

ANTIQUITY AND EVOLUTIONARY STATUS OF BACTERIAL SULFATE REDUCTION: SULFUR ISOTOPE EVIDENCE*

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Abstract. The presently available sedimentary sulfur isotope record for the Precambrian seems to allow the following conclusions: (1) In the Early Archaean, sedimentary $\delta^{34}\text{S}$ patterns attributable to bacteriogenic sulfate reduction are generally absent. In particular, the $\delta^{34}\text{S}$ spread observed in the Isua banded iron formation (3.7×10^9 yr) is extremely narrow and coincides completely with the respective spreads yielded by contemporaneous rocks of assumed mantle derivation. Incipient minor differentiation of the isotope patterns notably of Archaean sulfates may be accounted for by photosynthetic sulfur bacteria rather than by sulfate reducers. (2) Isotopic evidence of dissimilatory sulfate reduction is first observed in the upper Archaean of the Aldan Shield, Siberia ($\sim 3.0 \times 10^9$ yr) and in the Michipicoten and Woman River banded iron formations of Canada (2.75×10^9 yr). This narrows down the possible time of appearance of sulfate respirers to the interval $2.8 - 3.1 \times 10^9$ yr. (3) Various lines of evidence indicate that photosynthesis is older than sulfate respiration, the SO_4^{2-} utilized by the first sulfate reducers deriving most probably from oxidation of reduced sulfur compounds by photosynthetic sulfur bacteria. Sulfate respiration must, in turn, have antedated oxygen respiration as O_2 -respiring multicellular eucaryotes appear late in the Precambrian. (4) With the bulk of sulfate in the Archaean oceans probably produced by photosynthetic sulfur bacteria, the accumulation of SO_4^{2-} in the ancient seas must have preceded the buildup of appreciable steady state levels of free oxygen. Hence, the occurrence of sulfate evaporites in Archaean sediments does not necessarily provide testimony of oxidation weathering on the ancient continents and, consequently, of the existence of an atmospheric oxygen reservoir.

1. Introduction

The search for the antiquity, and the assessment of the evolutionary status, of dissimilatory sulfate reduction ('sulfate respiration') are important topics in current efforts to elucidate the early history of life (cf. Trudinger, 1976). There is no doubt that the advent of sulfate respiration must have constituted a paramount quantum step in bioenergetic evolution and, accordingly, a most important benchmark in the temporal framework of early organic evolution as a whole. Although the sequential relationship of the principal steps in the evolution of the respiratory pathway is still under debate (Egami, 1974, 1976; Broda, 1975a, 1977), we may reasonably assume that, as a result of photosynthetic activity by green and purple sulfur bacteria, sulfate as a mild oxidant must have preceded free oxygen in the ancient environment (Broda, 1975b, p. 77). Hence, SO_4^{2-} as a terminal electron acceptor for the oxidation of organic substrates ('foodstuffs') should have become available in the oceans long before the attainment of appreciable steady state

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levels of molecular oxygen in the atmosphere, with sulfate respiration thus certainly antedating the process of O_2 -respiration.

In contrast to nitrate respirers (whose evolutionary status dominates current bioenergetic discussions), sulfate reducing bacteria can be traced back in the geological record as they release H_2S as a principal metabolite which is susceptible to subsequent fixation as sedimentary sulfide (mostly as pyrite, FeS_2). Moreover, during bacterial sulfate reduction, i.e.,



the stable isotopes of sulfur are selectively metabolized, with ^{32}S preferentially accumulating in bacteriogenic H_2S as a result of a kinetic isotope effect inherent in this process. In terms of the conventional δ -notation, the $\delta^{34}S$ values of metabolic H_2S are markedly shifted to the negative side when compared to those of the parent sulfate pool, the magnitude of the effect ranging from a few per mil. to some 50‰ as a result of its dependence on a complex set of variables which govern the rate of reduction per bacterial cell (see, inter alia, Kaplan and Rittenberg, 1964; Kemp and Thode, 1968). Accordingly, the prime characteristics of the dissimilatory reduction of sulfate by sulfate reducers are (1) a general enrichment of the light sulfur isotope (^{32}S) and (2) a relatively large spread in $\delta^{34}S$ values of the resulting metabolic H_2S -phase.

Both these characteristics are basically preserved when hydrogen sulfide is incorporated in sulfide minerals. This happens in many sedimentary environments, notably in the 'euxinic' facies associated with sulfuretum-type anaerobic ecosystems. Thus, sedimentary sulfides inherit the characteristic isotope spread of bacteriogenic H_2S , providing mineralized vestiges of former life activities of microbial sulfate reducers. It has been shown, furthermore, that primary $\delta^{34}S$ gradients are unlikely to be smoothed out by subsequent metamorphic processes, even in high-grade terranes (Buddington *et al.*, 1969; Rye and Ohmoto, 1974).

