# CHAPTER 1 Sulphur Isotopes in Nature and the Environment: An Overview

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# 1.1 INTRODUCTION

By 1931 it had long been suspected that there were differences in the chemical properties of the isotopes of an element, but it was the discovery of the rare heavy isotopes of the light elements, <sup>13</sup>C, <sup>15</sup>N, <sup>17</sup>O, and <sup>18</sup>O, in 1929 and particularly that of deuterium by Urey and his coworkers in 1931 that led to the detection of such differences. It was correctly felt that the 100% difference in the masses of the hydrogen isotopes would give rise to appreciable chemical dissimilarities, and in the succeeding decade, Urey's group and others predicted and measured such differences. An extension of their studies to isotopic compounds of carbon, nitrogen, and oxygen showed that small differences in the chemical properties of the isotopes of these elements existed as well.

The laboratory measurement of chemical isotope effects, both equilibrium and kinetic, has developed into an extremely useful tool for the investigation of the mechanisms of chemical reactions. In addition, it has been recognized that isotope effects occur in nature, so that samples of an element will have variable isotope compositions or ratios reflecting differences in their chemical, biological, and geological histories. Over the past 40 years, extensive measurements of the isotope abundance variations of hydrogen, boron, carbon, oxygen, and sulphur have aided in the determination of geochemical properties of these elements and in the solution of many geochemical problems.

Sulphur isotope geochemistry has been a particularly rewarding field of investigation because of the relatively large percentage mass difference between the two principal isotopes, the variety of chemical forms of sulphur, and their widespread occurrences in the earth's lithosphere, hydrosphere, and atmosphere. Sulphur isotope geochemistry studies began in the late 1940s (Thode *et al.*, 1949; Trofimov, 1949).

Sulphur isotope ratio studies have been concerned with such problems as isotope fractionation in the biological sulphur cycle, the sulphur-bearing

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gases of volcanoes, the isotopic composition of present-day and ancient oceans, isotope distribution patterns in recent and ancient sediments and in coal and petroleum, the evolution of early life, and modes of formation and depositional histories of sulphide mineral deposits, etc. It is not surprising that sulphur isotope ratio measurements are now finding increased application in environmental studies.

## **1.2 THEORY AND MEASUREMENT OF ISOTOPE EFFECTS**

Sulphur has four stable isotopes ( ${}^{32}S$ ,  ${}^{33}S$ ,  ${}^{34}S$ ,  ${}^{36}S$ ) whose percentage abundances are approximately 95.0, 0.75, 4.20, and 0.017 respectively (MacNamara and Thode, 1950). Isotope abundance variations are generally considered in terms of the abundance ratio  ${}^{34}S/{}^{32}S$  of the two principal isotopes. Isotope effects are generally small and this makes it convenient to refer to fractional differences in isotope ratios ('del' values ( $\delta$ ) of samples relative to a standard, and to express these differences in parts per thousand (per mil):

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

The generally accepted standard is troilite from the Canyon Diablo meteorite for which  ${}^{34}S/{}^{32}S$  is assigned the value 1/22.22. There are several reasons for expressing sulphur isotope ratio variations in this manner. Firstly, the mass spectrometer techniques used for sulphur isotope abundance measurements make the determination of differences in <sup>34</sup>S/<sup>32</sup>S ratios between samples much more precise than the determination of the absolute values of the ratios for either sample. Using approximately 1 mg of sulphur, as sulphur dioxide, or a few tenths of a milligram of sulphur, as sulphur hexafluoride, it is possible to compare samples with a precision of the order of 0.1‰ (McKinney et al., 1950; Rees, 1978). Secondly, the use of Canyon Diablo troilite (which is extremely uniform in isotopic content) as a standard makes interlaboratory comparison of results much easier than if a number of personal standards are used. Finally, there is strong evidence that the ratio  ${}^{34}S/{}^{32}S$  in the troilite of iron nickel meteorites is the primordial value for the solar system and is the initial value of the earth's crust and mantle. It is therefore the natural base line to which terrestrial variations should be related.

#### 1.2.1 Equilibrium isotope effects

Isotope fractionation is a function of the relative masses of reacting molecules and in chemical systems may result during either isotopic exchange or unidirectional processes. Consider, for example, isotope exchange between sulphur dioxide and hydrogen sulphide. The exchange reactions are:

$$H_2^{32}S \rightleftharpoons {}^{32}SO_2$$

and

$$H_2^{34}S \rightleftharpoons {}^{34}SO_2$$

These equations can be combined to give the overall isotope exchange equation:

$$H_2{}^{34}S + {}^{32}SO_2 \rightleftharpoons H_2{}^{32}S + {}^{34}SO_2$$

The equilibrium constant K may be expressed in terms of concentration or of partition functions (Q) for the molecules involved (Urey and Greiff, 1935; Urey, 1947; Bigeleisen and Mayer, 1947):

$$K = \frac{\left[{}^{34}\text{SO}_2\right] / \left[{}^{32}\text{SO}_2\right]}{\left[\text{H}_2{}^{34}\text{S}\right] / \left[\text{H}_2{}^{32}\text{S}\right]} = \frac{Q^{34}\text{SO}_2 / Q^{32}\text{SO}_2}{Q\text{H}_2{}^{34}\text{S} / Q\text{H}_2{}^{32}\text{S}}$$

The expression involving ratios of partition functions for isotopic molecules is convenient for the prediction of K since such ratios may be evaluated solely in terms of the fundamental vibrational frequencies of the molecules concerned. The expression for K involving ratios of concentration for isotopic molecules shows that when K is not unity the ratio  ${}^{34}S/{}^{32}S$  will not be the same in the two equilibrated phases. Thus the extent to which K differs from unity is a measure of the equilibrium isotope effect.

