Chapter 6.1

THE BIOLOGICAL SULFUR CYCLE

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INTRODUCTION

Sulfur can exist in a number of valence states between +6 and −2. In the natural environment, the most abundant forms of sulfur have valencies of +6 (sulfates, sulfate esters), 0 (elemental sulfur) and −2 (sulfides, reduced organic sulfur) but sulfur dioxide and sulfites (+4) and polysulfur compounds with mixed valence states (e.g. thiosulfate, polythionates) are produced transiently.

About 90% of crustal sulfur occurs in the forms of minerals in deep oceanic and sedimentary rocks, the remainder being largely accounted for as oceanic sulfate (Table 6.1.1). The element undergoes continuous cycling between reservoirs (Holser and Kaplan, 1966; Chapter 6.4) and, within this broad geochemical frame-work, a well-defined biological oxidation-reduction cycle has become established (Goldhaber and Kaplan, 1974; Fig. 6.1.1), which may have had its origins during the early stages of biological evolution (Peck, 1966).

Since sulfur, in the form of cysteine, methionine and other organic molecules (Freney, 1967), is an essential component of living matter, all organisms play a role in the biological sulfur cycle, but certain classes of bacteria transform large amounts of sulfur in energy-yielding reactions. The major types of sulfur metabolism, and the associated organisms, are shown in Table

6.1.2 and have been the subjects for several reviews (e.g. Trudinger, 1969; Kelly, 1972) and a major Symposium (Van Egeraat and Huntjens, 1975).

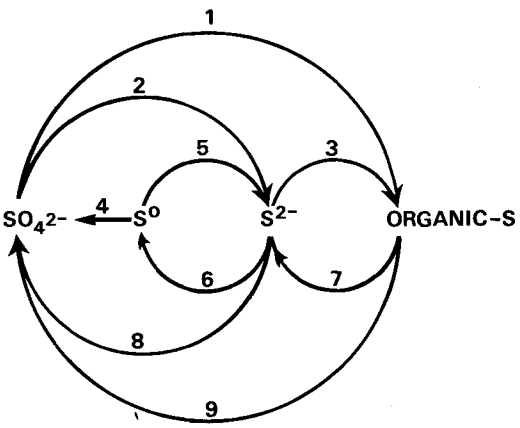

Fig. 6.1.1. Biological cycling of major sulfur pools. (Number explained in Table 6.1.2.)

TABLE 6.1.1

Estimated sulfur reservoirs (After Holser and Kaplan, 1966, Ref. 1, and Ericksson, 1963, Ref. 2.)

Ref.	Reservoir	Tg × 10^{-6} S
1	Deep oceanic rocks	
	Sediments	75 ± 20
	Mafic rocks	2300 ± 800
	Sedimentary rocks	
	Sandstone	250 ± 60
	Shale	2000 ± 580
	Limestone	380 ± 110
	Evaporites	5100 ± 1600
	Volcanics	50 ± 18
	Connate water	27 ± 5
	Total sediments	7800 ± 1700
	Freshwater	0.003 ± 0.002
	Ice	0.006 ± 0.002
	Atmosphere	3.6 ±
	Sea	1280 ± 55
2	Organic reservoir	
	Land plants	0.6 × 10^{-3}
	Marine plants	0.024 × 10^{-3}
	Dead organic matter	5.0 × 10^{-3}
	Total organic	5.62 × 10^{-3}

TABLE 6.1.2

Major classes of organisms involved in cycling of sulfur

Organism	Reactions [a]	Habitat	Remarks
Dissimilatory reducers [b]			
Desulfovibrio, Desulfotomaculum	2	Water-logged soils; anoxic waters and sediments (marine or fresh water).	Strict anaerobes; sulfur metabolism linked to energy production; *Dm. nigrificans* thermophilic.
Desulfuromonas	5	Anaerobic, H_2S-containing waters and muds of marine or estuarine environments	Strict anaerobes; sulfur metabolism linked to energy production.
Assimilatory reducers			
Bacteria, fungi, algae, plants	1, 3	Ubiquitous.	Aerobic or anaerobic; sulfur metabolised for synthesis of cellular constituents.
Chemolithotrophs [b]			
Thiobacillus, Beggiatoa	4, 6, 8	Wide variety of soils and H_2S-containing marine and fresh water environments.	Mainly strict aerobes — some utilize NO_3^{2-} anaerobically; autotrophic, facultatively autotrophic or mixotrophic deriving energy from sulfur oxidation; autotrophic status of *Beggiatoa* uncertain.
Photolithotrophs [b]			
Chlorobium, Chromatium	4, 6, 8	H_2S-containing muds and stagnant waters exposed to light; sulfur springs.	Photosynthetic, strict anaerobes; sulfur metabolism linked to energy fixation.
Heterotrophic microorganisms			
	7, 9 (some involved in 4, 6, 8).	Ubiquitous.	Reaction 7 may take place anaerobically; overall conversion to SO_4^{2-} aerobic.

