The Global Biogeochemical Sulphur Cycle
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CHAPTER 1
Principal Reactions of the Global Biogeochemical Cycle of Sulphur

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1.1 INTRODUCTION

The element sulphur with atomic number 16 and atomic mass 32.06 is in group VI of Mendeleev's periodic system. Terrestrial sulphur is a mixture of four stable isotopes with mass numbers 32, 33, 34, and 36 occurring in the proportions of 95.02, 0.75, 4.21, and 0.02% respectively. It occurs in the earth's crust to the extent of 0.047% and is widely distributed in nature in free and combined forms; it can be found in a range of valence states from the highly reduced sulphide (−2) to the oxidized form in sulphate (+6). The most abundant forms of sulphur are sulphate, sulphide, polysulphide, and elemental sulphur.

1.2 LOW-TEMPERATURE CHEMICAL REACTIONS OF THE GLOBAL SULPHUR CYCLE

The global biogeochemical cycle is a complex network of chemical and biochemical reactions in which sulphur participates in various forms with different physicochemical properties and aggregation states.

Of the gaseous forms of sulphur involved in this cycle the most important are hydrogen sulphide, sulphur dioxide, and sulphur trioxide. These gases are formed by various natural processes and as a result of man's activity. In the atmosphere hydrogen sulphide is quickly oxidized to sulphur dioxide which can take part in numerous reactions including oxidation, hydration, and combination with ammonia to form sulphate aerosols. An intricate complex of homogeneous and heterogeneous reactions involving sulphur-containing gases occurs in the atmosphere; many of these reactions are discussed in Chapter 4.

All of the sulphurous gases are soluble in water and their aqueous solutions are endowed with pronounced acidic properties, as a consequence of which sulphur plays an important role in the cycling of other elements, particularly the metals.

Sulphur dioxide, in both gaseous and hydrated forms, is readily oxidized to sulphur trioxide in the presence of oxygen (equation 1),

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad (1)$$

or reduced to elemental sulphur in the presence of reducing agents such as hydrogen sulphide (equation 2),

$$SO_2 + 2H_2S \rightleftharpoons 3S + 2H_2O \quad (2)$$

Sulphur trioxide dissolves in water to form the chemically active sulphuric acid which, even when diluted, reacts vigorously with many metals and their oxides to produce sulphates. These reactions are of paramount importance in the processes of weathering and corrosion of metals, as well as in many technological processes. Most sulphates are fairly soluble in water and thus are widespread in nature.

Of the poorly soluble sulphates, the most important geochemically are the calcium sulphates, anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$). Oxidized sulphur is mainly removed from the cycle in one of these forms; consequently, deposits of gypsum and anhydrite are the biggest reservoirs of natural sulphur, being formed principally in the first stages of sea-water evaporation during very hot weather.

Sulphides, which form in aqueous solutions of hydrogen sulphide, have quite different chemical properties and geochemical peculiarities. As can be seen from Fig. 1.1, the zone of stability of hydrogen sulphide and bisulphide ion for all pH values is situated in the field of low partial pressures of oxygen, i.e. under anaerobic conditions. Most metal sulphides, with the exception of the alkali and alkaline earth metals, are poorly soluble in water, and thus the geochemical behaviour of both sulphur-containing compounds and many metals changes at the aerobic–anaerobic interface. When anaerobic conditions change to aerobic, sulphides are oxidized to form soluble and migratory sulphates, but when the reverse occurs, poorly soluble sulphides are formed and metals are immobilized.

The mechanisms of these geochemical reactions are rather complex, but under low-temperature conditions they become even more complicated because of the involvement of micro-organisms. Examples of such processes are given in Chapter 5 where the formation and oxidation of iron disulphide (FeS_2) is discussed. It should be noted that iron disulphide, represented in nature mainly by the mineral pyrite, is one of the most abundant compounds of sulphur and is widely used for technological purposes. Together with elemental sulphur it is one of the raw materials used for the production of sulphuric acid.

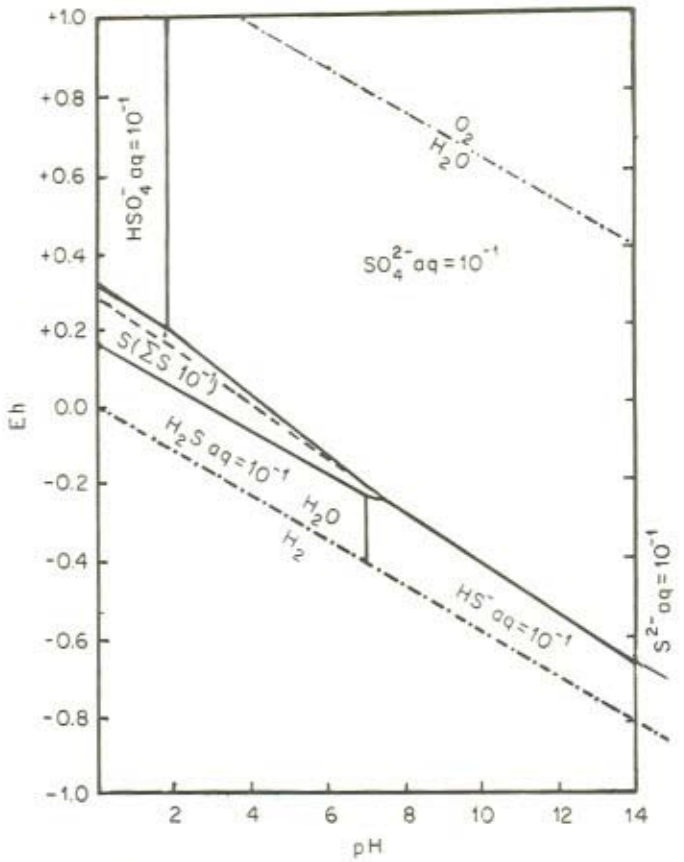

Fig. 1.1 The equilibrium distribution of sulphur species in water at 25 °C and 1 atm total pressure for activity of dissolved sulphur equal to 10^{-1}. The dashed lines indicate equal values of dissolved species within sulphur field (from Garrels and Christ, 1965)

Elemental sulphur (S^0) is the sole relatively stable natural form of sulphur with an intermediate state of oxidation. Under natural conditions it is formed mainly at the expense of hydrogen sulphide oxidation (equations 2 and 3).

$$2H_2S + O_2 \rightleftharpoons 2S + 2H_2O \qquad (3)$$

The zone of stability for sulphur (see Fig. 1.1) stretches slightly beyond the upper limit of hydrogen sulphide and bisulphide stability, which means that sulphur is unstable in the presence of oxygen. As with pyrite, micro-organisms appear to be of paramount importance for the low-temperature oxidation of elemental sulphur.