During the last decade or so, sulfur isotope have accrued for a fair amount of Precambrian and notably Archaean sediments which seem to suggest certain limits for the time of emergence of dissimilatory sulfate reduction (see, inter alia, Thode *et al.*, 1962; Perry *et al.*, 1971; Vinogradov *et al.*, 1976; Goodwin *et al.*, 1976; Donnelly *et al.*, 1977). The recent accumulation of the first sulfur isotope values (Monster *et al.*,

Fig. 1. Isotopic composition of sulfides from igneous rocks of Archaean age as compared with sulfur from the troilite phase of meteorites. The narrow clustering of $\delta^{34}S$ values around zero per mil. as observed in several mafic bodies [(2), (3)] indicates 'primitive' sulfur of mantle derivation, while the moderate spreads displayed by (4), (5) and (6) reflect already incipient isotope differentiation (either by intramagmatic fractionation processes or as a result of contamination with sedimentary sulfur). — (1) Troilite in various types of meteorites (Hulston and Thode, 1965); (2) sulfides in Isua orthoamphibolites (3.76×10^9 yr) of tholeiitic affinities (Monster *et al.*, 1979); (3) sulphides in Ameralik basalts (between 3.1 and 3.7×10^9 yr) of Isua region (Monster *et al.*, 1979); (4) sulfides in mafic and ultramafic intrusions at base of Archaean Iengra Series ($\sim 3.5 \times 10^9$ yr), Aldan Shield, Siberia (Vinogradov *et al.*, 1976); (5) sulfides in felsic volcanics intercalated in Michipicoten banded iron formation of Canada (Goodwin *et al.*, 1976); (6) nickel sulfides in ultramafic/mafic sequences (2.6 – 2.8×10^9 yr) of Yilgarn Block, Australia (Donnelly *et al.*, 1977).

1979) from the oldest terrestrial sediments from Isua, West Greenland (3.76×10^9 yr) (Moorbath *et al.*, 1973) as well as from other Archaean sequences (Fripp *et al.*, 1978; Lambert *et al.*, 1979) makes this perhaps an appropriate time for a review of the ancient sulfur cycle. In the following, an overview will be given on the presently known