For the H<sub>2</sub>S and SO<sub>2</sub> system above, the isotope equilibrium constant is 1.0064 at 800 K (Thode *et al.*, 1971). Thus at 800 K under equilibrium exchange conditions, the  $\delta^{34}$ S value of SO<sub>2</sub> will be 6.4‰ heavier than that of H<sub>2</sub>S (Figure 1.1). The decrease in the equilibrium isotope effects (*K* – 1) with increasing temperature, as seen for the SO<sub>2</sub>–H<sub>2</sub>S exchange reaction in Table 1.1, is the basis for isotope thermometry.

Exchange reactions between sulphur compounds theoretically predict enrichment of  ${}^{34}S$  in the more oxidized species, the largest fractionation factor occurring in the exchange between H<sub>2</sub>S and SO<sub>4</sub><sup>2-</sup>, the two extreme oxidation states.

It must be noted that although an isotope equilibrium constant may be calculated for a pair of sulphur compounds, there is no guarantee that isotope equilibrium will in fact be set up. If conditions are such that no reaction paths are possible, then the isotopic compositions of the two compounds will necessarily remain unaltered. In the case of the  $SO_2$  and



Figure 1.1 Changes in  $\delta^{34}$ S values as isotopic equilibrium is approached

Table 1.1 Equilibrium constants for some sulphur isotope exchange reactions (from Tudge and Thode, 1950)

Isotope exchange reactions	<i>T</i> (°C)	K (calc.)	<i>K</i> (exp.)
$H_2{}^{34}S + {}^{32}SO_4{}^{2-} \rightleftharpoons H_2{}^{32}S + {}^{34}SO_4{}^{2-}$	25	1.074	_
$H_2^{34}S + {}^{32}SO_3 \rightleftharpoons H_2^{32}S + {}^{34}SO_3$	25	1.070	
$H_2^{34}S + {}^{32}SO_2 \rightleftharpoons H_2^{32}S + {}^{34}SO_2$	0	1.037"	
$H_2^{34}S + {}^{32}SO_2 \rightleftharpoons H_2^{32}S + {}^{34}SO_2$	25	1.032"	
$H_2^{34}S + {}^{32}SC_2 \rightleftharpoons H_2^{32}S + {}^{34}SO_2$	527	1.0064"	1.006"
$+ H^{34}SO_{3}^{-}(aq) = -SO_{2}(g)$	25		$1.019^{b}$
$H_2^{32}S + H^{34}S^- \rightleftharpoons H_2^{34}S + H^{32}S^-$	25		1.006
$\frac{1}{8} \frac{32}{5} S_8 + H_2^{34} S \rightleftharpoons \frac{34}{5} S_8 + H_2^{32} S$	25	1.003	

" From Thode et al. (1971).

<sup>b</sup> From Thode et al. (1945).

 $H_2S$  exchange system, for example, it is necessary to have water present and to go to high temperatures so that reaction paths may be established between two sulphur compounds. In other cases, the time required to establish equilibrium may be long even on the geological time scale. The system would then have an isotopic distribution between that of its prior condition and equilibrium (Figure 1.1).

#### 1.2.2 Kinetic isotope effects—isotope fractionation in unidirectional process

For systems undergoing unidirectional chemical reactions, the situation is somewhat more complicated than that for equilibrium processes and more attention must be paid to the reaction mechanism and possible intermediates involved in the formation of final products.

Isotope fractionation in a unidirectional process results from differences in reaction rates of the different isotopic species. In a single-step, zero, or firstorder reaction, the isotope fractionation factor between the instantaneously generated product and remaining reactant is simply given by the ratio of rate constants for the two competing isotopic reactions. For example, in the chemical reduction of sulphate the ratio of rate constants  $k_{32}/k_{34}$  for the competing reactions:

$${}^{32}\mathrm{SO}_4{}^{2-} \xrightarrow{k_{32}} \mathrm{H}_2{}^{32}\mathrm{S}$$

and

$${}^{32}\mathrm{SO}_4{}^{2-} \xrightarrow{k_{34}} \mathrm{H}_2{}^{34}\mathrm{S}$$

has been measured and is  $\sim 1.022$  at room temperature (Harrison and Thode, 1957).

Since the  ${}^{32}SO_4{}^{2-}$  species reacts 1.022 times faster than the  ${}^{34}SO_4{}^{2-}$ , the H<sub>2</sub>S produced at any instant is depleted in  ${}^{34}S$  by about 22‰ relative to the remaining  $SO_4{}^{2-}$ .