The major processes in the biogeochemical cycle of sulphur which have

been reported in this book take place in the upper horizons of the earth's crust under normal conditions of temperature and pressure. Therefore in this chapter we shall confine ourselves mainly to a brief survey of the low-temperature reactions of the sulphur cycle.

1.3 HIGH-TEMPERATURE REACTIONS OF THE BIOGEOCHEMICAL CYCLE OF SULPHUR

In silicate melts sulphur may be present as sulphide and sulphate ions. Experimental studies by Katsura and Nagashima (1974) showed that the ratio of these forms in basaltic melts at 1200 °C depended on the partial pressure of oxygen: at pressures in excess of 10^{-8} atm the basic sulphur form was sulphate, while at pressures less than 10^{-8} atm sulphide was the predominant form in the melt.

It is believed that the principal reaction in high-temperature melts is the substitution of sulphur for oxygen in metal oxides (Esin and Geld, 1966; equation 4):

$$S_2(\text{gas}) + 2\text{MeO(melt)} \rightleftharpoons 2\text{MeS} + O_2 \qquad (4)$$

Major factors which control the course of this reaction are the melt composition, temperature, and partial pressures of oxygen and sulphur in the gaseous medium in equilibrium. An elevation of the partial pressure of sulphur increases its solubility, but the impact of a change in the partial pressure of oxygen is not as clear cut (Katsura and Nagashima, 1974). An increase in the FeO and Na_2O concentrations in silicate melts leads to an elevation in sulphur solubility in these melts (Nagashima and Katsura, 1973; Haughton *et al.*, 1974; Kuznetsova and Krigman, 1978).

Under conditions of rapid melt cooling, e.g. during submarine basalt eruptions, the erupted matter is rapidly crystallized and sulphur is isolated in the form of sulphide inclusions (Moore and Fabbi, 1971). However, during slow basalt cooling, in subaerial conditions, most sulphur compounds are lost in the form of sulphurous gases.

These gases form as a result of high-temperature interaction of water with the sulphides and ferrous silicates of melts (equations 5, 6, and 7):

$$FeS + H_2O \rightleftharpoons FeO + H_2S \qquad (5)$$

$$FeS + FeSiO_3 + H_2O \rightleftharpoons Fe_2SiO_4 + H_2S \qquad (6)$$

$$FeS + FeSiO_3 + 3H_2O \rightleftharpoons Fe_2SiO_4 + SO_2 + 3H_2 \qquad (7)$$

In the course of temperature and pressure variations sulphurous gases react with each other (equations 3, 8, and 9), as well as with the other magmatic gases:

$$SO_2 + 2CO \rightleftharpoons 2CO_2 + S \qquad (8)$$

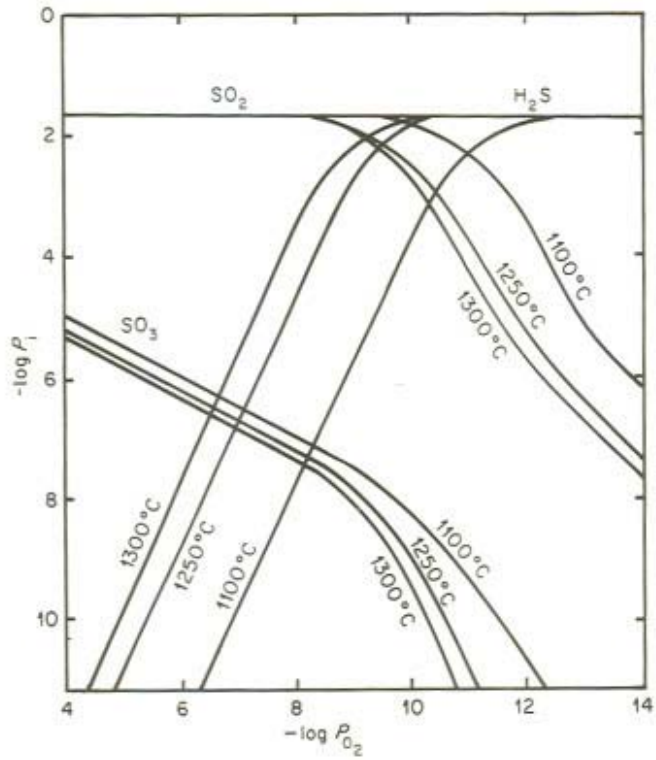

Fig. 1.2 Relationships between calculated partial pressures of SO_2, SO_3, and H_2S and calculated P_{O_2} at 2.1% $(SO_2)_i$ under various temperatures. $(SO_2)_i$ is the initial SO_2 concentration (from Katsura and Nagashima, 1974)

$$H_2S + 2H_2O \rightleftharpoons SO_2 + 3H_2 \qquad (9)$$

The calculated partial pressures of three basic components of magmatic gases (SO_2, SO_3, and H_2S) at different partial pressures of oxygen are presented in Fig. 1.2. Under real conditions the ratio of gases depends strongly on the composition of the magma (Matsuo, 1960), while the total content of sulphur compounds in magmatic gases decreases with decreasing temperature (Sokolov, 1966).

1.4 BIOLOGICAL PROCESSES FOR THE FORMATION AND DECOMPOSITION OF SULPHUR-CONTAINING ORGANIC COMPOUNDS

Sulphur is a constituent of a number of amino acids, and therefore may be referred to as one of the so-called biogenic elements whose metabolism is

inherent in all living organisms. The overwhelming majority of micro-organisms and plants utilize the process of assimilatory sulphate reduction, in which sulphate sulphur is reduced and incorporated into the sulphur-containing amino acids—cysteine, cystine, and methionine (Zinder and Brock, 1978; Krouse and McCready, 1979). Another important group of live organisms including most animals and some micro-organisms is incapable of assimilatory sulphate reduction and requires ready-made sulphur-containing amino acids for metabolism and growth. Finally, some micro-organisms not endowed with the ability of assimilatory sulphate reduction may use sulphur compounds in other states of reduction—from sulphite to sulphide ions for their metabolism (Krouse and McCready, 1979).