[a] Numbers refer to stages in Fig. 6.1.1.

[b] Representative organisms only — for comprehensive listing of specialized sulfur microorganisms see Buchanan and Gibbons (1974).

ASSIMILATION OF SULFUR

The most important metabolic reaction is the assimilation of sulfur into organic forms which ultimately require the reduction of oxidized sulfur to the oxidation level of sulfide. This reduction is effected by the majority of microorganisms (bacteria, algae, fungi) and plants and, because of its abundance, sulfate is the dominant precursor of reduced sulfur. Pathways of assimilatory sulfate reduction are discussed briefly in Chapter 6.2 and depicted in Fig. 6.2.1 (p. 317).

Animals represent an extension of the assimilatory chain in that, although unable to reduce sulfate, they utilize preformed sulfur amino-acids synthesised by plants and other organisms.

The consequences of assimilation of sulfur in terms of mineral cycling are hard to assess. Although only a small fraction of crustal sulfur is at any time present in organic form (Table 6.1.1) its turnover, in a geological sense, is extremely rapid. Fresh organic matter commonly has a C : S ratio of about 50 : 1. Current estimates of global primary organic matter production are in the order of 150 PgC y^{-1} (Riley, 1944) which would require the annual assimilation of 1—2 Pg of sulfur. In terms of elemental sulfur, this is equivalent to the annual deposition of an 0.2 mm layer over the entire land and ocean surface of the earth. There is experimental evidence that organic sulfur may be a potential source of sulfur for sulfide mineralization (Weil, 1955, 1958; Weil et al., 1954; Lambert, 1973), but it is probable that most assimilated sulfur is rapidly reoxidized to sulfate.

DISSIMILATORY SULFATE REDUCTION

Of more immediate geochemical relevance is the *dissimilatory* reduction of sulfate to hydrogen sulfide which is a major topic for discussion in Chapter 6.2. Sometimes called "sulfate respiration" the process involves oxidation of organic matter (or hydrogen) with the transfer of electrons to sulfate instead of oxygen as in the majority of respiratory systems. The process is accompanied by a net release of free energy which is utilized by the organism for growth (e.g. eqn (1), Wake et al., 1977).

$$2 \text{ lactate} + SO_4^{2-} \rightarrow 2 \text{ acetate} + 2\ H_2O + 2\ CO_2 + S^{2-} (\Delta G' = 88 \text{ kJ}) \qquad (1)$$

Dissimilatory sulfate reduction is a rare metabolic process which is carried out by a few bacterial species belonging to the genera *Desulfovibrio*, *Desulfotomaculum* and the newly-described *Desulfomonas*. The bacteria, however, are widely distributed in the natural environment and they are probably responsible for most of the H_2S formation on earth at temperatures below about 100°C. Their activities have been detected under environmental conditions of Eh, +350 to —500 mV; pH, 4.2 to 10.4; pressure, 0.1 to 100

MPa; temperature, 0 t0 104°C and salinity <1% to saturated NaCl (ZoBell, 1958), although conditions for optimal activity are considerably more restricted (Trudinger et al., 1972).

A major constraint is an absolute requirement for anoxic conditions and the organisms are particularly active in sediments, aqueous basins and water-logged soils where restricted water movement and oxidation of organic matter by aerobic organisms has led to a depletion of oxygen. Nevertheless, bacterial sulfate reduction may occur in oxidized sediments due to the presence of reduced microniches (Jørgensen, 1977a).

Laboratory studies on dissimilatory sulfate-reducing bacteria indicate that only lactate, pyruvate and a few other simple organic molecules are capable of serving as energy-yielding substrates (Postgate, 1959; Skyring et al., 1977). Cappenberg (1974) reported that β-fluorolactate inhibited H_2S production in bottom deposits of Lake Vechten and caused the accumulation of lactate. This suggests that lactate was the main organic substrate during sulfate reduction in the muds. These results imply that complex organic matter produced by living organisms must first be degraded by fermentative and other processes before being available for the reduction of sulfate. This notion is supported by experiments of Sorokin (1962) indicating that the absence of sulfate reduction in the sub-surface layers of Black Sea sediments was due to the absence or "depression" of saprophytic organisms. Nedwell and Floodgate (1972a) noted a correlation between increased sulfate reduction activity and increased numbers of heterotrophic bacteria during summer in the 19—20 cm sub-surface layer of sediments near Menai Bridge, Anglesey.