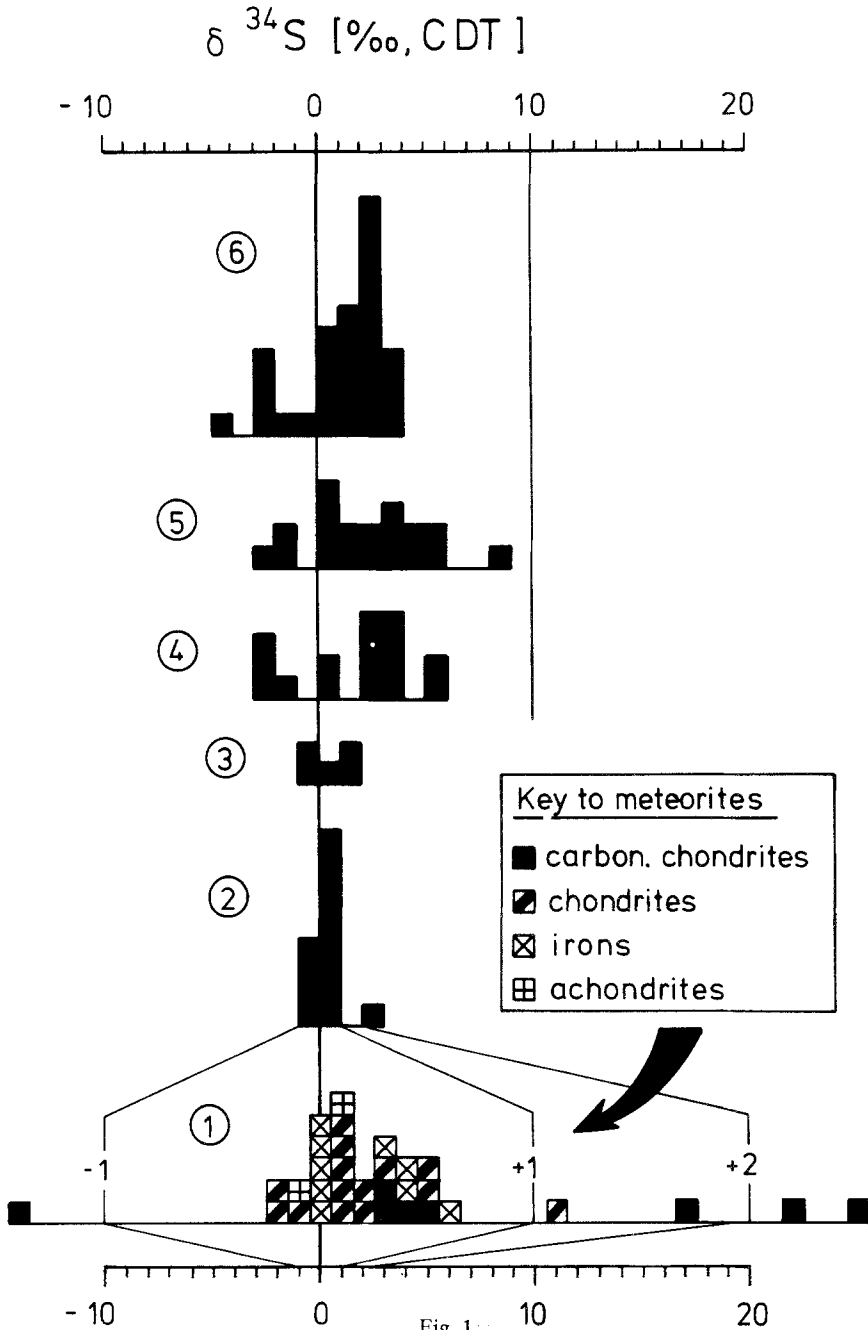


Fig. 1.

Precambrian sulfur isotope record which — though incomplete over large periods — should allow us to decidedly narrow in time the possible rise of sulfate respirers during the Early Precambrian.

2. Isotopic Composition of Sulfur in Archaean Primary Rocks

The sulfur isotope abundances observed in several mafic igneous rocks of Archaean age (see Figure 1) provide a natural base-line for the interpretation of the early sedimentary sulfur isotope record. Sulphur with $\delta^{34}\text{S}$ values close to zero per mil. as encountered in sulfides from both the 3.7×10^9 yr-old Isua amphibolites of tholeiitic affinities and the somewhat younger (between 3.1 and 3.7×10^9 yr) Ameralik basalts of the same region [see Figure 1, (2), (3)] is generally supposed to reflect the average isotopic composition of mantle sulfur, coming very close to sulfur in the troilite phase meteorites. It is reasonable to assume that isotopic differentiation of terrestrial sulfur had originally started with primordial sulfur of this type. As is attested by the sizeable spread around zero per mil. of the $\delta^{34}\text{S}$ values yielded by several primary rocks [see Figure 1, (4), (5), (6)], isotopic fractionation of primitive sulfur may actually commence at a very early stage, either as a result of intramagmatic differentiation processes or by assimilation of isotopically fractionated sulfur from the surrounding sediments.

3. Precambrian Sedimentary Sulfur Isotope Record

Figure 2 is a compilation of the principal sedimentary sulfur isotope data (for sulfide and sulfate) hitherto available for the time span between the beginning of the record some 3.7×10^9 yr ago and Grenville age (about 10^9 yr) Except for those from the Grenville Province, these data reflect the isotopic geochemistry of sulfur from *common* sedi-

Fig. 2. Sedimentary sulfur isotope record for the time range $3.7-1.0 \times 10^9$ yr. ago (time axis not to scale; note that (2), (3) and (4) are approximately coeval). — (1) Isua, West Greenland, banded iron formation (3.76×10^9 yr); (2) Pilbara Block, Australia ($\sim 3.5 \times 10^9$ yr); sulfate occurring as bedded barite); (3) Fig Tree Group, Swaziland System, South Africa ($3.0-3.3 \times 10^9$ yr; sulfate occurring as bedded barite); (4) Archaean of Aldan Shield, Siberia (lower suites approaching 3.5×10^9 yr): (a) Upper Aldan and Nimnyr Suites of Iengra Series, (b) and (c) Fedorov Suite of Iengra Series (sulfate occurring as barite and anhydrite), (d) and (e) Taeshnoe and Pionerskoe iron ore deposits in Fedorov Suite of Iengra Series, (f) and (g) Dsheltula Series; (5) various banded iron formations from Rhodesia (mostly $> 2.8 \times 10^9$ yr); (6) black shales from greenstone belts within Yilgarn Block, Australia ($2.6-2.8 \times 10^9$ yr); (7) and (8) Michipicoten and Woman River banded iron formations, Superior Province, Canada ($\sim 2.75 \times 10^9$ yr); (9) black shales from Outokumpu, Finland (between 1.8 and 2.3×10^9 yr), (10) Sudbury Precambrian: (a) Froid Series ($\sim 2.2 \times 10^9$ yr), (b) Onwatin Slates of Sudbury basin ($\sim 1.9 \times 10^9$ yr); (11) Grenville Province of Canadian Shield ($1.0-1.2 \times 10^9$ yr): (a) Adirondack sedimentary sulfide deposits, (b) sphalerite-pyrite deposits of Balmat-Edwards, (c) bedded anhydrite, Balmat-Edwards. — Data from Brown, 1973 (11b,c); Buddington *et al.*, 1969 (11a); Donnelly *et al.*, 1977 (6); Fripp *et al.*, 1978 (5); Goodwin *et al.*, 1976 (7,8); Lambert *et al.*, 1978 (2); Mäkelä, 1974 (9); Monster *et al.*, 1979 (1); Perry *et al.*, 1971, 1975 (3,2); Thode *et al.*, 1962 (10); Vinogradov *et al.*, 1976 (3,4).

mentary environments, with major stratiform ore bodies (e.g., Broken Hill, Mt. Isa) and assemblages of detrital sulfides (Witwatersrand) deliberately excluded (for a review of the isotope geochemistry of these latter occurrences see Schidlowski, 1973).