The involvement of mineral sulphur in the synthesis of organic compounds by micro-organisms and plants is a large-scale biogeochemical process, whose quantitative assessment is hampered by the lack of coherent information on the concentrations of the various forms of sulphur in plants and animals. However, the extent of this process may be judged from the amount of sulphur removed from soil in harvested crops. According to Kilmer's (1979) data based on the annual reports of the US Department of Agriculture, the world-wide removal of sulphur in harvested crops amounts to 2.5 TgS annually.

Part of the organic sulphur of plants is consumed by man and animals, while the remainder, after the death of vegetative tissue, is decomposed by saprophytic micro-organisms and is returned to the mineral part of the cycle in the form of sulphate under aerobic conditions, and as hydrogen sulphide under anaerobic conditions.

During decomposition the sulphur-containing amino acids, cysteine and methionine, are released and then degraded by the action of certain enzymes. Cysteine, for example, reacts with cysteine desulphhydrase and ammonia and hydrogen sulphide are released. The reaction may be represented by equation (10) (Segal and Starkey 1969):

$$\underset{\text{cysteine}}{HS{-}CH_2{-}CH(NH_2){-}COOH} + H_2O \longrightarrow \underset{\text{pyruvic acid}}{CH_3{-}CO{-}COOH} + NH_3 + H_2S \quad (10)$$

In recent years, due to the discovery of organic sulphur compounds such as methyl mercaptan (CH_3SH) and dimethyl sulphide (CH_3SCH_3) in the atmosphere, scientists became interested in the biological reactions which lead to their production in the biosphere. These compounds are produced by many bacteria, yeasts, and moulds on media containing methionine and other sulphur-containing organic compounds (Krouse and McCready, 1979):

$$\underset{\text{methionine}}{CH_3{-}S{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH} + H_2O \longrightarrow \underset{\alpha\text{-ketobutyric acid}}{CH_3{-}CH_2{-}CO{-}COOH} + NH_3 + \underset{\text{methyl mercaptan}}{CH_3SH} \quad (11)$$

In addition, certain micro-organisms, in particular the fungi *Schizophyllum commune*, have been reported to produce dimethyl sulphide and methyl mercaptan on media containing glucose with sulphate as the sole source of sulphur (Young and Maw, 1958). A more detailed analysis of the literature on the microbiological formation of volatile organic sulphur compounds may be found in the reviews of Krouse and McCready (1979) and Zinder and Brock (1978).

1.5 OXIDATION OF SULPHUR COMPOUNDS BY MICRO-ORGANISMS

The oxidation of reduced sulphur is always accompanied by the release of energy, e.g. in the oxidation of thiosulphate (equation 12; Roy and Trudinger, 1970):

$$S_2O_3^{2-} + 2O_2 + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ + 211 \text{ kcal} \quad (12)$$

Various groups of chemolithotrophic micro-organisms are capable of using this energy for synthesizing their organic constituents from carbon dioxide. Chemolithotrophic sulphur organisms have been classified into three important groups on the basis of their morphology: (1) Thiobacteriaceae, colourless coccoid, straight or curved rod-shaped bacteria; (2) Beggiatoaceae, colourless cells occurring in trichomes within which they are arranged in chains; and (3) Achromatoaceae, large spherical, ovoid or short cylindrical cells containing sulphur granules (Roy and Trudinger, 1970).

The *Beggiatoa* are filamentous organisms commonly found in marine and freshwater environments containing hydrogen sulphide. Micro-organisms of this group oxidize hydrogen sulphide to elemental sulphur which is often deposited inside the cells. When hydrogen sulphide in the media becomes unavailable, the accumulated sulphur is oxidized to sulphate and removed from the cells. The physiology of *Beggiatoa* has not been well studied and even the fact of obligatory chemolithotrophy has not been proven (Trudinger, 1979) especially as Strohl and Larkin (1978) have separated five groups of *Beggiatoa* from freshwater sediments, all of which grew heterotrophically.

In contrast to the filamentous sulphur-bacteria, numerous representatives of the *Thiobacillus* genus have been investigated in every detail (Ralph, 1979). Members of this group of bacteria which take an active part in the

oxidation of natural compounds of sulphur, differ in their response to pH and temperature and in their ability to grow when organic compounds are present in the medium. The autotrophic bacteria *Thiobacillus thioparus, T. denitrificans*, and *T. neapolitanus*, together with the closely related *T. novellus* and *T. perometablis*, grow preferentially in alkaline and slightly acidic conditions, whereas *T. thiooxidans*, *T. denitrificans*, and *T. intermedius* prefer acidic and ultra-acidic conditions. Under these acidic conditions many reduced compounds of sulphur are unstable and thus elemental sulphur and metal sulphide are usually oxidized by these organisms.

Unlike other unicellular sulphur-bacteria, the acidophilic bacteria *T. ferrooxidans* and *Sulfolobus acidocaldarians* are also capable of oxidizing ferrous iron in acidic media. The peculiarity makes *T. ferrooxidans*, in particular, one of the most important geochemical agents participating in the aerobic decomposition of sulphide ores. This ability is used in the bacterial leaching of ores to recover metals, e.g. the extraction of iron from pyrite.

The biological and chemical reactions involved in the dissolution of pyrite may be represented by the following equations (Temple and Delchamps, 1953):

$$2FeS_2 + 2H_2O + 7O_2 \rightleftharpoons 2FeSO_4 + 2H_2SO_4 \quad (13)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightleftharpoons 2Fe_2(SO_4)_3 + 2H_2O \quad (14)$$

$$Fe_2(SO_4)_3 + FeS_2 \rightleftharpoons 3FeSO_4 + 2S \quad (15)$$

$$2S + 3O_2 + 2H_2O \rightleftharpoons 2H_2SO_4 \quad (16)$$

In this process the second and fourth reactions follow the biological pathway with the participation of *T. ferrooxidans* and *T. thiooxidans*, whereas the third reaction appears to be strictly chemical; metal sulphide is oxidized by ferric ion which in turn is reduced to ferrous ion. One of the most important reactions of the whole oxidation cycle in the natural dissolution of metal sulphides or the bacterial leaching of metals is the microbial oxidation of ferrous iron to ferric iron (equation 14).

Growing at the interface between the aerobic and anaerobic zones, the *Thiobacilli* and *Beggiatoa* play an important part in the oxidation of various reduced sulphur compounds to both elemental sulphur and sulphate (Trudinger, 1979).

1.6 OXIDATION OF REDUCED SULPHUR UNDER ANAEROBIC CONDITIONS

The importance of micro-organisms in oxidative reactions of the sulphur cycle is not, however, solely confined to aerobic conditions. Two groups of micro-organisms exist which are capable of oxidizing hydrogen sulphide, ele-

mental sulphur, and other partially oxidized compounds of sulphur in the absence of free oxygen.