Predictions of rates of chemical reactions are made within the framework of the transition state theory (Eyring, 1935; Evans and Polanyi, 1935) where it is assumed that reactant molecules are in equilibrium with molecules known as 'activated complexes' in a transition state through which the reaction proceeds to products. Using the framework of this theory, the ratio of rate constants for the above two competing isotopic reactions may be written (Bigeleisen, 1947; Bigeleisen and Wolfsberg, 1958) as

$$\frac{k_1}{k_2} = \left\{ \frac{Q^{34} \mathrm{SO_4}^{2-}}{Q^{32} \mathrm{SO_4}^{2-}} \middle/ \frac{(Q^{34} \mathrm{SO_4}^{2-})^*}{(Q^{32} \mathrm{SO_4}^{2-})^*} \right\} \frac{\upsilon_1}{\upsilon_2}$$

The ratio of rate constants for the reaction of light and heavy isotopic species is therefore expressed, as in the case of equilibrium constants, simply in the form of two partition function ratios, one for the two isotopic

reactants  $SO_4^{2-}$  and one for the two isotopic species of 'activated complexes'. The factor  $v_1/v_2$  in the expression is a mass term ratio for the two isotopic species, where v may be related to a vibrational mode in the activated complex. By making certain assumptions concerning the nature of the transition state, estimates for the ratio of rate constants for two competing isotopic reactions can be made. Therefore relative rate constants determined experimentally when combined with theoretical calculations provide information on the nature of the activated complex. For example, the large kinetic isotope effect obtained in the chemical reduction of sulphate can only be understood if we assume the breaking of a S—O bond in the initial rate-determining step, e.g.

$$SO_4^{2-} \rightleftharpoons (SO_3^{2-} - O)^* \rightarrow SO_3^{2-}$$

In a multistep reaction, the situation may be more complex. In general, isotope fractionation occurs in the initial rate-determining step. However, in the case of a rapid equilibrium step followed by a unidirectional step, the equilibrium isotope effect in step 1 and the kinetic isotope effect in step 2 are additive.

## **1.2.3 Fractionation factors**

For purposes of understanding isotope abundance variations, it is important to distinguish between simple process factors as given by equilibrium constants or by ratios of rate constants for a given isotopic reaction and fractionation observed for systems where the simple process factors may be multiplied many times. Commercial processes for the separation of isotopes depend on this kind of multiplication (Urey and Greiff, 1935). Where such systems occur in nature, apparent isotope fractionation factors will be observed that are significantly larger than those calculated or measured for simple processes.

A batch process is one such system that can give rise to large fractionation. In the case of kinetic isotope effects, the changes in isotope ratios of both reactants and products with time depends on the extent of reaction (Bigeleisen and Wolfsberg, 1958). In Figure 1.2, reduction of sulphate to hydrogen sulphide is assumed to have a ratio of rate constants for the <sup>32</sup>S and <sup>34</sup>S molecular species of 1.024. For small fractions of reaction, the sulphide product will be depleted in <sup>34</sup>S by approximately 24‰ with respect to the initial sulphate. As the reaction proceeds this depletion becomes smaller until at 100% reaction, the sulphide produced will have the same isotopic composition as the initial sulphate. For a small fraction of reaction, the sulphate isotopic composition will be virtually unaltered, but as the reaction proceeds, because of the continuing preferential reduction of

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 ${}^{32}SO_4{}^{2-}$ , the remaining sulphate will become more and more enriched in  ${}^{34}S$  and will so attain higher and higher  $\delta^{34}S$  values (Figure 1.2). The curves in Figure 1.2 are consistent with Rayleigh distillation equations.

In natural batch systems the ultimate extent of fractionation depends on the supply of reactant, and the terms 'open' and 'closed' systems have been used to differentiate between 'infinite' and 'limited' reactant reservoirs (Nakai and Jensen, 1964).

In an 'open' system the isotopic composition of the reactant remains essentially unchanged and the product will be depleted in <sup>34</sup>S by one simple process factor given by the ratio of rate constants for the two isotopic species. In a 'closed' system the isotopic composition of both reactant and product change with time as the reaction proceeds, as seen in Figure 1.2.

Clearly batch processes of this type can occur in nature and give rise to a variety of observable fractionation factors which will depend on the



Figure 1.2 Changes in  $\delta^{34}$ S values of remaining reactant and accumulated product where  ${}^{32}$ SO<sub>4</sub><sup>2-</sup> is being reduced 1.024 times faster than  ${}^{34}$ SO<sub>4</sub><sup>2-</sup>

completeness of reaction. This must be taken into account in the interpretation of natural isotope distribution patterns.

# **1.3 SULPHUR ISOTOPE VARIATIONS IN NATURE**

Figure 1.3 shows the ranges of  $\delta^{34}$ S values found in nature for a number of different forms of sulphur. The zero point of the  $\delta^{34}$ S scale is troilite from the Canyon Diablo meteorite (Thode, 1963). Some terrestrial samples fall outside the range of Figure 1.3, such as barite concretions from the ocean floor at +87‰ (Sakai, 1971) and marcasite associated with petroleum at -53.1‰ (Austin, 1970). However, 98% of all samples analysed fall in the range -40 to +40‰) (Nielsen, 1979).