As is obvious from Figure 2, the isotope data from the Isua banded iron formation

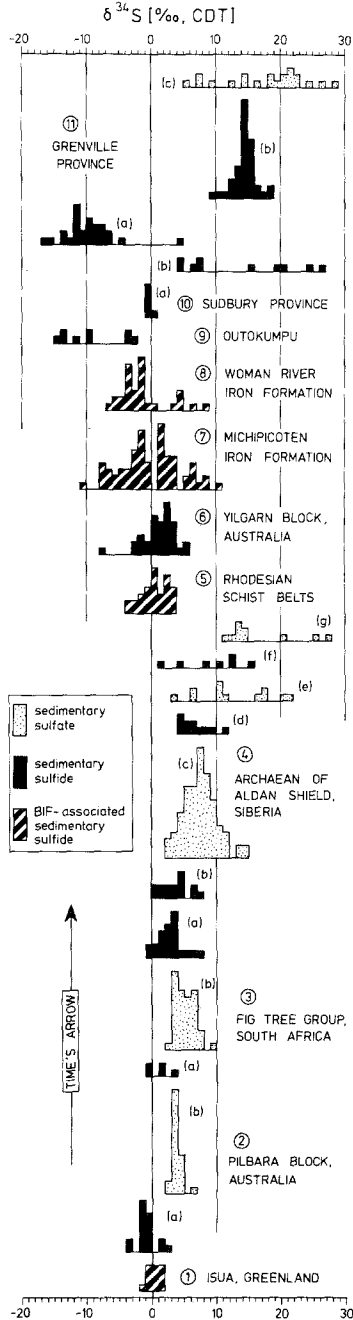


Fig. 2.

represent the lowermost benchmark in the sedimentary sulfur isotope record. With an average $\delta^{34}\text{S}$ of $+0.5 \pm 0.9\%$ [CDT] (Monster *et al.*, 1979), the sulfides of the various BIF-members investigated (belonging mostly to the sulfide and oxide facies) are virtually identical in their isotopic composition with magmatogenic sulfur as present, for instance, in the tuffaceous Isua amphibolites ($\delta^{34}\text{S} = +0.3 \pm 0.9\%$) and the basaltic Amealik dykes of the Isua region [$\delta^{34}\text{S} = +0.6 \pm 1.1\%$; cf. Figure 1, (2), (3)]. Hence, the sulfide constituents of the Isua banded iron formation are clearly made up of very primitive sulfur resembling primordial sulfur from the Earth's mantle (cf. Shima *et al.*, 1963; Schneider, 1970). The most probable source of this sulfur were volcanogenic sulfide emanations which, during the passage to their final sites of emplacement within the sedimentary sequence, have experienced minor isotopic fractionation accounting for the observed maximum spread of $\delta^{34}\text{S}$ values between -1.0 and $+2.0\%$. It should be noted that there is no isotopic evidence whatsoever that the sulfur of the Isua iron formation has passed through a stage of bacteriogenic H_2S with subsequent precipitation as sedimentary sulfide. Accordingly, the observed sulfur isotope distribution in these sulfides would be consistent with the absence of microbial sulfate respirers prior to some 3.7×10^9 yr ago.

Such a conclusion is apparently substantiated by a triad of somewhat younger occurrences of sedimentary sulfur which all fall roughly into the time interval 3.0 to 3.5×10^9 yr [Pilbara Block, Australia; Barberton greenstone belt, South Africa; Aldan Shield, Siberia; see Figure 1, (2), (3) and (4)]. These occurrences are characterized by the coexistence in the same sedimentary sequence of both sulfide and sulfate, the latter occurring mostly as barite currently interpreted as either an original relic or a later replacement of the oldest evaporite series preserved in the sedimentary column (Perry *et al.*, 1971; Vinogradov *et al.*, 1976; Lambert *et al.*, 1979). Although the sedimentary origin notably of the Barberton barites has been repeatedly questioned, there seems to be convincing evidence by now that these sulfates were originally deposited as chemical sediments (Heinrichs and Reimer, 1977). Further, Lowe and Knauth (1977) have reported from the underlying Onverwacht cherts abundant spindle-shaped crystallites resembling pseudomorphs after gypsum ('gypsum ghosts'). From the barite-chert series of the North Pole (Pilbara) deposits Dunlop (1978) has also described textural features suggesting that the barites were essentially formed by diagenetic replacement of an evaporitic calcium sulfate precursor by Ba^{2+} -bearing intrastratal solutions (without significantly affecting the bulk isotope geochemistry of the sulfates). The original precipitation of a fairly soluble calcium sulfate phase would, necessarily, imply relatively high SO_4^{2-} -concentrations in the Archaean oceans, this lending further support to concepts of a conservative sea water chemistry through the ages (cf. Garrels and Mackenzie, 1974; Holland, 1974).

