965) and sulphate evaporites exhibit $\delta^{34}S$ values close to those of the sulphate from which they were derived. Thus, if it is assumed that the evaporites were deposited from a mixed ocean, the results in figure 4 imply that there have been major changes in the isotopic composition of ocean sulphate over geological time.

The only process in the geochemical cycle known to cause significant sulphur isotope fractionation is the reduction of sulphate (figure 1) (Rees 1970), which, in most marine sediments, is catalysed by bacteria. It therefore follows that shifts towards high δ^{34}S values in evaporites represent periods when an excess of ^{32}S was transferred from the oceans to the pyritic shale reservoir, while the shifts in δ^{34}S in the opposite direction correspond to periods when the transfer of ^{32}S from shales to the oxidized reservoirs predominated. The amounts of sulphur transferred are considerable. For example, Holser & Kaplan (1966) calculated that the change of δ^{34}S from $+10‰$ in the late Permian (*ca.* 2.2 Ma B.P.) to $+20‰$ in the Tertiary must have involved a net transfer of about 5.6×10^8 Tg of sulphur from the oceans to the shale reservoir. This represents about 45 % of the sulphur in the present oceans.

Opinions differ as to the particular model to be applied to the ocean–evaporite–shale system. Rees (1970) considers that the major net transfers of sulphur were between shales and evaporites. He implies that, apart from the isotopic shifts, there were not necessarily marked changes in oceanic sulphur chemistry. On the other hand, Holser & Kaplan (1966) suggest that the isotopic changes were associated with (p. 129) 'large shifts in the concentration of the total sulfur of the sea'. They further suggest that the accumulation of ^{32}S in the oceans (for example, at *ca.* 400 Ma B.P.) may have been caused by a decline in bacterial sulphate reduction activity due to unfavourable climatic conditions, oxygenation of the oceans, or lack of nutrients. It is important to note, however, that the critical factor is the *fixation* of sulphide into sediments, which is not necessarily related to the rate of sulphate reduction: it could equally be controlled by the supply of metals.

A third model has been proposed by Holser (1977), who suggests that earlier models would require an unacceptably high rate of sulphide deposition to account for the rapid rises in δ^{34}S that began at *ca.* 600, 300 and 200 Ma B.P. He takes the view that these must have been caused by 'catastrophic' influxes of ^{34}S-enriched sulphate generated in large Mediterranean seas that had been isolated from the oceans for considerable periods of time.

Nevertheless, regardless of the model employed, it is clear that, if the interpretation of the evaporite isotopic record in terms of oceanic sulphate is correct, dissimilatory sulphate reduction and presumably biological pyrite oxidation have played significant roles in the transfer of sulphur between the principal geochemical reservoirs, at least since the late Proterozoic.

6. INTERACTIONS BETWEEN THE CYCLES OF SULPHUR AND OTHER ELEMENTS

Biogeochemical cycles are interdependent (see, for example, Trudinger *et al.* 1979). The interdependence is a consequence not only of the physiological needs of organisms for a large number of elements but also of the fact that organisms alter the chemistry of the environment in which they grow, thereby affecting previously established chemical equilibria. Examples of links between the sulphur cycle and the iron and carbon cycles have already been mentioned.

The quantitative importance of sulphate reduction in carbon cycling has become evident in recent years. A large proportion of organic matter reaching anoxic sediments can be mineralized in this way. In deep basins, such as the Black Sea, this may represent only a small percentage of the total organic carbon input to the basin because most organic matter is degraded during sedimentation through the oxic zone of the water column (Deuser 1971). However, in shallow-water coastal environments, sulphate-reducing bacteria develop in close proximity to sites of organic matter input and may use more than 50% of the total organic carbon (Jørgensen 1977; Jørgensen & Cohen 1977; Howarth & Teal 1979; Skyring *et al.* 1982).

The apparent relation between sulphate reduction and carbonate mineral formation that emerged from examination of elemental sulphur deposits is confirmed by the results of studies on modern marine sediments. The oxidation of average organic matter by sulphate generates one equivalent of alkalinity for each equivalent of sulphate reduced:

TABLE 4. CHANGES IN PORE-WATER CHEMISTRY IN THE UPPER 5 cm OF A CORE FROM THE BALI TROUGH

(L. A. Chambers, P. J. Cook & P. A. Trudinger, unpublished results.)

component	change†/(meq/l)
SO_4^{2-}	−29.4
alkalinity	+14.9
NH_4^+	+1.5
Ca^{2+}	−10.8
Mg^{2+}	−7.2

† Relative to the overlying ocean water.