The possibility of hydrocarbon utilization by sulfate-reducing bacteria is of interest in view of the association of H_2S and sulfate-reduction with petroliferous environments (see Chapters 6.2 and 6.4). Such utilization has been reported on a number of occasions (Tausson and Alishima, 1932; Tausson and Veselov, 1934; Novelli and ZoBell, 1944; Rosenfeld, 1947; ZoBell, 1950) but many of the results have been criticized by Postgate (1959) on the grounds that authentic pure cultures were not used and the purity of reagents was not specified. These criticisms may not apply to the experiments of Davis and Yarbrough (1966) who demonstrated the formation of radioactive carbon dioxide from ^{14}C-labelled methane, ethane and n-octadecane in cultures of *Desulfovibrio desulfuricans*. The oxidations, however, took place to only a small extent (less than 0.002% in 22 days) and required the presence of additional organic matter (lactate). Recently, Wade et al. (1977) concluded, on thermodynamic grounds, that only short-chain alkynes are potential hydrocarbon substrates for sulfate-reducing bacteria. On present evidence, therefore, crude oils appear unlikely to be primary organic sources for bacterial sulfate reduction, but may possibly be utilized after partial degradation by other hydrocarbon-degrading organisms.

Most dissimilatory sulfate-reducing bacteria appear incapable of oxidizing

organic matter beyond the level of acetate. Recently, however, Widdel and Pfennig (1977) isolated an organism, *Desulfotomaculum acetoxidans*, from anaerobic fresh and seawater muds which couples sulfate reduction to the oxidation of acetate to CO_2 and water. In some situations, therefore, sulfate may be the terminal electron acceptor for the complete oxidation of organic matter.

OXIDATION OF REDUCED SULFUR

While some reduced sulfur, either of biogenic or non-biogenic origin, may accumulate in the environment as metal sulfides and elemental sulfur, or be incorporated into fossil organic matter, most is eventually oxidized to sulfate, a process in which microbial activities play a major role.

The mechanism of oxidation of organic sulfur in nature is somewhat problematical. Cysteine, the principal organic sulfur component of living systems, is readily hydrolysed to H_2S by a wide range of heterotrophic microorganisms and it is often assumed that this reaction, followed by sulfide oxidation, is a major route for mineralization of organic sulfur. Nedwell and Floodgate (1972b) reported that rates of H_2S production from organic matter in an intertidal mud flat were greater than (at 5—10°C) or comparable with (at 20—30°C) those of sulfate reduction although the extent of organic-sulfur mineralization by this route was not determined.

There is evidence, however, that in soils at least some organic sulfur is oxidized while remaining attached to the organic moiety (Freney, 1960, 1967). Volatile methylated sulfides are known products of organic sulfur degradation (Challenger, 1951; Freney, 1967) and have been proposed as components of the global sulfur cycle (Lovelock et al., 1972). Organisms utilizing methyl sulfides as sole sources of energy have recently been described (Sivelä and Sundman, 1975). The quantitative significance of the latter processes, however, has yet to be evaluated and at the present time most of our information relates to the oxidative transformations of *inorganic* sulfur compounds.

Two classes of bacteria are specially adapted for sulfur oxidation (Table 6.1.2): *Chemolithotrophic sulfur bacteria* which utilize the energy released during oxidation by oxygen for fixation of CO_2 into organic matter (e.g. eqn (2))

$$CO_2 + H_2S + O_2 + H_2O \rightarrow [CH_2O] + SO_4^{2-} + 2\,H^+ \qquad (2)$$

and *Photolithotrophic sulfur bacteria* which carry out photosynthetic carbon fixation using sulfide (and other sulfur compounds) as an "oxidant sink" (e.g. eqns (3) and (4)).

$$CO_2 + 2\,H_2S \xrightarrow{\text{light}} [CH_2O] + H_2O + S^0 \qquad (3)$$

$$2\,CO_2 + H_2S + 2\,H_2O \xrightarrow{\text{light}} 2[CH_2O] + SO_4^{2-} + 2\,H^+ \quad (4)$$

Typical chemolithotrophic bacteria are the thiobacilli (Vishniac and Santer, 1957; Trudinger, 1967). Many of these are strict autotrophs but facultative autotrophs and mixotrophic species have been described (e.g. Trudinger, 1969; Rittenberg, 1969).

As a genus, the thiobacilli occupy a range of ecological niches. *Thiobacillus thioparus* and *Thiobacillus neapolitanus*, for example, grow best under neutral to mildly alkaline conditions while *Thiobacillus thiooxidans* is acidophilic with an optimum pH close to 2. Some thiobacilli (e.g. *Thiobacillus denitrificans*) can utilize nitrate and an alternative electron acceptor and can, therefore, function under anaerobic conditions. In general, the thiobacilli oxidize most reduced forms of inorganic sulfur including sulfides, elemental sulfur, thiosulfate and polythionates: *Thiobacillus ferroxidans* can also grow at the expense of the oxidation of ferrous iron under acidic conditions. These properties equip the organisms for activities of considerable geochemical and economic importance which are discussed in detail in Chapter 6.3.