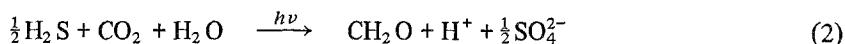
A conspicuous feature of these Early Archaean sulfur occurrences is the very small isotopic fractionation between sulfide and sulfate amounting to only 3 to 4% on average. This contrasts markedly with fractionations of $30 \pm 5\%$ encountered in younger, and notably Phanerozoic, sediments (cf. Holser and Kaplan, 1966; Holland, 1973;

Schidlowski *et al.*, 1977). With their $\delta^{34}\text{S}$ means lying between +4 and +7%, the sulfates are not too far in their isotopic composition from primordial sulfur, while the sulfides largely fall into the range of this latter. It would seem reasonable, therefore, to concur in the statement by Lambert (1978) that juvenile sulfur with $\delta^{34}\text{S} \cong 0\%$ was the most probable source of *both* sulfur species.

If sulfide and sulfate in these sediments are *genetically related* (which interpretation would exclude, for instance, the presence of substantial amounts of detrital pyrite), then the sulfur isotope geochemistry of these Archaean sequences could, in principle, be explained in two alternative ways:

1. First, the minor shift of the $\delta^{34}\text{S}$ values from zero to averages between +3 and +7% as displayed by the Early Archaean sulfates might be interpreted as heralding the beginnings of bacterial sulfate reduction (which, when in full control of the exogenous sulfur cycle, will push the mean for sulfate evaporites much further into the positive field). However, the isotopic composition of sulfides in the enclosing sediments is not consistent with this explanation, showing neither the characteristic magnitude of fractionation between bacteriogenic sulfide and the contemporaneous sulfate source nor the distribution pattern typical of bacteriogenic $\delta^{34}\text{S}$ values. Although experimental work by Harrison and Thode (1957) has shown that, under specific conditions (notably low sulfate concentrations of the order of 10^{-5} molar), the isotope effect in bacterial sulfate reduction may indeed approach zero, it seems unlikely that such conditions are relevant to our case (with evidence piling up in favor of an original presence in these series of calcium sulfate which would necessitate fairly high SO_4^{2-} -concentrations in the waters of the evaporitic basin). Altogether, the $\delta^{34}\text{S}$ distribution patterns displayed by the sedimentary sulfides certainly have closer affinities to magmatic sulfur than to the respective patterns of bacteriogenic sulfides.

2. An alternative explanation may be based on the assumption that the bulk of the sulfate ions stems from photosynthetic oxidation of primordial (reduced) sulfur by green and purple sulfur bacteria. With $\text{SO}_2 \ll \text{H}_2\text{S}$ in juvenile sulfur emanations, and SO_2 just ending up as sulfite (SO_3^{2-}) in low redox environments, the formation of sulfate will be contingent upon a subsequent oxidation of reduced sulfur compounds as well as of SO_2 to the sulfate stage. Although local inorganic oxidation processes cannot be completely discounted even under the reduced conditions prevalent on the primitive Earth, the most important contribution towards the early terrestrial SO_4^{2-} -budget was probably made by photosynthetic sulfur bacteria (Broda, 1975b, p. 77). Providing optimum conditions for the proliferation of anaerobic microbial ecosystems, the Archaean might have even been the 'golden age' of green and purple sulfur bacteria. In processes of bacterial photosynthesis, e.g.,



minor to moderate enrichments of the heavy sulfur isotope have been observed in the resulting sulfate and polythionate fractions, the effect being usually very small (0–1%) for SO_4^{2-} , but significant (up to about 11%) for the transient (metastable) $\text{S}_x\text{O}_4^{2-}$ -phase

(Kaplan and Rittenberg, 1964). As already proposed by Perry *et al.* (1971), the moderately positive $\delta^{34}\text{S}$ values displayed by the bulk of the Archaean barite deposits could, therefore, be consistent with an origin of their SO_4^{2-} -component by photosynthetic oxidation of reduced primordial sulfur.