$$2CH_2O + SO_4^{2-} \longrightarrow H_2S + 2CO_2 + 2OH^-. \qquad (2)$$

As a result, the equilibrium of the system

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

is displaced in favour of carbonate ions and the solubility product of carbonates such as those of calcium and magnesium may be exceeded. Numerous studies on sediment cores have demonstrated that decreases in pore-water sulphate concentration are accompanied by increases in total alkalinity and decreases in calcium and magnesium ions (Gieskes 1975). An example is shown in table 4, which describes changes in some chemical parameters in the pore waters of the upper 5 cm of an anoxic sediment core from 3560 m depth in the Bali Trench. Carbonate deposition is formally equivalent to the utilization of two equivalents of alkalinity per mole of carbonate produced:

$$Ca^{2+} + CO_2 + 2OH^- \longrightarrow CaCO_3 + H_2O. \qquad (3)$$

Changes in measured alkalinity and in calcium and magnesium ions should therefore provide a measure of the total alkalinity generated by biochemical reactions operating within the sediments. For the example cited in table 4, the change in total alkalinity, after compensation for ammonium ions, was calculated to be 31.3 meq/l. This is close to the value (29.4 meq/l) for sulphate depletion, providing strong evidence that sulphate reduction was the major factor responsible for the observed changes in calcium and magnesium content.

To explain these chemical changes it is inferred that carbonate minerals are formed within sediments. Carbon isotopic data provide independent evidence for the association of sulphate reduction with carbonate deposition. Organic carbon is enriched in ^{12}C owing to the preferential utilization of $^{12}CO_2$ by photosynthetic organisms. Carbon dioxide produced during the degradation of organic matter is similarly enriched and thus carbonate minerals precipitated from a carbonate pool that contains a significant proportion of biogenic CO_2 should tend to be lighter than normal. Carbonates in modern marine sediments generally have $\delta^{13}C$ values of within 1–2‰ of zero relative to the PDB standard. These values are close to those of oceanic bicarbonate, indicating that the chemical precipitation of carbonates involves little or no carbon isotope fractionation. On the other hand, ^{12}C-enriched bicarbonate (Claypool & Kaplan 1974) and carbonate minerals have been detected within zones of sulphate reduction of anoxic sediments. An example of the latter is at a deep-sea site off Baja California where dolomites with $\delta^{13}C$ values as low as −30‰ (Pisciotto & Mahoney 1981), and a rapid depletion of pore-water sulphate (Gieskes *et al.* 1981), coincide at a sub-bottom depth of *ca.* 200–300 m. A direct relation between carbonate deposition and sulphate reduction activity was reported by Ivanov *et al.* (1980). Carbonates in sediments of the northwestern part of the Indian Ocean have $\delta^{13}C$ values ranging from −1.1 to −11.9‰, and there is a general inverse correlation ($r = -0.794$) between $\delta^{13}C$ and the rate of sulphate reduction.

The above examples demonstrate that dissimilatory sulphate reduction leads to the localized formation of calcium and magnesium carbonates in marine sediments. Where sulphate reduction occurs in regions of high evaporation it is possible that more soluble carbonates would be precipitated. Such a mechanism has been proposed for the formation of extensive natron (Na_2CO_3) deposits in the Wadi Natrûn in the Libyan desert (Abd-el-Malek & Rizk 1963).

There is also evidence that the sulphur cycle has played a more profound role in the global redistribution of carbon between organic and inorganic pools and in the regulation of atmospheric oxygen. Veizer *et al.* (1980) reported that, from the late Proterozoic to the Quaternary, $\delta^{13}C$ values of marine carbonates vary with time and correlate negatively ($r = -0.839$) with $\delta^{34}S$ values of sulphate evaporites over the same period (see figure 4). Thus when sulphate reduction was the dominant process in the sulphur cycle leading to ^{34}S enrichment in ocean, the pool of sedimentary organic matter became depleted and ^{12}C-enriched CO_2 was released to the hydrosphere and atmosphere leading to the formation of ^{12}C-enriched marine carbonates. Conversely, periods dominated by pyritic weathering were those in which ^{12}C-enriched organic matter was sequestered in sediments. These antipathic changes in the overall redox states of carbon and oxygen led Veizer *et al.* (1980) to conclude that photosynthesis, sulphate reduction and pyrite weathering were major factors in maintaining oxygen levels in the Phanerozoic atmosphere. This conclusion is supported by numerical models developed by Schidlowski & Junge (1981), who had earlier proposed that shifts in the redox state of the sulphur cycle must have been accompanied by marked changes in atmospheric oxygen (Schidlowski *et al.* 1977).