The thiobacilli are generally restricted to temperatures below about 50°C. The geothermal habitats where temperatures may reach 95°C a new genus of sulfur-oxidizing bacteria, *Sulfolobus*, has recently been reported (Brock et al., 1972; Fliermans and Brock, 1972; de Rosa et al., 1975; Bohlool, 1975) members of which have an optimum growth temperature of 70–75°C and may remain active at 85°C. They are acidophilic (pH optimum 2–3) and according to Mosser et al. (1973) may be responsible for the generation of sulfuric acid in solfataras. In the Yellowstone National Park solfataras, Moose Pool and Sulfur Caldron, Mosser et al. recorded oxidation rates of 67 and 190 g $S^0\ m^{-2}\ d^{-1}$, respectively, which appeared to be entirely under biological control.

Two principal groups of photolithotrophic sulfur organisms are the green and the purple bacteria (Pfennig, 1977) exemplified by *Chlorobium* and *Chromatium*, respectively. They are obligate anaerobes and, therefore, occupy a relatively restricted niche in the natural environment. In meromictic lakes, for example, were sulfate is reduced in the bottom waters and sediments, photosynthetic bacteria may be sharply stratified at the H_2S-O_2 boundary the depth of which is determined by the light gradient (Kuznetsov, 1959; Sorokin, 1970a).

A geochemically significant property of the photolithotrophic sulfur bacteria is the production of sulfur from sulfide when the latter is in excess (van Neil, 1932). Sulfur may accumulate extracellulary, as is the case with *Chlorobium*, or as intracellular globules (in *Chromatium*) and subsequently is oxidized to sulfate when the supply of sulfide becomes limited.

Although the association of lithotrophic bacteria and sulfur oxidation is

clear-cut there is growing evidence that a good deal of the oxidative transformations of inorganic sulfur compounds in the natural environment may be brought about by heterotrophic microorganisms for which the physiological function of sulfur metabolism has yet to be defined. Tuttle and Jannasch (1972) reported that "typical" thiobacilli are rare in the marine environment while Caldwell et al. (1975) described enrichment of fluorescent pseudomonds in thiosulfate-media inoculated with decomposing plant material from a sub-tropical sulfur spring. Vitolins and Swaby (1969), in an analysis of Australian soils, detected relatively few thiobacilli but large numbers of sulfur- and thiosulfate-oxidizing heterotrophs which, they concluded, were mainly responsible for sulfur oxidation in such soils. Recently, Jørgensen (1977) reported high population densities (av. 5—20 g m^{-2} over a period of 1 year) of the colourless sulfur bacteria, *Beggiatoa* spp., in the sediments of the brackish fjord, Limfjorden, Denmark. He suggested that these heterotrophs may play a significant role in sulfur cycling in the sediments. The roles of the various classes of colourless and photosynthetic sulfur bacteria in the sulfur cycle have recently been discussed by Kuenen (1975) and Pfennig (1975).

In laboratory systems, sulfur-oxidizing bacteria often produce thiosulfate and polythionates from sulfide and elemental sulfur (Trudinger, 1967; Kelly, 1968) but the extent to which these reactions take place in the natural environment is uncertain. Although significant concentrations of thiosulfate have been detected in natural waters such as the Black Sea (Sorokin, 1962; Tuttle and Jannasch, 1973) and meromictic freshwater lakes (Sorokin, 1970a), much of this may arise by chemical oxidation of H_2S (Cline and Richards, 1969; Chen and Morris, 1972; Avrahami and Golding, 1968) and it has been suggested (Sorokin, 1970b, c; 1964a) that the main function of bacteria in these environments is to oxidize the products of chemical sulfide oxidation to sulfate.Whatever its origin, thiosulfate may reach concentrations in natural waters comparable with those of sulfide (Sorokin, 1970a, b). Little attention has been given, however, to possible geochemical reactions involving thiosulfate although a possible role in pyrite formation has been suggested (Volkov and Ostroumov, 1957).

SULFURETA

Baas Becking (1925) introduced the term "sulfuretum" to describe an ecological community of sulfate-reducing and sulfur-oxidizing organisms. Simple sulfureta may be constructed by mixing pure cultures of *Desulfovibrio* spp. with photosynthetic sulfur bacteria (*Chromatium* spp. or *Chlorobium* spp.) and providing a suitable source of carbon and electrons for the sulfate reducer (Butlin and Postgate, 1954; Gemerden, 1967). Reoxidation of sulfide produced by the reduction of sulfate supports the

growth of the photoautotroph and organic matter synthesized by the latter organism may provide additional oxidizable carbon for the sulfate-reducer. Matheron and Baulaigue (1976) recently described a stable mixed culture of *D. desulfuricans*, *Chlorobium* sp. and the non-sulfur heterotroph, *Escherichia coli*. The mixture utilized glucose and the biochemical sequence may be formulated as follows:

E. coli

$$2 \text{ glucose} + H_2O \rightarrow 2 \text{ lactate} + \text{acetate} + \text{ethanol} + 2\ CO_2 + 2\ H_2$$