Figure 1.3 Sulphur isotope distribution in nature

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It can be seen that a broad distinction may be made between sulphur which has and sulphur which has not become involved in the sedimentary cycle. Sulphur in meteorites, ultrabasic and basic sills, granitic intrusions, and igneous rocks of primary origin have  $\delta^{34}$ S values in a narrow range close to zero (Shima *et al.*, 1963; Thode *et al.*, 1962; Ryznar *et al.*, 1967; Schwarcz, 1973; Grinenko *et al.*, 1970; Mitchell and Krouse, 1975).

Volcanic gases and rocks tend to have a wider range of  $\delta^{34}S$  values distributed symmetrically about  $\delta^{34}S = 0$ . This significant range of values is due to a variety of inorganic chemical reactions and equilibria which tend to enrich oxidized forms of sulphur and deplete reduced forms of sulphur in <sup>34</sup>S (Sakai, 1957; Rafter *et al.*, 1960; Heald *et al.*, 1963; Oana and Ishikawa, 1966; Grinenko and Thode, 1970; Puchelt *et al.*, 1971; Hoefs, 1973). Also some volcanoes eject not only primary material ( $\delta^{34}S = 0$ ) but act as pumps for sea water and other sources of sulphur compounds. Inorganic reactions with isotopic equilibria in hydrothermal fluids theoretically lead to oxidized and reduced forms of sulphur which are respectively enriched and depleted in <sup>34</sup>S (Ohmoto, 1972).

In comparison, sulphur in sediments, in sea water, and in materials such as coal and petroleum that have participated in the biological sulphur cycle, displays a much wider range of  $\delta^{34}$ S values. This distinction provides a basic diagnostic technique in sulphur isotope studies. When an igneous rock is found that displays a wide range of  $\delta^{34}$ S values or a narrow range well removed from zero, it is possible to state with some certainty that the rock is not of primary origin but is a reworked sediment or at least has a component of sedimentary sulphur.

#### 1.3.1 Biological sulphur cycle

In general, evaporites (sulphates) tend to be enriched and sedimentary sulphides depleted in <sup>34</sup>S, as one might expect from thermodynamic considerations. However, there is no evidence of isotopic exchange between sulphate and sulphide below temperatures of ~100 °C. Further, although the chemical reduction of sulphate to hydrogen sulphide takes place readily at room temperature in the presence of strong reducing agents and acids, chemical reduction under more realistic geochemical conditions has not been demonstrated below temperatures of ~100 °C.

It is now well established that these large deviations of  $\delta^{34}$ S from zero are due largely to the fractionation of the sulphur isotopes in biologically mitigated reactions at low temperatures. The biological cycle of sulphur is in part characterized by the activity of sulphur oxidizing and reducing bacteria which together account for the bulk of contemporary turnover rates in the biosphere (Baas-Becking, 1925; Postgate, 1959; Alexander, 1971). Whereas photosynthetic/photolithotrophic sulphur bacteria oxidize reduced sulphur, *desulphovibrio desulphuricans* or 'sulphate respirers' reduce sulphate to sulphide in anaerobic ecosystems in the presence of organic matter.

Sulphate reduction in the sulphur cycle may be assimilatory or dissimilatory. During assimilatory reduction, such as occurs in the plant metabolism of sulphate, the sulphur is reduced from a valence of +6 to a valence of -2 in the synthesized products (amino acids and proteins). On the other hand, dissimilatory reduction of sulphate with the release of hydrogen sulphide often occurs in the bacterial reduction of sulphate. The turnover rates of sulphur in these latter dissimilatory processes exceed those during assimilatory reduction by several orders of magnitude. Accordingly the decisive biological control of the sulphur cycle is exercised by the sulphate reducing bacteria.

It is during this dissimilatory reduction of sulphate to  $H_2S$  carried out by a few extant genera (viz. desulphovibrio, desulphotomaculum and desulphomotas) that relatively large isotope effects occur. The bacterial reduction which takes place under anaerobic conditions in the presence of organic matter is therefore a major factor in the geochemical cycle of sulphur and accounts for the large fluxes of sulphur depleted in <sup>34</sup>S into the lithosphere from the hydrosphere (Thode *et al.*, 1951; Jones and Starkey, 1957; Kaplan and Rittenberg, 1964).

# 1.3.1.1 Isotope fractionation by assimilatory reduction of sulphate

Assimilatory reduction of sulphate by plants and animals in both freshwater and marine environments results in only slight isotope fractionation, the  $\delta^{34}$ S of reduced organic sulphur ranging from +0.5 to -4.4‰ relative to the sulphate in the external milieu (Ishii, 1953; Kaplan *et al.*, 1963; Mekhtiyeva and Pankina, 1968; Mekhtiyeva, 1971). Similar small fractionations between cellular sulphur and sulphate have been noted during growth of a number of microorganisms (Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1978). These fractionations varied from -0.9 to 2.8‰, the reduced cellular sulphur being isotopically light relative to the sulphate nutrient, whereas Ishii (1953), quoted by Kemp and Thode (1968), reported that metabolism of sulphate by plants (algae) involved little or no isotope fractionation < 1.2‰.