Almost certainly the sulphur bacteria have a much wider range of effects on element cycling than indicated by those cited above. For example, sulphuric acid produced by acidophilic thiobacilli has been shown in the laboratory to facilitate the weathering of granite (Wagner & Schwartz 1967) and may be involved in the dissolution of carbonate minerals in Nature (Golubić & Schneider 1979). Sulphate reducers have been implicated in the formation of roll-type uranium deposits, where it is suggested that they create the reducing conditions necessary for the formation of insoluble U^{IV} minerals (see, for example, Granger & Warren 1969). As with sulphide oxidation, however, it is unlikely that these processes would leave any unique imprint on the geological record by which their operation in the past could be recognized.

7. The age of the biogeochemical sulphur cycle

In the light of the foregoing discussions the question arises: when in geological history was the present biogeochemical sulphur cycle established? Unless geochemical or other evidence for the past activities of sulphide-oxidizing organisms is eventually forthcoming this question will remain unanswerable, although it can be argued on comparative biochemical grounds that some form of photosynthetic sulphur oxidation evolved during the early, essentially anoxic, phase of Earth history (see, for example, Klein & Cronquist 1967; Broda 1978; Trüper 1982).

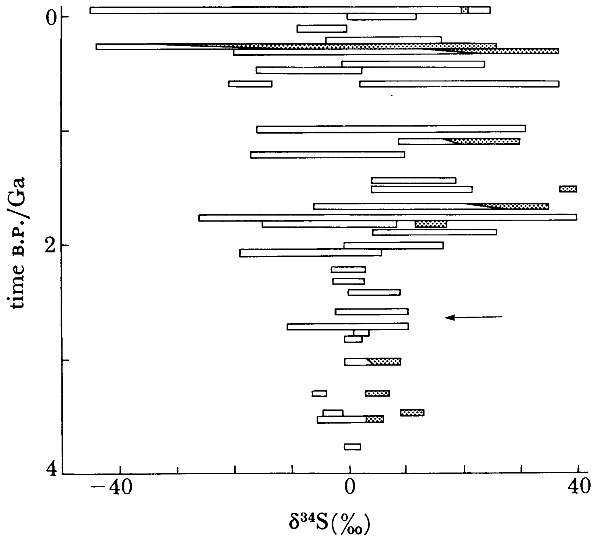

Figure 5. Isotopic composition of sedimentary sulphur as a function of time. The bars represent the best estimates of times of deposition, or the mid-points of ranges where the exact time is uncertain: open bars, sulphide; stippled bars, sulphate. (Data from references cited by Sangster (1968), Monster *et al.* (1979) and Skyring & Donnelly (1982).)

The development of the modern biogeochemical cycle must of course have postdated, or at least been contemporaneous with, the emergence of dissimilatory sulphate reduction. A comparison of global sulphur isotopic patterns in sedimentary minerals of different ages provides some insight into the secular development of sulphate reduction.

We have already seen that the modern biogeochemical cycle has generated sulphides in Holocene sediments that exhibit a wide range (*ca.* 80‰) of δ^{34}S values. We have also deduced that dissimilatory sulphate reduction is the principal factor responsible for the formation of ^{32}S-enriched sulphides and for ^{34}S enrichment in marine sulphate. A clue to the age of sulphate reduction could be provided by the appearance of similar isotopic patterns in the sedimentary record.

Figure 5 shows the secular trend in isotopic patterns of minerals in sedimentary rocks ranging in age from the oldest known (the 3.8 Ga old Isua rocks in Greenland) (Monster *et al.* 1979) to the Holocene. From 1.8–2.0 Ga B.P. onwards, δ^{34}S values of sulphides are highly variable, and shortly after this time (*ca.* 1.5 to 1.7 Ga B.P.) sulphate evaporites strongly enriched in ^{34}S were present. This is interpreted to mean that by about 2.0 Ga B.P. dissimilatory sulphate reduction had developed to the stage where it became a major factor in the geochemistry of sulphur.

Before 2.0 Ga B.P. the picture is not so clear. Nevertheless, available evidence does suggest that sulphides in these older rocks are generally much more uniform in isotopic composition, with $\delta^{34}S$ values within 6‰ of zero. Thus for roughly the first half of Earth's history, terrestrial sulphide may have been almost exclusively magmatic in origin. Apparently anomalous $\delta^{34}S$ distribution patterns are noted in rocks about 2.6–2.75 Ga old, represented by the Deer Lake greenstone sequence in Minnesota and the Michipicoten and Woman River iron-formations of the Canadian Shield (indicated by the arrow on figure 5). These patterns have been taken as indicating an early stage of bacterial sulphate reduction (Goodwin *et al.* 1976; Monster *et al.* 1979; Ripley & Nicol 1981; Thode 1980) but Skyring & Donnelly (1982) have recently presented biological and geochemical arguments to suggest that these rocks contain both magmatic sulphide and biogenic sulphide derived from the reduction of *sulphite* by an evolutionary precursor of the dissimilatory sulphate reducers.