D. desulfuricans

$$2 \text{ lactate} + \text{sulfate} \rightarrow 2 \text{ acetate} + \text{sulfide} + 2\ CO_2 + 2\ H_2O$$

$$\text{ethanol} + 0.5 \text{ sulfate} \rightarrow \text{acetate} + 0.5 \text{ sulfide} + H_2O$$

$$2\ H_2 + 0.5 \text{ sulfate} \rightarrow 0.5 \text{ sulfide} + 2\ H_2O$$

Chlorobium

$$2 \text{ sulfide} + 4\ CO_2 + 4\ H_2O + n \text{ acetate} \rightarrow 4 + n[CH_2O] + 2 \text{ sulfate}$$

Since glucose and other fermentable compounds are products of photosynthesis, this system probably represents an approximation to the reality of the natural environment.

A "natural' mixed population, or consortium, "*Chloropseudomonas ethylica*", was isolated from H_2S-containing stagnant waters (Shaposhnikov et al., 1960) and originally classified as a novel photosynthetic sulfur autotroph. It later proved to be a syntrophic mixture of *Chlorobium limicola* and an heterotrophic H_2S-producing bacterium (Gray et al., 1973). A similar situation may apply to two other "natural" mixed populations, *Chlorochromatium* and *Pelochromatium* (Pfennig, 1975). Both represent an association of photosynthetic organisms (*Chlorobium*) with, as yet uncharacterized, colourless bacteria. Mixed populations of the type described often grow at faster rates than the individual organisms in isolation and their viability may be maintained for extended periods of time without subculturing (Pfennig, 1975). This suggests that each organism provides factors, nutritional or otherwise, which favour the development and survival of its companion, a fact which could have important ecological implications.

Further examination of "*Chloropseudomonas*" (Pfennig and Biebl, 1976) revealed an interesting variation of the sulfuretum. A new organism, designated *Desulfuromonas acetoxidans*, which reduces sulfur at the expense of acetate, ethanol or propanol, was isolated from "*Chloropseudomonas*" cultures and from an anaerobic, sulfide-containing marine mud: more oxidized forms of sulfur were not metabolized. Together with photosynthetic green sulfur bacteria, *Desulfuromonas* forms a syntrophic mixture in which sulfur is continually recycled between sulfide and its

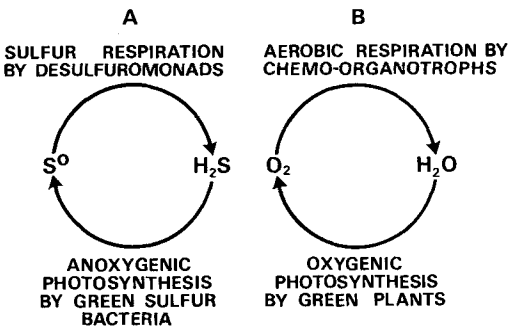

Fig. 6.1.2. Comparison of elemental sulfur-linked and oxygen-linked respiratory-photosynthetic cycles.

elemental form (Fig. 6.1.2A). This property is also shared by the newly described spirillum 5175 which reduces sulfur, sulfite and thiosulfate, but not sulfate, at the expense of oxidation of formate or hydrogen (Wolfe and Pfennig, 1977). It may also apply to strains of sulfate-reducing bacteria which have the ability to reduce elemental sulfur (Biebl and Pfennig, 1977). Pfennig and Biebl (1976) recognized the analogy between the cycle shown in Fig. 6.1.2A and that of planetary oxygen cycle (Fig. 6.1.2B) and one may speculate whether the former not only plays a role in the cycling of sulfur in present-day anaerobic environments but may be representative of a primitive stage in the evolution of the sulfur cycle and photosynthesis during the early anoxic period of earth's history. This speculation perhaps takes on added significance in view of the current concept that photosynthetic bacteria were the evolutionary precursors of oxygen-evolving cyanophytes (blue-green algae *) (Klein and Cronquist, 1967; Margulis, 1970) and of the recent discovery that the cyanophyte, *Oscillatoria limnetica*, can carry out both oxygenic photosynthesis and anaerobic bacterial-type photosynthesis linked to H_2S oxidation (Cohen et al., 1975a, b).

In the natural environment, large scale, and more complex sulfureta develop wherever sulfate reduction has become established (Fenchel and Riedl, 1970; Caldwell and Tiedje, 1975; Fenchel and Jørgensen, 1977). Numerous terrestrial, freshwater and marine examples have been reported in the literature but rarely has an attempt been made to analyse a single environment in terms of the biota and the chemical and biochemical processes associated with both the reductive and oxidative aspects of the sulfur cycle. One notable exception is the Black Sea where the work of Sorokin (1962, 1964b, 1970b) and Jannasch and his colleagues (Tuttle and Jannasch, 1973;

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* See footnote on p. 12.