In summary, the isotopic geochemistry of these Archaean sulfide-sulfate pairs seems to lend reasonable support to the assumption that photosynthetic sulfur bacteria were already thriving in the ancient seas, whereas there is little (if any) unequivocal evidence for the presence of sulfate respirers. On the other hand, incipient differentiation of $\delta^{34}\text{S}$ distribution patterns for both sulfide and sulfate has been reported for the upper Archaean suites of the Aldan Shield (Vinogradov *et al.*, 1976), the respective histograms (see Figure 2, 4d–g) showing indeed some salient features of bacteriogenic patterns. Since geological field evidence indicates, however, extensive metamorphic and metasomatic reconstitution of the host rocks of these sulfide-sulfate pairs, it is proposed that not too much significance be attached to these data at the present stage.

Any large-scale bacterial sulfate reduction is also discounted by the $\delta^{34}\text{S}$ distribution ($\delta^{34}\text{S} = +0.6 \pm 2.0\%$) displayed by sulphides from various banded iron formations from the Archaean schist belts of Rhodesia [Fripp *et al.*, 1978; see Figure 2, (5)]. As in the case of the Isua iron formation, there is no doubt that these sulfides are made up of 'primitive' sulfur of magmatic pedigree. The bulk of the Rhodesian samples stem from the Early Archaean Sebakwian Group underlying the Bulawayan, the latter having been recently dated at $2.6\text{--}2.8 \times 10^9$ yr by Hawkesworth *et al.* (1975).

A plot of 35 sulfide values from black shales within the $2.6\text{--}2.8 \times 10^9$ yr old greenstone belts of the Australian Yilgarn Block (Donnelly *et al.*, 1977) also shows a marked preponderance of magmatogenic sulfur [cf. Figure 2, (6)]. Although occurring as a constituent of typically 'euxinic' sediments, there is little isotopic evidence that the bulk of these sulfides has ever passed through a stage of bacteriogenic H_2S with subsequent precipitation as sedimentary sulfide. We would, therefore, concur in the interpretation by Donnelly *et al.* (*op. cit.*) that hydrothermal emanations must have constituted the principal sulfur source of these sulfides. It cannot be excluded, however, that some rare negative $\delta^{34}\text{S}$ values encountered possibly indicate minor contributions by biological sulfate reduction.

The decisive break in the presently known sedimentary sulfur isotope record is indicated by the sulfide patterns yielded by the 2.75×10^9 yr old Michipicoten and Woman River banded iron formations of Canada (Goodwin *et al.*, 1976). Here, both the large spread of $\delta^{34}\text{S}$ values over some 20% and their marked encroachment upon the negative field [Figure 2, (7), (8)] leave hardly any doubt that these are genuinely bacteriogenic patterns (perhaps with some superimposed magmatogenic values responsible for the peaks in the zero permil range). Variations of such patterns are shown by most younger Precambrian sedimentary sulfides hitherto investigated, notably those from black shales occurring in the immediate vicinity of the Outokumpu deposit, Finland (between 1.8 and 2.3×10^9 yr, cf. Mäkelä, 1974) and from the $1.0\text{--}1.2 \times 10^9$ yr old Grenville Province of the Canadian Shield [Figure 2, (9), (11)]. It is worth noting that, during

Grenville times, isotope values of seawater sulfate were rather modern as is attested by a $\delta^{34}\text{S}$ average of about 21‰ [Figure 2, (11c)] yielded by the bedded anhydrite in the surroundings of the Balmat-Edwards sphalerite-pyrite deposit (Brown, 1973). The similarity of the isotope geochemistry of the Balmat-Edwards sulfides [cf. Figure 2, (11b)] with the sulfates of their sedimentary frame is generally explained in terms of a total conversion into sulfide, by bacterial sulfate reduction, of a limited sulfate reservoir of above composition. In contrast, the Adirondack sulfide deposits of the same province (Buddington *et al.*, 1969) display a bacteriogenic isotope pattern typical of sulfate reduction in open systems, combining a relatively large spread of $\delta^{34}\text{S}$ values with an average lying well in the negative field [Figure 2, (11a)].

The two sulfide occurrences from the Sudbury district (Thode *et al.*, 1962) included in Figure 2 (10a and 10b) may serve as an example of sedimentary sulfur of different pedigree occurring in relatively close spatial and temporal vicinity. While the sulfides from the Froid Series (10a) south of the Sudbury basin (with $\delta^{34}\text{S}$ values close to zero per mil.) are obviously made up of primary sulfur derived from local volcanogenic sources, those from the Onwatin slates (10b) inside the basin display the wide isotope spread typical of biogenic material.

4. Time of Emergence and Evolutionary Status of Dissimilatory Sulfate Reduction

With the presently available Precambrian sulfur isotope record at hand (Figure 2), an attempt to determine the possible time of emergence of bacterial sulfate reduction seems to be called for. Because of the limits imposed by the scanty data base and the poor time resolution (notably for the Archaean part of the record), this event can be narrowed down at present only to a time interval of about 300–400 million years.