One group, represented by *Thiobacillus denitrificans*, are chemolithotrophic anaerobic bacteria which can oxidize reduced sulphur compounds in the absence of oxygen at the expense of nitrate which is simultaneously reduced to molecular nitrogen (equation 17):

$$5S_2O_3^{2-} + 8NO_3^- + H_2O \longrightarrow 10SO_4^{2-} + 4N_2 + 2H^+ \qquad (17)$$

The distribution and geochemical activities of *T. denitrificans* have not yet been studied in detail. Nevertheless it appears that these organisms are quite important for the oxidation of sulphur compounds in paddy soils (Baldensperger and Garcia 1975; Jacq and Roger, 1978) and in the upper horizons of marine and lacustrine reduced sediments where nitrate penetrates deeper than dissolved oxygen.

The second group of anaerobic bacteria which have the ability to oxidize reduced sulphur compounds are the photolithotrophs. Two families, Thiorhodaceae and Chlorobacteriaceae, have been recognized, with the best-known members being the purple sulphur bacteria, *Chromatium* and the green bacteria, *Chlorobium* (Roy and Trudinger, 1970). These organisms contain photosynthetic pigments analogous to those of green plants and fix carbon dioxide in the presence of light and a reduced sulphur compound which acts as an electron donor. Equation (18) represents the oxidation of hydrogen sulphide by the photolithotrophs:

$$2CO_2 + H_2S + 2H_2O \xrightarrow{\text{light}} 2CH_2O + SO_4^{2-} + 2H^+ \qquad (18)$$

Like all photosynthetic reactions these processes take place only in the presence of light which imposes certain restrictions on the distribution of the photosynthetic sulphur-bacteria. The zone of activity is limited to the upper part of the anaerobic zone of the biosphere into which light penetrates. This includes the uppermost horizons of shallow sediments of water bodies and the lower part of the photic zone of water columns containing hydrogen sulphide. In these ecosystems the photosynthetic bacteria grow in tremendous quantities and play an active part not only in the sulphur cycle but also in the carbon cycle.

More detailed information on the ecology and geochemical activity of these organisms can be found in the reviews of Pfennig (1975, 1977) and the monographs of Kondratyeva (1972) and Gorlenko *et al.* (1977).

1.7 REDUCTION OF SULPHATE BY MICRO-ORGANISMS

The low-temperature reduction of sulphate to hydrogen sulphide is conducted by an exclusive group of micro-organisms called desulphurizing or

sulphate-reducing bacteria; the process is termed 'dissimilatory sulphate reduction'. This reduction may be regarded as a redox process in which sulphate is used as a terminal electron acceptor in the oxidation of organic compounds or hydrogen. Physiologically, this process provides the bacterial cell with the necessary energy for metabolism.

Typically, dissimilatory sulphate reduction is expressed formally in the following way (equation 19):

$$2CH_3{-}CHOH{-}COOH + H_2SO_4 \longrightarrow 2CH_3{-}COOH + 2CO_2{-}2H_2O + H_2S \quad (19))$$

Three genera of sulphate-reducing bacteria have been described on the basis of their morphology and physicobiological properties: the *Desulfovibrio* are heterotrophic, obligate motile anaerobes which are generally curved rods; *Desulfotomaculum* are heterotrophic, anaerobic rod-shaped organisms that form heat-resistant spores; and *Desulfomonas* are non-motile rods.

All known species of sulphate-reducing bacteria grow well on nutritive media which include sulphate and lactate or pyruvate. However, under natural conditions this group apparently utilizes a much wider spectrum of organic compounds. For example, *Desulfovibrio africanus* can grow on ethanol, and *D. vulgaris* metabolizes methanol, ethanol propanol, and butanol. (See note added in proof.)

Of great importance for understanding the final stages in the anaerobic decomposition or organic compounds is the work of Widdel and Pfennig (1977) who isolated a new species of sulphate-reducing bacteria, *Desulfotomaculum acetoxidans*, which is capable of oxidizing acetate to carbon dioxide. Before this work appeared, it was believed that acetate was metabolized exclusively by methane-producing bacteria, and numerous schemes were proposed for the anaerobic decomposition of organic matter which included a succession of sulphate-reducing and methane-producing bacteria.

Before closing this brief review of the major biogeochemical reactions of the global sulphur cycle, it should be stressed that many living organisms are of paramount importance for the cycling of sulphur at low temperatures and pressures. They not only speed up the oxidation of reduced sulphur compounds but also perform various redox reactions under anaerobic conditions.

1.8 FRACTIONATION OF THE STABLE ISOTOPES OF SULPHUR

Originally, the aim of isotope abundance measurements was to identify the natural isotopes and to gain an understanding of the atomic weights of the elements. More recently they have been used to interpret the long-term geochemical changes in nature, to determine the origins of mineral deposits, and to study the diagenesis of sulphur in modern environments (Chambers and Trudinger, 1978).

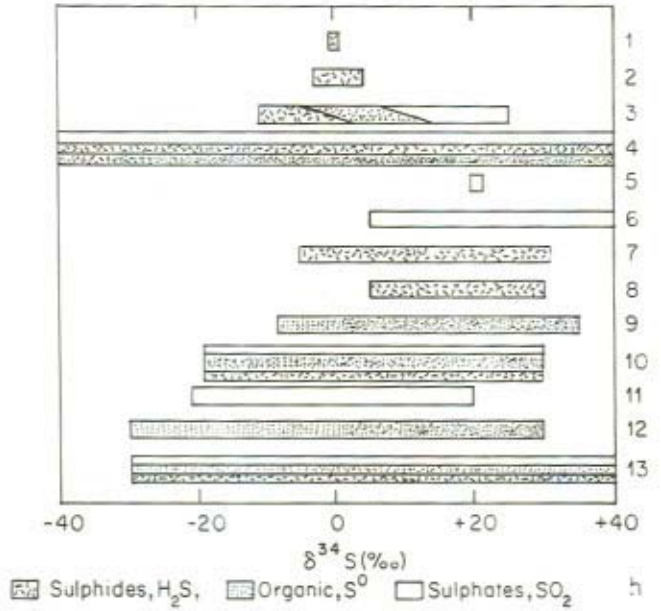

Fig. 1.3 Isotopic composition of sulphur in various natural substances. 1, Meteorites; 2, basic rocks; 3, volcanic rocks; 4, sedimentary rocks; 5, ocean-water; 6, evaporites; 7, zinc–lead deposits; 8, hydrogen sulphide from Devonian rocks, Alberta, Canada; 9, petroleum; 10, atmospheric compounds; 11, fresh water; 12, coal; 13, soil (from Krouse, 1970)