Assimilatory organisms rarely produce significant amounts of free hydrogen sulphide from sulphate. There is evidence, however, that abnormal nutritional factors may modify sulphur metabolic pathways and thus lead to traces of hydrogen sulphide formed and isotope fractionation. Krouse *et al.* (1984) have shown that vegetation under stress from high concentrations of sulphur in atmospheric plumes from sour gas wells show such effects (Section 7.2.7).

## 1.3.1.2 Isotope effects in the dissimilatory reduction of sulphate

Laboratory culture experiments performed with *Desulphovibrio desulphuricans* have shown that isotope effects associated with dissimilatory sulphate reduction vary between  $\delta^{34}$ S values of +3 and -46‰ depending in part on experimental conditions and possibly the organism (Ford, 1957; Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Chambers and Trudinger, 1978). In general, the degree of fractionation is an inverse function of the rate of reaction. The highest fractionations are obtained at low metabolic rates of sulphate reduction, whereas the minimum effect at high metabolic rates ranges close to 0‰. The influence of temperature and electron donors on isotope fractionation can generally be interpreted in terms of their effect on the rate of reduction. Also at very low sulphate concentrations (< 0.01 mM), the magnitude of the fractionation and Thode, 1958).

Various models of isotope fractionation during dissimilatory sulphate reduction have been proposed to account for the isotope effects obtained under various conditions in terms of the biochemistry and the reduction pathways (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Rees, 1973; see Chambers and Trudinger, 1978 review).

The pathway of dissimilatory sulphate reduction is composed of four principal enzyme catalysed steps as follows:

An essential feature of the Rees model is that steps 1, 2, and 3 are reversible so that the system, external sulphate  $\rightarrow$  sulphite, represents a pool allowing the kinetic isotope effect to be expressed during sulphite reduction. Rees assumed that only the forwards steps 1, 3, and 4 involved fractionation so that the overall isotope effect given by his steady-state model reduced to

$$\alpha = \alpha_1 + \alpha_3 x_1 x_2 + \alpha_4 x_1 x_2 x_3$$

where  $\alpha_1$ ,  $\alpha_3$ , and  $\alpha_4$  are the fractionation factors for the forward reactions 1, 3, and 4, and  $x_1$ ,  $x_2$ , and  $x_3$  are the ratios of the backward to forward flows associated with steps 1, 2, and 3 respectively.

The sizable isotope shifts in the negative direction associated with reaction series both in culture experiments and in natural environments are accordingly composites of the isotope effects inherent in the four numbered reaction steps depicted above. Attempts to account for the observed fractionation in principle consider four boundary conditions with one of the component reactions becoming rate controlling under specific conditions.

Thus when the reaction proceeds unidirectionally, the overall isotope effect is simply that in the first step  $\alpha_1$  (+3%). In contrast, a multistep, unidirectional, first-order sequence exhibits the isotope effect in the rate-determining step or slowest step. The other extreme experimental value, -46 to -50%, occurs when the parameters  $x_1$ ,  $x_2$  and  $x_3$  approach unity. This means that the reduction of sulphite to hydrogen sulphide has been slowed down to the point where there is a build-up of the back flows from sulphite to APS so that the value of  $x_3$  is no longer zero.

Although there is considerable uncertainty as to the kinetic isotope effects to be assigned to the various steps in the reaction sequence  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$ , it is generally agreed that the isotope effects associated with steps 1 and 2 are in the order of a few per mil only, the value for step 1 even becoming positive +3‰ at sulphate concentrations < 0.01 mM (Harrison and Thode, 1958). On the other hand, relatively large isotope effects are associated with reaction steps 3 and 4 which involve breaking of sulphur–oxygen bonds. Values proposed for step 3 vary between -25‰ (Rees, 1973) and -10 to -15‰ (Chambers and Trudinger, 1978), whereas the effect linked to sulphite reduction (step 4) should also be about -25‰.

#### 1.3.1.3 Isotope fractionation during oxidation of sulphide

In the biological sulphur cycle, several groups of bacteria produce sulphate by oxidation of reduced inorganic sulphur compounds. These include photosynthetic and chemosynthetic autotrophic organisms as well as heterotrophic organisms. Chemosynthetic sulphur bacteria (thiobacilli) utilize the energy released by the reactions of sulphide with free oxygen. Hence, thiobacilli are aerobes, whereas photosynthetic sulphur bacteria are strict anaerobes.

Isotope effects in the oxidation steps of the biological sulphur cycle in autotrophic processes involving both chemosynthetic and photosynthetic sulphur bacteria have been studied (see review by Chambers and Trudinger, 1978).