Sen Gupta and Jannasch, 1973; Jannasch et al., 1974) has revealed a semi-quantitative picture of the interrelationships of the sulfur, nitrogen and carbon (both photosynthetic and chemosynthetic) cycles and provided a preliminary description of the types or organisms involved.

Inevitably, however, analyses of complex natural environments are subject to considerable fluctuations and uncertainties and a large mass of data must be assembled over a long period of time before a statistically realistic model can be advanced. Jørgensen and Fenchel (1974) attempted to circumvent some of the problems associated with the natural environment by studying the kinetics of the sulfur cycle in an experimental system designed to resemble a natural, reduced, shallow sea-water sediment. The "sediment", consisting of sand mixed with chopped *Zostera marina* (eel grass) leaves, was deposited under circulating sea-water at 22°C and illuminated for 8 h d^{-1} for seven months. Rates of sulfate reduction obtained by direct measurements on core material with ^{35}S-sulfate were comparable with those reported for marine sediments (see p. 304) indicating that the system was reasonably analogous to a natural environment. In the early stages of the experiment, there was a successive development of chemolithotrophic sulfur bacteria (*Beggiatoa*) and purple sulfur bacteria (*Chromatium*) as had earlier been observed by Fenchel (1969) in artificial sulfureta. A significant finding of Jørgensen and Fenchel (1974) and Jørgensen (1977c) was that sulfate reduction can account for the oxidation of more than half the organic matter degraded in marine sediments. This indicates the potential importance of the sulfur cycle in the overall biochemical ecology of sediments.

Another experimental approach to the study of sulfureta in sediments was devised by Hallberg et al. (1976). Closed plexiglass boxes (Schippel et al., 1973) equipped with sampling ports and electrodes for continuous measurement of pH, Eh and sulfide-ion activity are anchored in soft bottom sediments, and physical, chemical and biological characteristics of the sediment-water system monitored over a period of time. In a 9-month experiment on Baltic Sea sediments, sulfate reduction proceeded rapidly in the early stages followed by sulfide reoxidation due to the development of the photosynthetic sulfur bacteria *Chromatium* and *Chlorobium*.

KINETICS OF BIOLOGICAL SULFUR CYCLING

Table 6.1.3 lists some rates of hydrogen sulfide production determined on ground waters and surface muds of sediments. The values range over about five orders of magnitude but, in general, the highest rates are found in saline sediments which may reflect, in part, the greater availability of nutrients in these environments compared with ground waters and freshwater sediments. Indeed, vigorous sulfate reduction is often a consequence of pollution of natural waters (e.g. Koyama et al., 1965).

TABLE 6.1.3

Rates of sulfate reduction in ground waters and surface muds of sediments [a]

	SO_4^{2-} content (mmol l^{-1})	Rate (μmol H_2S l^{-1} d^{-1})	Ref.
Ground waters (U.S.S.R.)			
Shor-su S deposit	0.7— 7.3	0.3— 5.3	1
Gaurdak S deposit	9.6—12.2	1.1— 14.3	1
Cis-Carpathian S deposits	1.2—10.2	0.3—112	1
Kosha-Naur oil fields	Flooded with sea water	2.9—58.8	1
Freshwater sediments (U.S.S.R.)			
Lake Beloe	0.5—2.1	$6—18 \times 10^{-3}$	1
Rybinski reservoir	0.4—6.2	2×10^{-2}—2.7	1
Gor'kii reservoir	0.3—1.4	1.2—86.5	1
Kiubyshev reservoir	1.1—5.3	3.3—89.4	1
Lake Belovod	4.5—6.5	2.0— 3.6	1
Lake Belovod	—	ca. 4.4	2
Lake Gel Gel	0.2—5.6	0.9—134	2
Lake Sakavo	7.7	22—140	3
Lake Chernyi Kichiyer	1.1	416	3
Lake Bol'shoy Kichiyer	0.45	193	3
Lake Konon'yer	0.4	123—163	3
Lake Kuznechikha	0.4	13—114	3
Lake Pomaretskoe	3.3	900	4
Saline sediments			
Lake Solenoe	up to 43.8	11—600	1
Lake Mogil'noe	27.1	29	1
Barents Sea littoral zone	up to 28.1	267—714	1
Krasnovodsk Bay	up to 22.9	114—247	1
Black Sea	up to 22.9	0.8— 72	5
Lake Veisovoe	31	86—600	6
Repnoe Lake		488	7
Lizard Island (Coral island)	30.1	40—100	8
Aarhus Bay	—	439—1013	9
Anglesey — intertidal and flat	—	178—2000	10
Experimental sedimentary systems			
Sea water sediment from Branford Bay, Connecticut	[b]	16 [c]	11
Baltic Sea sediment	[b]	32 [c]	12
Sand-eelgrass	[b]	82—95	13

References: 1 = Ivanov, 1968; 2 = Sorokin, 1970a; 3 = Chebotarev et al., 1975; Matrosov et al., 1975; 4 = Gorlenko et al., 1974b; 5 = Sorokin, 1962; 6 = Chebotarev et al., 1974; 7 = Chebotarev et al., 1973; 8 = Skyring and Chambers, 1976; 9 = Jørgensen, 1978); 10 = Nedwell and Floodgate, 1972a; 11 = Nakai and Jensen, 1964; 12 = Hallberg et al., 1976; 13 = Jørgensen and Fenchel, 1974.