Most workers in these fields have studied the sulphur isotopes with mass numbers 32 and 34 because of their more favourable abundances; numerous studies have demonstrated marked variations in the relative proportions of these isotopes in sulphur compounds from natural sources (Fig. 1.3). The isotopic compositions are often expressed as $\delta^{34}S$ values which relate the isotopic composition of a sample to that of a standard according to equation (20):

$$\delta^{34}S(‰) = \left[\frac{(^{34}S/^{32}S)\ \text{sample}}{(^{34}S/^{32}S)\ \text{standard}} - 1\right] \times 1000 \qquad (20)$$

The standard for the analysis of terrestrial samples is usually troilite from the Canon Diablo meteorite which has a $\delta^{34}S$ value of 0‰. Positive values of $\delta^{34}S$ mean that the sample is enriched in the ^{34}S isotope while negative values denote an enrichment in ^{32}S compared to the meteorite standard.

In natural systems the fractionation of stable isotopes of sulphur occurs in the course of oriented chemical reactions under normal temperatures (termed the kinetic isotopic effect), and in isotope exchange reactions proceeding, as a

rule, at raised temperatures and possibly in biological systems (referred to as the thermodynamic isotopic effect).

Knowledge of the behaviour of sulphur isotopes in low-temperature oxidation and reduction of sulphur compounds is important for a better understanding of the geochemistry of sulphur in the sedimentary process.

Harrison and Thode (1957) were the first to show the kinetic isotopic effect during the chemical reduction of sulphate. In their experiments sulphate was reduced to hydrogen sulphide by hydriodic acid in the presence of hydrochloric and hypophorous acids. Generally, no more than 2% of the sulphate was reduced to determine the fractionation factor of this reaction. In these experiments hydrogen sulphide was enriched in the ^{32}S isotope by 21–22‰ compared to sulphate, and the isotopic effect was independent of the concentration of the reducing agent and the temperature within the range 17–50 °C.

The effect of temperatures between 100 °C and 300 °C on the magnitude of the kinetic effect was determined by studying the reduction of sulphuric acid by hydrogen (Grinenko *et al.*, 1969). The results of this study are given in Fig. 1.4. It should be noted that at temperatures above 150 °C isotopic exchange may be induced between the reaction products which would lead to an isotope redistribution at the expense of the thermodynamic isotopic effect.

Grinenko and Thode (1970) demonstrated a kinetic isotopic effect during the partial reduction of sulphur dioxide by hydrogen sulphide (equation 21):

$$2H_2S + nSO_2 \longrightarrow 3S + 2H_2O + (n-1)SO_2 \qquad (21)$$

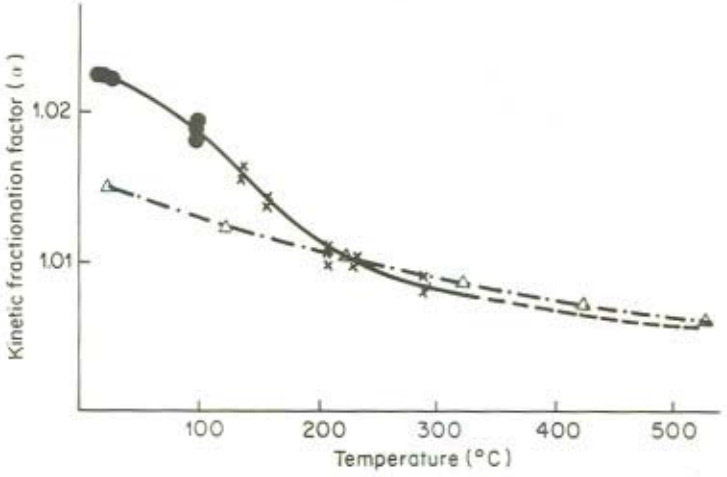

Fig. 1.4 Effect of temperature on the kinetic fractionation factor in the reduction of sulphate to sulphur dioxide and hydrogen sulphide. ●, Reduction to hydrogen sulphide; ×, reduction to sulphur dioxide; △, calculated curve (from Harrison and Thode, 1957 and Grinenko and Grinenko, 1974)

As expected, the remaining sulphur dioxide was enriched in the heavy sulphur isotope. The fractionation factor for the temperature interval from 25 °C to 280 °C calculated by the Rayleigh formula was 1.015 (Grinenko and Thode, 1970).

At ambient temperatures oxidation of reduced sulphur compounds is not generally accompanied by a substantial fractionation of sulphur isotopes. In experiments conducted by Vinogradov and Grinenko (1964) a stream of oxygen was passed into sulphur dispersed in water; sulphur was oxidized to sulphate which was slightly enriched in the light isotope while the heavy isotope accumulated in the residual sulphur. A significant fractionation of isotopes was observed only when more than 80% of the original sulphur was oxidized; the fractionation factor calculated from the experimental data did not exceed 1.0014. A slight fractionation of isotopes was observed during the reaction of water with elemental sulphur at 80–100 °C with the simultaneous production of hydrogen sulphide and oxidized sulphur compounds (Monster *et al.*, 1965). Compared to the original sulphur, the oxidized compounds were slightly enriched in ^{32}S and hydrogen sulphide was enriched with ^{34}S.

Therefore, the kinetic isotopic effects occurring in both oxidation and reduction reactions lead to products that are enriched in the light isotope and residues that are enriched with the heavy isotope of sulphur. During the chemical reduction of oxidized sulphur compounds, any hydrogen sulphide formed cannot be enriched in ^{32}S by more than 22‰ compared to the initial sulphur. However, the heavy isotope may accumulate in the residue and reach high values according to the Rayleigh formula.

$$N = N_0\left(\frac{V_0}{V}\right)^{(\alpha-1)/\alpha}$$

where N_0 and N are the contents of ^{34}S in the original compound and residue, V_0 and V are the amounts of original compound and residue, and α is the fractionation factor.

An important conclusion that can be drawn from the review of work on the kinetic isotopic effect is that sulphate formed by oxidation of sulphide and elemental sulphur has essentially the same isotopic composition as the sulphur compounds undergoing oxidation.