Studies of isotope effects during sulphide oxidation by photosynthetic organisms have produced conflicting results, perhaps due to different techniques for measuring the isotope effects and to the formation of intermediates in some cases. However, in general these isotope effects are small and inverse. Early laboratory experiments with *Chromatium* sp. photosynthetic oxidizing bacteria indicated isotope effects of less than 1‰ in the oxidation of hydrogen sulphide and sulphur and to sulphate by either

growing cultures or resting cell suspensions (Ford, 1957). Later, Kaplan *et al.* (1960) using *Chromatium* sp. and Mekhtiyeva and Kondrateva (1966) using *Rhodopseudomonas* sp. reported that sulphate became slightly reduced in <sup>34</sup>S (inverse effect) and that there was little or no isotope effect associated with sulphur formation. On the other hand, D.P. Kelly *et al.*, as reported by Chambers and Trudinger (1978), found that sulphur produced during sulphide oxidation by *Chlorobium thiosulphatophilum* became enriched in <sup>34</sup>S by up to 5‰, a result similar to that obtained during abiogenic oxidation of sulphide to sulphur by Kaplan and Rafter (1958). Both sulphur and sulphate became enriched in <sup>34</sup>S during sulphide oxidation by photosynthetic bacterium (E. Shaposhnikovii, reported by Ivanov *et al.*, 1976). Finally, Kaplan and Rittenberg (1964) showed that in contrast to their earlier results, significant enrichment of <sup>32</sup>S in sulphur resulted during sulphide oxidation by *Chromatium* sp., whereas no significant fractionation was found in sulphate.

Recently Fry *et al.* (1983) reported isotopic enrichment factors for both photoheterotrophic or photoautotrophic oxidation of sulphide to elemental sulphur by *Chromatium vinosum*. Their results showed the product sulphur to be enriched in <sup>34</sup>S (inverse isotope effect) by  $2.4 \pm 0.7\%$ . This is in reasonable agreement with the average for the earlier work referred to above. Fry *et al.* (1983) point out that the small inverse isotope effect observed during sulphide oxidation is likely to be associated with proton equilibria in the sulphide system. The equilibrium isotope effect in the exchange reaction

$$H_2^{32}S + H^{34}S^- \rightleftharpoons H_2^{34}S + H^{32}S^-$$

is 6‰ (Table 1.1), favouring <sup>34</sup>S in the H<sub>2</sub>S. Thus if the <sup>34</sup>S enriched H<sub>2</sub>S is the active component utilized by the cell, in the photosynthetic oxidation of sulphide, small inverse isotope effects will result. The actual magnitude will be of the order of 2–3‰ depending on the pH and proportions of H<sub>2</sub>S and HS in the medium.

Chemosynthetic oxidation of sulphide in the presence of oxygen may involve larger isotope effects. This is suggested by the data of Kaplan and Rittenberg (1964), where large normal isotope effects ( $^{32}$ S species reacting faster) of up to -18% were observed with aerated cultures of *Thiobacillus concretivorous*. Extensive formation and accumulation of polythionates occurred in the cultures of these experiments enriched consistently in heavier isotopes by 0.6–19.0‰.

In the geological record, therefore, oxidized forms of sulphur thought to be derived from particular sulphide phases may be expected to differ isotopically from the precursor only if the mechanism of oxidation has been aerobic.

# **1.3.2** The marine sedimentary cycle

Clearly the major isotope fractionation in the sedimentary cycle occurs in the bacterial reduction of seawater sulphate to  $H_2S$  in anaerobic bottom waters and shallow sediments. The reduced sulphur in marine sediments, largely fixed as FeS and FeS<sub>2</sub>, is therefore isotopically light or depleted in <sup>34</sup>S relative to seawater sulphate by up to 70‰ (SCOPE 19, 1983).

The actual  $\delta^{34}$ S value of the sedimentary sulphides relative to sea water will depend on several factors. Firstly, it will depend on the isotope effect in the bacterial reduction of sulphate under the environmental conditions prevailing, such as available organic matter, etc. Secondly, it will depend on the fraction of the sulphides that may be considered formed in an 'open' system at the sea sediment interface with an infinite pool of sulphate and on the fraction that may be considered in a 'closed' system after burial. In an 'open' system, the full isotope effect will be realized, whereas in the 'closed' system, there is no net isotope fractionation after complete reduction of residual sulphate.

The extent to which sulphate reduction takes place in an 'open' or 'closed' system will depend largely on reducing conditions and sedimentation rates. Two extreme cases are Black Sea sediments, in which  $\delta^{34}$ S values for sulphide are displaced by up to 55% relative to the sea sulphate (sea anoxic and sedimentation rates are low—at 0.1 mm yr<sup>-1</sup>; Vinogradov *et al.*, 1962), and sediments off the coast of Venezuela, in which  $\delta^{34}$ S values of the sulphides are displaced by only 15‰ relative to the sea sulphate (water column oxygenated sedimentation rate is 25 cm yr<sup>-1</sup>; Thode *et al.*, 1960). Some reduced sulphur in sediments is derived from plant decay. Plant metabolism of marine sulphate does not involve sulphur isotope selectivity. However, in view of the low sulphur content of plant organic matter (generally 0.1–1%), this component of reduced sulphur in marine sediments is usually relatively small.

The fractionation of sulphur isotopes in the bacterial reduction of marine sulphate and the flux of reduced sulphur depleted in <sup>34</sup>S into the sediments has led to a build-up of <sup>34</sup>S in the oceans, beginning with the rise of sulphate reducers possibly in the late Archean starting with  $\delta^{34}S_{ocean}SO_4^{2-} = 0$  (Thode and Goodwin, 1983).