As already proposed elsewhere (Lambert, 1978; Monster *et al.*, 1979), the isotope distribution patterns of the sulfides from the Michipicoten and Woman River iron formations of Canada (2.75×10^9 yr) are likely to provide the oldest clear-cut evidence of bacterial sulfate reduction. On the other hand, the triad of Early Archaean sulfide-sulfate pairs represented in Figure 2 (2, 3, 4b and c) does not furnish convincing proof of contemporaneous sulfate respirers as has been fully set out before. Accordingly, the rise of microbial sulfate reducers should have antedated the Michipicoten and Woman River iron formations and postdated the sulfate occurrences of the Pilbara Block, the Barberton greenstone belt and the Iengra Series of the Aldan Shield respectively, thus leaving the time interval between 2.8 and some 3.1×10^9 yr as the most probable age limit for this event. Consequently, efforts to further narrow down in time this important step in bioenergetic evolution should concentrate on this particular time span.

The absence of bacteriogenic isotope patterns in the Isua iron formation decidedly fits into the general trend of the Archaean $\delta^{34}\text{S}$ record. Although the lack of bacteriogenic features in one particular sedimentary environment does, per se, not preclude bacterial activity in coeval sediments, it would be unrealistic, in view of the above findings, to

expect evidence of biological sulfur isotope fractionation as early as 3.7×10^9 yr ago. Because of this consistency with the Archaean sulfur isotope record as a whole, the interpretation of the Isua data in terms of an absence of bacterial sulfate reduction can be hardly invalidated by the occasional encounter of 'primitive' isotope patterns in geologically younger sediments and notably BIF series [caused by a preponderance in local environments of hypogenic sulfur; see, for instance, Figure 2, (5) and (10a)].

Hence, sedimentary sulfur isotope data presently available for the Archaean would suggest that sulfate respiration was a relatively late achievement in the evolution of bioenergetic processes. In particular, there is hardly any doubt that photosynthesis must have preceded sulfate respiration. This is prompted by both paleontological (Muir and Grant, 1976; Knoll and Barghoorn, 1977) and geochemical evidence (Junge *et al.*, 1975; Sidorenko and Sidorenko, 1975), with latest investigations dating back the probable beginnings of photosynthesis to at least Isua times (Schidlowski *et al.*, 1979). It is in keeping with such conjectures that photosynthetic (S-oxidizing) sulfur bacteria are presently being regarded as the most likely ancestors of sulfate reducers (Peck, 1974; Broda, 1975b, p. 112). This notion is supported, *inter alia*, by sequence analysis of ferredoxins from photosynthetic and sulfate-reducing sulfur bacteria (Schwartz and Dayhoff, 1978). In the phylogenetic tree of ferredoxins, photosynthetic sulfur bacteria diverge from primitive anaerobic heterotrophs (like *Clostridium*) at a very early stage, while sulfate reducers later branch from the base of the line leading to the blue-green algae (Figure 3).

Since the availability of sufficient quantities of sulfate is a necessary prerequisite for dissimilatory sulfate reduction, we may infer that photosynthetic sulfur bacteria must have set the stage for sulfate reducers, the advent of the latter heralding the establishment of a complete biological sulfur cycle ultimately powered by solar radiation. Since O_2 -respiring multicellular eucaryotes have appeared late in the Precambrian (cf. Cloud, 1976; Schopf, 1974), there is no doubt that sulfate respiration has antedated oxygen respiration, the most important quantum step in bioenergetic evolution (Schidlowski, 1978). The assumed sequence sulfate respiration \rightarrow oxygen respiration would necessarily imply that sulfate had become available in the ancient environment considerably earlier than free oxygen which would follow directly from the priority of bacterial photosynthesis to the more differentiated (O_2 -releasing) cyanophytic process.

5. Environmental Significance of Archaean Sulfate Evaporites

Since the bulk of sulfate participating in the *present* geochemical cycle unquestionably owes its origin to oxidation weathering of reduced sulfur compounds, the occurrence of bedded sulfates in Archaean sediments has been repeatedly taken as testimony of the existence of a contemporaneous atmospheric oxygen reservoir (Chukhrov *et al.*, 1970; Vinogradov *et al.*, 1976). However, with photosynthetic sulfur bacteria extant during the Archaean, inferences along these lines should be treated with due reserve.