Table 1.1 groups the theoretically calculated thermodynamic characteristics of various sulfur compounds; these data enable us to predict the distribution of sulphur isotopes in isotope exchange reactions at equilibrium. At equilibrium the heavy isotope of sulphur should accumulate to a large degree in oxidized compounds, because the fractionation factor is greater when there is a large difference between the oxidation states of sulphur (Table 1.1). The highest fractionation (82‰ at 27 °C) should be expected at equilibrium in a system containing sulphate and sulphide ions (Table 1.1).

When assessing thermodynamic isotopic effects from the data of Table 1.1,

Table 1.1 Isotopic properties of sulphur compounds (Sakai, 1968)

	Temperature (K)					
	300	*400*	*500*	*600*	*700*	*800*
Compound	*1000 · ln f^a (‰)*					
SO_4^{2-} aq.	82.1	51.7	35.2	25.3	18.8	14.0
SO_3^{2-} aq.	71.2	43.1	28.6	20.4	15.2	11.7
SO_2 gas	43.0	27.6	19.1	13.9	10.6	8.2
H_2S	13.0	8.9	6.6	5.1	4.0	3.2
HS^-	9.2	6.7	5.1	3.7	3.0	2.4
S_8 (1/8)[b]	15.8	8.9	5.7	4.0	2.9	2.2
S_2 (1/2)	10.1	6.0	4.0	2.8	2.1	1.6
FeS_2 (1/2)	18.4	10.9	7.0	4.8	3.6	2.7
ZnS	14.3	8.0	5.2	3.6	2.6	2.0
SiS[c]	12.8	7.5	5.0	3.5	2.6	2.0
PbS	3.6	2.0	1.3	0.9	0.6	0.5
S^{2-} aq.	0	0	0	0	0	0

[a] f is the reduced partition function ratio.
[b] Values for 300 K are calculated for rhombic sulphur by Tudge and Thode (1950). Values for other temperatures were calculated by assuming proportionality to $1/T^2$.
[c] Data of Hulston (1964).

it should be understood that these data allow the precise estimation of the degree of fractionation; they do not, however, enable us to determine whether a reaction will reach equilibrium. To obtain evidence for isotopic fractionation due to the thermodynamic effect, experimental studies on rates of isotopic exchange should be conducted.

The main problem in the interpretation of isotopic data on volcanic gases, fumarole emissions, and hydrothermal minerals is to decide whether equilibrium has been attained between oxidized and reduced compounds of sulphur at the various temperatures.

Thode *et al.* (1971) obtained evidence for a rather high rate of isotopic exchange between hydrogen sulphide and sulphur dioxide at temperatures above 500 °C, as did Grinenko and Thode (1970) for the temperature interval of 300–450 °C. The experimentally established dependence of the equilibrium constant for the distribution of sulphur isotopes between these compounds on temperature is shown in Fig. 1.5. These data show that sulphur dioxide is slightly more enriched in ^{34}S than hydrogen sulphide in the high-temperature gases, but at 300 °C the difference in isotopic composition amounts to 9‰. When a temperature drop occurs hydrogen sulphide and

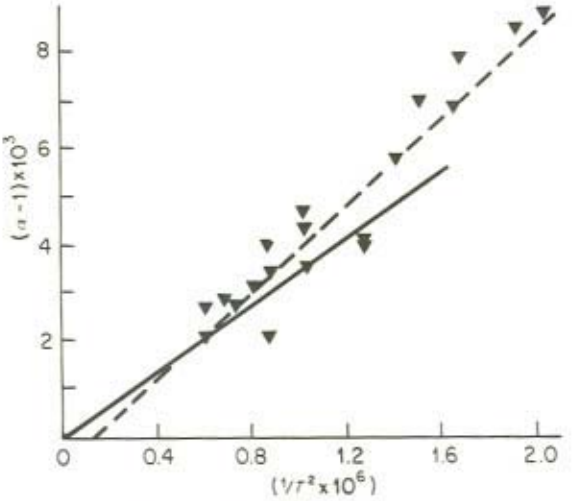

Fig. 1.5 Effect of temperature on the equilibrium constant for the isotope exchange reaction, $H_2{}^{34}S + {}^{32}SO_2 \rightleftharpoons H_2{}^{32}S + {}^{34}SO_2$. Continuous line—theoretical; broken line—experimental (α = equilibrium isotopic factor, T = absolute temperature) (from Thode *et al.*, 1971 and Grinenko and Thode, 1970)

sulphur dioxide react rapidly to form elemental sulphur. At 200 °C the rate of sulphur exchange between hydrogen sulphide and sulphur dioxide is quite low, and therefore the isotopic composition may change because of a kinetic isotopic effect. All of these effects result in a greater enrichment of the residual sulphur dioxide in the heavy sulphur isotope.

In acidic solutions rapid isotopic exchange has been demonstrated between hydrogen sulphide and sulphate at 200 °C. The dependence of the isotope fractionation factor for hydrogen sulphide and sulphate on temperature is illustrated in Fig. 1.6. These data suggest that in solution at high temperatures sulphate will be enriched in the ^{34}S isotope compared to the hydrogen sulphide present.

Some experimental data have been obtained showing that crystallization and recrystallization of sulphides above 250 °C proceed under conditions of isotopic equilibrium. This results in a definite distribution of sulphur isotopes between co-crystallizing sulphides, and such a distribution is temperature-dependent (Rye and Czamanske, 1969, Kajiwara and Krouse, 1971). The content of the ^{34}S isotope decreases in the series.

pyrite → (pyrotite-sphalerite) → chalcopyrite → galena

The greatest difference observed was for the pyrite–galena pair which amounted to only 4‰ at 250 °C. At ordinary temperatures, isotopic equili-