[a] Where necessary, 1 kg of sediment has been taken as 1 litre.

[b] Sulfate concentration of sea water decreasing during experiment.

[c] Initial apparently zero-order rate.

Note: The values in this Table were determined by direct measurements of sulfate reduction (usually of $^{35}SO_4^{2-}$). Other rates, calculated on the basis of sedimentation and diffusion models, may be found in Berner (1972) and Goldhaber and Kaplan (1975).

A major parameter leading to variability of sulfate reduction is the supply of utilizable organic matter (Sorokin, 1962; Ivanov, 1968; Berner, 1970; Ramm and Bella, 1974), and deposition of particulate organic matter at the sediment-water interface probably accounts to a large extent for the fact that, even in anoxic basins, the rates of reduction in surface muds may be several orders of magnitude greater than in the overlying waters (Chebotarev et al., 1974; Matrosov et al., 1975; Sorokin, 1962). Sweeney (1972) noted a general correlation between the organic carbon and pyrite contents of recent marine sediments while Goldhaber and Kaplan (1975) demonstrated a positive relationship between rates of sulfate reduction and sedimentation which accords with the trend towards higher organic carbon contents of rapidly depositing sediments (Berner, 1972).

Bacterial sulfate reduction appears to proceed to considerable depths in marine sediments but rates computed from changes in interstitial water sulfate concentrations, with suitable corrections for diffusion and sedimentation, are generally orders of magnitude below those in surface muds (Goldhaber and Kaplan, 1975). Again, this probably reflects a depletion of utilizable organic matter in the deeper layers by microbial utilization and conversion to more intractable humates and kerogens.

The variability of reduction rates reported in Table 6.1.3 is probably not due solely to differences in organic matter availability, but the nature of other controlling factors cannot be readily assessed. While Postgate (1951) reported that the rate of sulfate reduction by *D. desulfuricans* was independent of sulfate concentration above 1 mM, the results of Nakai and Jensen (1964) and Hallberg et al. (1976) suggest deviation from zero-order kinetics below about 2—3 mM sulfate in experimental sedimentary systems. Nevertheless, it is unlikely that sulfate limitation is a major kinetic barrier in the natural sulfur cycle except perhaps in some ground waters and freshwater sediments. Further speculation on the reasons for variable sulfate reduction rates in these complex systems is, however, not warranted at this stage.

It should be emphasised that most of the data in Table 6.1.3 are point measurements which are not necessarily representative of the overall rates of sulfate reduction in a particular environment. Nevertheless, Trudinger et al. (1972) and Rickard (1973) considered that the average rates in the Black Sea and other sediments may be "typical" of euxinic environments and concluded that they were of sufficient magnitude to account for synsedimentary sulfide ore deposition (see also, Temple, 1964).

Since, at the present time, there is no general large-scale accumulation of reduced sulfur in sediments and soils, the combined rates of biological and chemical oxidation of sulfide can be assumed to be in the same order as those of sulfate reduction. Unfortunately, the few recorded rates of sulfide oxidation in the environment are not directly comparable with those of sulfate reduction. Aside from difficulties posed by the experimental

methods, in most cases considerable time intervals elapsed between analyses of the two reactions. Sorokin (1970a), reported rates of up to 10 μmol l^{-1} d^{-1} for ^{35}S-labelled sulfide oxidation in the freshwater, meromictic Lake Belovod: in the most active zone, chemical, chemosynthetic and photosynthetic oxidations each accounted for about one third of the overall rate. Similar overall oxidation rates were observed in Lake Gel Gel. In the Black Sea rates of up to 16 μmol S^{2-} m^{-2} d^{-1} have been recorded in the oxic-anoxic transition zone of the water column (Sorokin, 1970b). Extremely high rates (about 15 mmol l^{-1} d^{-1}) for photosynthetic sulfide oxidation were recorded by Blackburn et al. (1975) in the upper 3 mm of sediment from an organic-rich, sandy marine area in Denmark under laboratory conditions and artificial light.

An indirect assessment of photosynthetic sulfide oxidation in Lake Repnoe, U.S.S.R., was made by Chebotarev et al. (1975). Using data from Gorlenko et al. (1974a) on CO_2 fixation by phototrophic bacteria, they calculated H_2S oxidation according to eqn (3), on the assumption that sulfur, not sulfate, was the oxidation product. The calculated rate of 22 mmol m^{-2} d^{-1} was considerably higher than that found in the Black Sea (see above) but agreed well with the rate of sulfate reduction (25 mmol m^{-2} d^{-1}) measured in the sediment plus water column in the same area of the lake.