Current evidence suggests that the period from about 2.8 to 1.7 Ga B.P. witnessed the gradual development of free oxygen in the hydrosphere and atmosphere (Schopf *et al.* 1982). A possible reason for the apparent escalation of sulphate reduction around 2 Ga B.P. is that free oxygen was necessary for the widespread formation of sulphate in the oceans. This would also imply that at about the same time an oxygen-linked sulphur cycle was in existence, although whether or not this involved sulphur-oxidizing organisms cannot be determined. Nevertheless, there are a few occurrences of sulphate evaporites in much older rocks dating back to about 3.5 Ga B.P. (Thorpe 1979). One possibility is that these formed in restricted environments where localized formation of sulphate by oxidation of magmatic sulphide took place, perhaps by photosynthetic sulphur bacteria (Lambert *et al.* 1978).

These arguments, based as they are on purely isotopic evidence, must be viewed with caution. Moreover, the decline in the sedimentary record with geological time means that the data become statistically less significant the further back in the sedimentary record we go. Nevertheless, there is additional evidence that the early Proterozoic was a period that witnessed a major change in sulphur geochemistry. Cameron & Garrels (1980) noted that, in shales of Archaean (more than 2.5 Ga B.P.) and Aphebian (2.5–1.7 Ga B.P.) ages, there is a linear correlation between organic carbon and sulphide–sulphur contents. However, in Archaean shales the C:S ratio, on a percentage dry mass basis, is 1:1, whereas for Aphebian shales the value is 1:0.36 – similar to the average C:S ratio of a variety of modern marine sediments (Goldhaber & Kaplan 1974). According to Berner (1970) the linear relation between carbon and sulphur is a consequence of a direct proportionality between the degree of sulphate reduction (and pyritization) and the amount of available organic matter. It is assumed that, on average, the ratio of available to intractable organic carbon is constant so that the latter is an index of the amount of carbon utilized by sulphate reduction. On this reasoning Cameron & Garrels (1980) conclude that the change in the C:S ratio in the Aphebian was the result of the onset of bacterial sulphate reduction. They also suggest that the 1:1 relation between carbon and pyrite sulphur in the Archaean 'may be the result of volcanic H_2S or other reduced S compounds being used by S-oxidizing bacteria' (p. 196), the implication being that the latter were the source of carbon. It is not readily evident, however, why this should result in a *stoichiometric* relation between carbon fixed and sulphide remaining.

The general conclusion to be reached from these studies is that dissimilatory sulphate reduction became widespread sometime after about 2.8 Ga B.P. and may have approached its present significance at around 2.0 Ga B.P. Then, or soon after, an oxygen-linked geochemical sulphur cycle became established. It is, of course, conceivable that anaerobic cycling of sulphur by dissimilatory sulphate reducers and photosynthetic sulphur bacteria was in existence earlier in Earth's history but failed to leave its imprint on the sedimentary record (or perhaps this imprint has not been, or cannot be, recognized). Even today a close coupling between sulphate reduction and photosynthetic sulphide oxidation appears to exist in certain meromictic lakes where bacterial photosynthesis contributes substantially to total primary organic carbon (Pfennig 1978). In Green Lake, New York, for example, the contribution can be as high as 85% and a rapid decline in dissolved sulphide content within the zone of bacterial photosynthesis (Deevey *et al.* 1963) indicates that, during daylight, most of the sulphide produced by bacterial sulphate reduction is consumed by the phototrophic bacteria.

8. Concluding remarks

In this paper an attempt has been made to illustrate the geological implications of sulphur oxidoreductions by bacteria by reference to some of the major transfers of sulphur between oxidized and reduced reservoirs. Dissimilatory sulphate reduction has probably been a significant geochemical process since the late Archaean or early Proterozoic and, by analogy with the modern environment, we can conclude that sulphur-oxidizing organisms have made significant contributions to the oxidative weathering of pyrite and other sulphidic minerals. These activities also have direct implications with respect to the geochemistry of other elements such as carbon, oxygen and metals. From the economic viewpoint the importance of sulphur bacteria is less certain. It seems likely that sulphate reducers were involved in the formation of some elemental sulphur deposits but there is no clearcut evidence that they made any direct contribution to genesis of base metal sulphide ores.

All conclusions regarding biological activity in palaeoenvironments, however, must be viewed cautiously since the geochemical evidence on which they are based is rarely, if ever, unambiguous. Moreover, uncertainties about the composition of the hydrosphere and atmosphere, particularly in the Precambrian, must inevitably cast some doubts on whether present ecosystems are strictly analogous to those that existed in the past. It is therefore unlikely that definitive statements on the past geochemical activities of microorganisms will be forthcoming. We rely instead on reaching 'most probable' conclusions that are consistent with all the available geochemical, mineralogical and biological data.

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