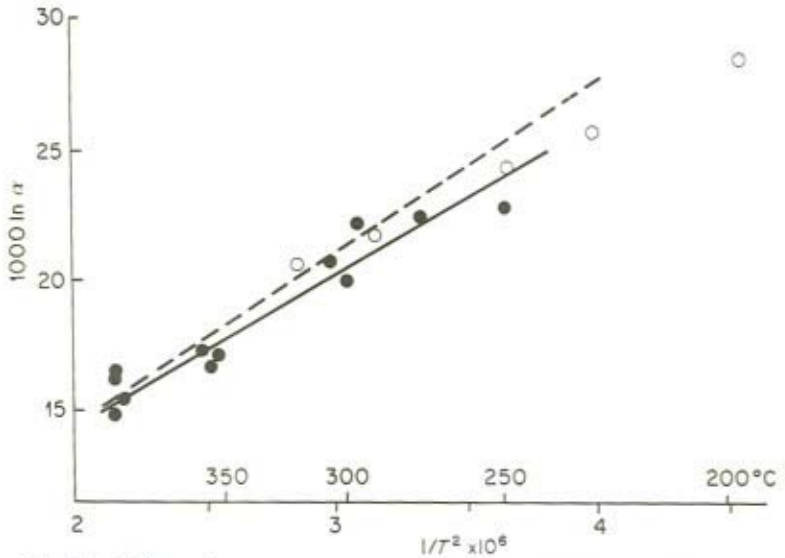

Fig. 1.6 Effect of temperature on equilibrium isotopic factor (α) for the exchange between hydrogen sulphide and sulphate. ●, from Igumnov *et al.* (1977); ○, from Robinson (1973); broken line, calculated curve (Sakai, 1968)

brium is not attained during the crystallization of sulphides and pyrite is only slightly enriched in the ^{32}S isotope (1–2‰) compared with the co-crystallizing sphalerite and chalcopyrite. Crystallization of gypsum from a saturated solution results in a 1.6‰ increase in the ^{34}S content of the crystals compared to the solution (Thode and Monster, 1965).

In the geochemistry of isotopes special attention is paid to the processes of fractionation in biological systems, since these processes engender the greatest isotopic fractionation in nature.

The process of sulphate assimilation from solution by bacteria, algae, and plants is accompanied by a slight isotopic effect; the total sulphur of these organisms is enriched in ^{32}S by 1–3‰ (Kaplan and Rittenberg, 1964; Mekhtieva and Pankina, 1968).

The partial decomposition of cysteine or other sulphur-containing amino acids in bacterial processes leads to a slight fractionation of sulphur isotopes; the first hydrogen sulphide released is enriched in ^{32}S by 5‰.

No detectable isotopic fractionation of sulphur occurs during the reduction of elemental sulphur to hydrogen sulphide by yeasts, nor during the oxidation of elemental sulphur by thiobacilli (Jones and Starkey, 1957; Kaplan and Rafter, 1958; Eremenko and Mekhtieva, 1961). However, oxidation of ele-

mental sulphur and pyrite by mixed cultures produced sulphates which were enriched in ^{32}S by a maximum of 1.7‰ (Nakai and Jensen, 1964).

In the case of oxidation of sulphide by thiobacilli a slight enrichment in ^{32}S is observed for elemental sulphur and a greater one for sulphates (up to 18‰), while the heavy isotope accumulates in intermediary products (Kaplan and Rittenberg, 1964). Studies on photosynthetic oxidation of hydrogen sulphide by purple bacteria have produced conflicting results on isotopic fractionation. In one series of experiments the elemental sulphur produced showed a low enrichment in the heavy isotope, while in another series sulphur

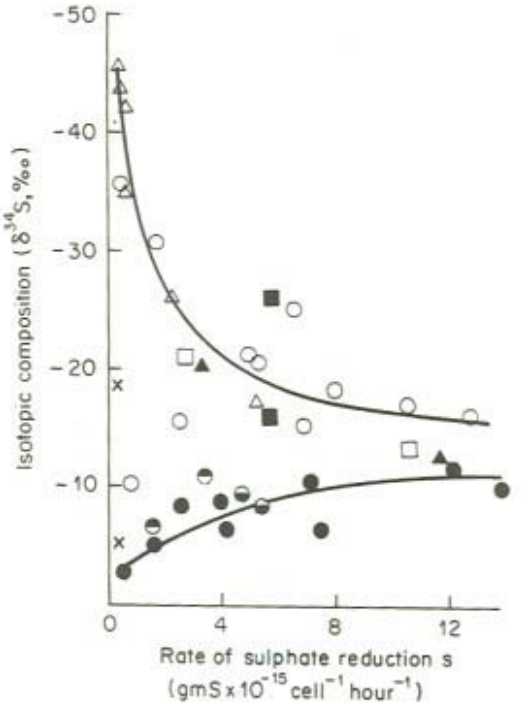

Fig. 1.7 Effect of sulphate reduction rate and electron acceptor on the isotopic composition of hydrogen sulphide formed during sulphate reduction by *Desulfovibrio desulfuricans*. ○, lactate at 10–45 °C, 0.06 M SO_4^{2-}; △, ethanol at 10–45 °C, 0.06 M SO_4^{2-}; ●, hydrogen at 10–45 °C, 0.06 M SO_4^{2-}; ×, lactate at 0 °C; ▲, lactate + 0.01 M SO_4^{2-}; □, lactate + 0.02 M SO_4^{2-}; ■, lactate + 0.12 M SO^{2-}; ◓, hydrogen + 0.02 M SO_4^{2-}; ◒, hydrogen + 0.18M SO_4^{2-} (from Kaplan and Rittenberg, 1964)

was enriched in the light isotope by up to 10‰; in the latter experiment no significant fractionation was observed in the sulphate (Kaplan and Rittenberg, 1964). One may conclude from the discussion above that essentially no fractionation of sulphur isotopes occurs during the oxidation of sulphur compounds.

The greatest fractionation of sulphur isotopes occurs during the microbial reduction of sulphate. As early as 1951, Thode *et al.* reported that the bacterial reduction of sulphate produced hydrogen sulphide enriched in the light isotope of sulphur. As a number of reviews have been published on the details of sulphur isotope fractionation during bacterial sulphate reduction (e.g. Grinenko and Grinenko, 1974; Krouse and McCready, 1979), only the basic conclusions will be discussed below.

Variations in sulphate concentration in nutrient media within the range 1×10^{-3}–3×10^{-2} moles litre^{-1} have no impact on the isotopic effect. However, for concentrations below 6×10^{-4} moles litre^{-1}, the isotopic fractionation factor decreases and approaches 1.00.

The type of electron donor used by bacteria has an important impact on the isotopic effect; viz. the use of organic donors rather than hydrogen under otherwise identical conditions results in a greater fractionation. Changes in pH and temperature do not produce regular effects in all cases.

In general the isotopic effect seems to depend on the sulphate reduction rate: with the use of organic electron donors an isotopic effect increased as the intensity of hydrogen sulphide emission per cell decreased. When hydrogen was used, however, there was a direct relationship between the degree of fractionation and the rate of reduction (Fig. 1.7).