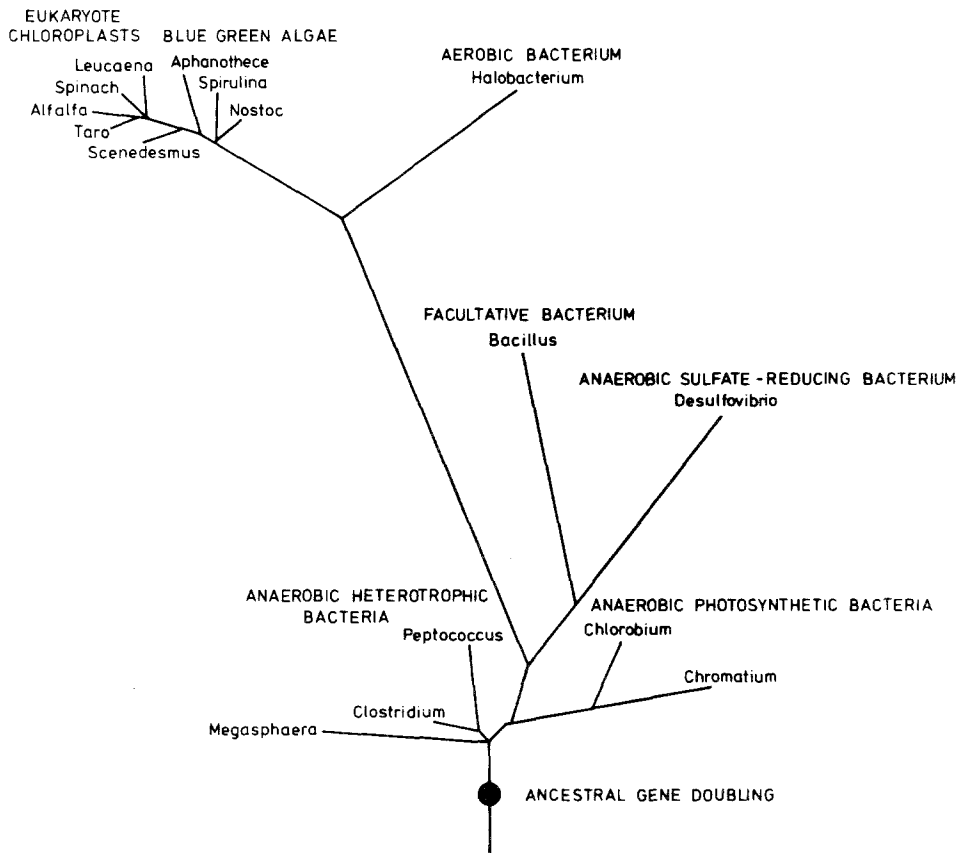


Fig. 3. Simplified evolutionary tree of ferredoxins (adapted from Schwartz and Dayhoff, 1978). Note that photosynthetic sulfur bacteria (*Chlorobium*, *Chromatium*) have branched very early from heterotrophic anaerobes (*Megasphaera*, *Clostridium*, *Peptococcus*) whose ferredoxins show the strongest evidence of the ancestral gene doubling observed in all ferredoxin sequences (hence, this event must have antedated the species divergences pictured in the tree). The *Desulfovibrio* line, on the other hand, has diverged from the root of the subtree which has consequently branched into aerobic bacteria, blue-green algae (cyanophytes), and plants.

As already pointed out above (Equation 2), photosynthetic bacteria utilize hydrogen sulfide (primarily H_2S from volcanic sources) instead of water as electron donor for the reduction of carbon dioxide. Since hydrogen sulfide was probably more abundant in the reducing environment of the Early Archaean than it is today, it may not be unreasonable to look at this time as the possible 'golden age' of photosynthetic sulfur bacteria. With the bulk of sulfate within the Archaean oceans stemming almost certainly from the life activities of these photolithotrophs, SO_4^{2-} as a mild oxidant should have become plentiful in the ancient seas long before the attainment of appreciable steady-state levels of molecular oxygen in the atmosphere (cf. Broda, 1975b, p. 77). Consequently, the occurrence of sulfate evaporites in Archaean sediments does not necessarily constitute

evidence of oxidation weathering on the ancient continents and thus of the existence of a contemporaneous atmospheric oxygen reservoir.

On the other hand, the isotopic composition of the oldest sedimentary carbonates (Schidlowski *et al.*, 1979) suggests a rather modern ratio of organic carbon to carbonate carbon in the Earth's sedimentary shell already some 3.7×10^9 yr ago, this implying the existence of a sizeable reservoir of oxidation equivalents of the reduced carbon constituents. If we are correct in assuming that the presence in the Isua supracrustals of oxide-facies banded iron formation is indicative of cyanophytic (O_2 -releasing) photosynthesis, then a major part of these oxidation equivalents could have been molecular oxygen. Accordingly, free oxygen could have indeed appeared very early in the Earth's history, but is unlikely to have accumulated in the atmosphere before the saturation of the principal oxygen sinks (notably the Fe^{2+} -burden of the ancient seas). An inconsistency between the position of cyanophytes in the evolutionary scheme of Figure 3 and their inferred presence during Isua times would deserve further inquiry.

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