Jørgensen and his colleagues have made assessments of sulfur fluxes in sediments based on analyses of rates of sulfate reduction and the concentrations of reduced and oxidized sulfur compounds. Jørgensen and Cohen (1977) examined in the littoral sediments of Solar Lake on the Sinai coast of the Gulf of Elat. The sediments consist of stromatolitic cyanophytic mats up to 1 m in depth (Cohen et al., 1977a, b, c; Krumbein et al., 1977) which appear to supply the organic substrate for sulfate reduction. The most active zone was the upper 10 cm, corresponding to the first 10–20 years of the life of the mat. Rates of sulfate reduction in this zone were in the order of 67 mmol S m^{-2} d^{-1} and accounted for well over 90% of the total reduction of sulfate by the sediment: only 0.15% of H_2S produced was fixed in the sediments the remainder, presumably, being reoxidized at the sediment surface. Below 20 cm, rates of sulfate reduction fell to 10–50 μmol S m^{-2} d^{-1} with most of the H_2S being trapped within the sediment as iron sulfides.

A similar study to the one just described was undertaken by Jørgensen (1977c) on the coastal marine sediments of Limfjorden, Denmark. Sulfate reduction (on average 9.5 mmol m^{-2} d^{-1}) was largely confined to the upper 20 cm of sediment and over 90% of the H_2S produced appeared to be reoxidized at the sediment-water interface: only about 7% of H_2S was converted to iron sulfides. The development of the sulfur cycle in sediments has been described by Jørgensen and Fenchel (1974) using the experimental system described earlier (see p. 303). The results, illustrated in Fig. 6.1.3, showed that the rate of sulfate reduction remained almost constant over the period studied and was accompanied by increasing pools of H_2S, FeS and S^0

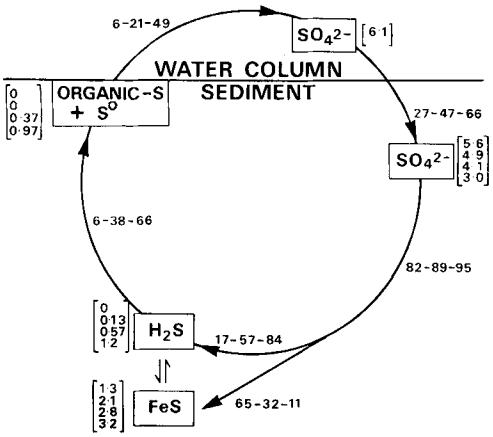

Fig. 6.1.3. Evolution of the sulfuretum in a model sediment (modified and redrawn from Jørgensen and Fenchel, 1974). Figures in brackets are the mean pool sizes in μmol cm^{-3} on days 7, 19, 41 and 76 of the experiment. Other figures are the mean fluxes in μmol cm^{-3} d^{-1} between these days.

(+ organic-S) and rates of oxidative processes. Although it is a reasonable assumption that the deficit between H_2S produced by sulfate reduction and sulfide trapped in sediments represents reoxidation, this may not necessarily take place in situ: a variable amount of H_2S may escape to the atmosphere to be oxidised elsewhere. Hansen et al. (1978) demonstrated H_2S-emission from two shallow coastal areas in Denmark averaging 1.5 and 38 mmol m^{-2} d^{-1}. The emissions took place largely at night when photosynthetic sulfide oxidation was suppressed, and represented a significant proportion of H_2S produced by sulfate reduction: possible contributions from organic sulfur and reduction of elemental sulfur were, however, not determined. Nriagu and Coker (1976) estimated that the emission of sulfur from Lake Ontario sediments (1.3 mmol m^{-2} y^{-1}) was only about 1% of the annual input of sulfur. The loss was, however, sufficient to cause marked enrichment in ^{34}S in the sulfur which remained fixed in sediments. (For a discussion of isotope effects, see Chapter 6.2.)

Realistic fluxes of sulfur (or indeed any element) in the natural environment are difficult to obtain. The environment itself is inhomogeneous and the biochemical systems complex, and there are major problems associated with the extrapolation of point measurements of limited duration to a regional, long-term scale. Nevertheless, the recent studies in the field are giving at least a semiquantitative picture of some of the biogeochemical reactions of sulfur which have important implications in the mineral formation and dissolution (see Chapters 6.2–6.4).

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Note added in proof

Since this chapter was prepared, six new genera of strictly anaerobic sulfate-reducing bacteria have been identified. They include coccoidal, rod-shaped and filamentous organisms, chemolithotrophs which grow on CO_2, H_2 and sulfate, and organisms capable of completely oxidizing higher fatty acids (N. Pfennig, 1979, personal communication).