The maximum isotopic effects observed in laboratory experiments on reduction of sulphates and sulphites are summarized in Table 1.2. As can be seen from these data, hydrogen sulphide may be enriched in the light isotope by up to 50‰ compared with sulphate. Under natural conditions even greater isotopic effects have been registered (60–70‰). As biogenic isotopic effects have proved to be much greater than those observed during the chemical reduction of sulphate, questions have arisen concerning the mechanisms of the fractionation and several hypotheses have been suggested. At present most investigators share the belief (Rees, 1973; Grinenko and Grinenko, 1974) that isotopic exchange occurs between the intermediary products of reduction in the bacterial cell which produces the thermodynamic isotopic effect under ordinary temperatures. The reality of such a mechanism is supported by recent experiments on the exchange of radioactive sulphur between $H_2{}^{35}S$ and Na_2SO_4 in the presence of sulphate-reducing bacteria (Trudinger and Chambers, 1973), and by the dependence of the isotopic composition of oxygen in the residual sulphate on that of oxygen in the water in which the reaction occurred.

The sulphur isotopic composition of natural samples can vary up to 160‰

Table 1.2 Maximum isotopic effects of various bacterial processes in laboratory experiments

Process	Organism	Initial reactant	Final product	Maximum isotopic effect	Reference[a]
Sulphate reduction	*Desulfovibrio desulfuricans*	SO_4^{2-}	H_2S	−46	1
	Desulfovibrio desulfuricans	SO_4^{2-}	H_2S	−35	2
	Desulfovibrio vulgaris	SO_4^{2-}	H_2S	−24	3
	Desulfotomaculum nigrificans	SO_4^{2-}	H_2S	−12	4
	Saccharomyces cerevisiae	SO_4^{2-}	H_2S	−25	5
	Desulfovibrio gigas	SO_4^{2-}	H_2S	0	6
Sulphate assimilation	*Escherichia coli*	SO_4^{2-}	Organic S	−2.8	1
	Saccharomyces cerevisiae	SO_4^{2-}	Organic S	−2.4	11
	Desulfovibrio desulfuricans	SO_4^{2-}	Organic S	−2.7	4
Sulphite reduction	*Desulfovibrio desulfuricans*	SO_3^{2-}	H_2S	−14	1
	Desulfovibrio desulfuricans	SO_3^{2-}	H_2S	−13	10
	Desulfovibrio vulgaris	SO_3^{2-}	H_2S	−33	3
	Saccharomyces cerevisiae	SO_3^{2-}	H_2S	−50	5
	Salmonella sp.	SO_3^{2-}	H_2S	−42	7
	Desulfotomaculum nigrificans	SO_3^{2-}	H_2S	−8	4
Cysteine decomposition	*Proteus vulgaris*	Cysteine	H_2S	−5.1	1
Chemosynthetic oxidation	*Thiobacillus concretivorus*	H_2S	S^0	−2.5	1
	Thiobacillus concretivorus	H_2S	SO_4^{2-}	−18	
	Thiobacillus concretivorus	H_2S	$S_xO_y^{2-}$	+19	
	Thiobacillus concretivorus	S^0	SO_4^{2-}	−1.4 to 0.4	1
	Thiobacillus denitrificans	S^0	SO_4^{2-}	−1.1 to +0.4	8
	Thiobacillus sp.	S^0	SO_4^{2-}	−2	9
Photosynthetic oxidation	*Chromatium*	H_2S	S^0	−10	1
	Chromatium	H_2S	SO_4^{2-}	0	
	Chromatium	H_2S	$S_xO_y^{2-}$	+11	

[a]1. Kaplan and Rittenberg (1964); 2. Chambers *et al.* (1975); 3. Kemp and Thode (1968); 4. McCready (1975); 5. McCready *et al.* (1974); 6. Smejkal *et al.* (1971); 7. Krouse and Sasaki (1968); 8. Mekhtieva (1964); 9. Nakai and Jensen (1964); 10. Harrison and Thode (1958); 11. McCready *et al.* (1974).

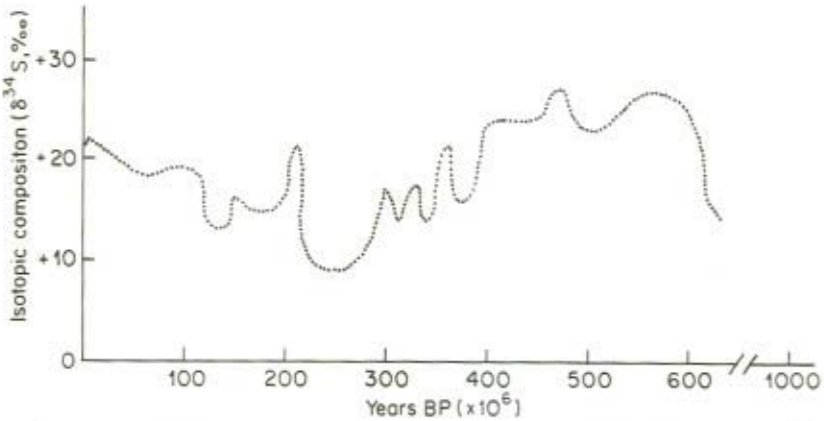

Fig. 1.8 Isotopic composition of sulphur in evaporites of different age (from Grinenko and Grinenko, 1974)

although most samples vary within 70‰ (Fig. 1.3). This range far exceeds the fractionation that can be related exclusively to chemical and physical processes. Undoubtedly, the major processes responsible for the fractionation are related to the biological activity during sulphur turnover in the sedimentary cycle.

The mechanisms of microbial isotopic fractionation, in which the light isotope is transferred to sulphide and the heavy isotope accumulates in sulphate, became operational some 2 billion years ago. This resulted in an accumulation of ^{34}S in sea-water and marine evaporites.

Variations in the sulphur isotopic composition of oceanic sulphate evaporites are shown in Fig. 1.8. It appears that the isotopic composition in evaporites of different age is irregular due to the differing rates of sulphate influx with river-water and sulphur exhalation from volcanoes and also because of the temporal variations in bacterial reduction and evaporite deposition.

NOTE ADDED IN PROOF

Since this report was proposed 5 additional genera of sulphate-reducing bacteria have been reported. Among these are organisms capable of completely oxidizing fatty acids from C_1 to C_{18} and some aromatic compounds. (Pfennig, N., Widdel, F. and Trüper, H. G. (1981) The dissimilatory sulphate-reducing bacteria. In: Starr, M. P., Stolp, H., Trüper, H. G., Balows, A., and Schlegel, H. G. (eds), *The Prokaryotes* Vol. 1. Springer-Verlag, Berlin. pp. 926–940.)

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