Except near freshwater contributaries, present-day ocean sulphate is remarkably uniform with  $\delta^{34}$ S values near +21‰ (this value is based on the latest findings using SF<sub>6</sub> by Rees (1978). Earlier workers using SO<sub>2</sub> reported values around +20.3‰.) However, data from evaporite deposits attest to significant temporal isotopic variations in the ancient oceans (Thode and Monster, 1964; Nielsen and Ricke, 1964; Thode and Monster, 1965; Holser and Kaplan, 1966; Davies and Krouse, 1975). Figure 4.2, Section 4.2.2.2 shows the spread in  $\delta^{34}$ S values for evaporites of a given age. Both the lowest and mean values have been considered as the closest approach to the value for the contemporaneous ocean. The higher  $\delta^{34}S$  values result for evaporites deposited from restricted or inland seas where the time constant for change in  $\delta^{34}S$  is small relative to the oceans.

The  $\delta^{34}$ S values for marine sulphate, uniform at +21‰ today, has varied between a minimum of about +10‰ and a maximum of about +30‰ over the last 400 million years (see Section 4.2). Rees (1970) and Holland (1973) have modelled these changes which have been caused by biological activity and changes in relative fluxes of sulphide and sulphate mineral precipitation.

Further, biological isotope fractionations superimposed on the  $\delta^{34}$ S variations of the ancient oceans accounts for the large spread in  $\delta^{34}$ S values found for sulphides in sedimentary rocks. Deposits related to ancient oceans such as Pb–Zn ores (Campbell *et al.*, 1968; Sasaki and Krouse, 1969; Sangster, 1968; Vredenberg and Cheney, 1971) are generally enriched in <sup>34</sup>S upwards to the  $\delta^{34}$ S values identified with associated evaporites.

## 1.3.3 Fossil fuels

Thode and Monster (1965) found petroleum and associated H<sub>2</sub>S to be on the average some 16‰ depleted in <sup>34</sup>S as compared to related evaporites. However,  $\delta^{34}$ S values for petroleum may be altered during certain oil transformation processes (Orr, 1974; Thode, 1981). In certain hightemperature transformations, hydrogen sulphide formed by the thermochemical reduction of evaporitic sulphate, with little or no isotope fractionation, is introduced into the petroleum, thus altering its  $\delta^{34}$ S values. Similar hightemperature reduction of sulphate can account for the high  $\delta^{34}$ S values of H<sub>2</sub>S in the sour gas wells of Alberta, Canada, in the range of those for the associated evaporites (Krouse, 1980). Although petroleum  $\delta^{34}$ S values vary from -10 to +40% (Figure 1.4), individual large pools and pools of genetically related deposits are exceedingly uniform in isotopic content (Thode and Rees, 1970). Sulphur isotope variations in petroleum have been reviewed by Krouse (1977) (see also Sections 4.5.3 and 4.5.4).

Coal originates from plants in continental or swamp areas. In most coals, the sulphur occurs primarily as organic and pyrite sulphur. In freshwater coastal plain peats and many lignites, organic sulphur dominates; sulphate is important and pyrite is minor. Thus the transformationi of peat to coal appears to involve an increase in pyrite principally at the expense of organic sulphur. Recent studies of sulphur transformation in peat across the Everglades basin in Florida indicate that pyrite formation in organic-rich swamps depends on the use of organic oxysulphur compounds in dissimilatory respiration by sulphur reducing bacteria (Altschuler *et al.*, 1983). Since this process would take place essentially in a closed system, the net sulphur isotope fractionation would in most cases be small. Thus in low sulphur

coals, the  $\delta^{34}$ S values would essentially reflect that of the sulphate nutrient in the swamp area.

The total sulphur and pyrite become more prominent in peats of brackish or marine environments and in coal derived from such peats. However, most of the sulphur in high sulphur coals (> 1% sulphur) comes from pyrite inclusions and the  $\delta^{34}$ S ranges of coal of different ages and origins vary greatly, as indicated in Figure 4.15 (see also Sections 4.5.1 and 4.5.2).

# **1.4 SULPHUR ISOTOPES IN THE ATMOSPHERE**

The concentration and isotopic composition of sulphur in the atmosphere can be highly variable and highly source dependent (see also Chapter 5). Nielsen (1974) has summarized the major contributors to atmospheric sulphur and in addition has given estimates of their isotopic compositions.

According to Nielsen the major natural contributors to the global atmospheric sulphur budget are as follows:

- (a) Volcanic exhalations. The present-day addition of volcanic sulphur is probably rather minor (estimates range from 2–5%), although of course most of the sulphur on the surface of the earth had as its origin the outgassing of the deep crust and mantle. As mentioned previously, volcanic sulphur exhalations probably centre around  $\delta^{34}S = 0$  with a total spread of ~15‰ (see also Section 4.6).
- (b) Hydrogen sulphide from anoxic ocean waters. Transfer of such hydrogen sulphide to the atmosphere can only take place under special circumstances, as, for example, when deeper water masses are stirred by heavy storms. Under normal conditions, any hydrogen sulphide released from anoxic bottom waters will be oxidized to sulphate by dissolved oxygen in the water column long before it can reach the ocean surface. The  $\delta^{34}$ S value of any hydrogen sulphide released in this manner will be negative with respect to seawater sulphate, reflecting its biological origin.
- (c) Hydrogen sulphide from sea marshes and intertidal flats. Again because of the fast oxidation of hydrogen sulphide in the presence of oxygen, this has been considered a minor source of isotopically light sulphur. However, direct measurements by Hansen *et al.* (1978) indicate very significant emissions from shallow littoral sediments of the North Sea ranging from 18 g S m<sup>-2</sup> yr<sup>-1</sup> from sediments with 1% organic matter to 450 g S m<sup>-2</sup> yr<sup>-1</sup> for sediments highly enriched in organic matter. These results are in agreement with those of other investigations obtained for sediments on the coasts of the Barentzov and Caspian seas and the sea of Azov. The  $\delta^{34}$ S values obtained for the release of H<sub>2</sub>S by 'sulphate reducers' from similar littoral sediments of the Eastern Sivash (Chukhrov *et al.*, 1975) have an average value of 4‰ as compared to seawater

sulphate at 21‰. Estimates of global emissions of light gaseous reduced sulphur compounds into the atmosphere range up to 34 Tg yr<sup>-1</sup> or  $\sim 6\%$  of total emissions (Granat *et al.*, 1976; Rjaboshapko *et al.*, 1978).

- (d) Sea spray. Sulphate is transferred from the ocean to the atmosphere by wave action at the ocean surface producing aerosols. This sulphate has a  $\delta^{34}$ S value of +21‰, reflecting its ocean water source, and can be transported by wind onto continental regions.
- (e) Biogenic volatile sulphur compounds in continental areas from decay of organic matter. In a given area, this sulphur must isotopically reflect its derivation from sulphate in rain water, rivers, lakes, soils, etc. Such emissions are absent in arid regions but may be high in tropical swamps. In general this sulphur is isotopically lighter than seawater sulphate.

It is necessary to add one further category to those considered by Nielsen.

(f) Dimethyl sulphide. According to Maroulis and Bandy (1977) and Graedel (1979), for example, dimethyl sulphide is probably a major source of atmospheric sulphur. This compound, which can be produced by marine algae, is a more likely source of reduced sulphur from the oceans than is hydrogen sulphide. Little is known about the isotopic composition of dimethyl sulphide. An estimate is given in Section 5.5.6.

The anthropogenic fluxes of sulphur to the atmosphere result from the utilization in industry of sulphur compounds themselves and from the utilization of other materials that contain sulphur as an unwanted or unavoidable by-product. These sources may be summarized as follows:

(a) Native sulphur and hydrogen sulphide. These compounds are produced as a concomitant of natural gas use or from large sulphur deposits in salt domes of the Gulf Coast area and other parts of the world, and have  $\delta^{34}$ S values ~15‰ light relative to associated sulphates, reflecting their biological origin (see Section 4.4).

Sulphur dioxide and traces of hydrogen sulphide from the processing of 'sour' gas wells can be a major source of atmospheric sulphur in certain locations (see Section 8.2).

- (b) Sulphide ores. The δ<sup>34</sup>S values of sulphide ores are highly variable and atmospheric contributions will be highly source dependent. Specific ore bodies are usually homogeneous and have distinctive δ<sup>34</sup>S values (see Section 4.3). Sulphur from sulphide ore is emitted to the atmosphere from smelters and in the emission can be either as sulphate formed directly in high-temperature processes or as sulphur dioxide which can be oxidized further to sulphate during its atmospheric residence.
- (c) Coal. As mentioned above, most of the sulphur in coal comes from

pyrite inclusions and its values therefore vary widely. However, low sulphur coals  $<\sim 1\%$  will have  $\delta^{34}S$  values, reflecting that of the organic matter from which the coal was formed.

(d) Petroleum. Although the isotopic composition of sulphur in petroleum is variable (Thode and Rees, 1970), the sulphur in particular oil reservoirs and horizons tends to be rather homogeneous isotopically. In general  $\delta^{34}$ S oils tend to be 15‰ light relative to the sulphate in the oceans at the time of oil formation.



Figure 1.4 Synopsis of  $\delta^{34}$ S distributions in major source materials of atmospheric sulfur (Nielsen, 1974)

Figure 1.4 gives a synopsis of  $\delta^{34}S$  distribution patterns in the major source materials of atmospheric sulphur. Thus the  $\delta^{34}S$  value of a particular atmospheric sample reflects the averaging of many inputs. To the extent that there is mixing and long-distance transport, characteristic  $\delta^{34}S$  values should be expected for continental, maritime, and transitional regions, particularly in remote areas from dominant local sources.

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## 1.5 RAIN WATER

The principal source of sulphate in rain water over ocean is sea spray. The  $\delta^{34}$ S values of the ocean atmosphere (Atlantic and Pacific) far offshore range from +12 to +18‰ (Chukhrov *et al.*, 1980). These low values relative to sea sulphate have been explained by the mixing of the atmosphere with biogenic sulphur carried over from the continents. There is also the possibility of a biogenic source of sulphur from the ocean itself, perhaps involving both hydrogen and sulphur and dimethyl sulphide. Rainwater sulphate over the continents is, on the other hand, isotopically much lighter, indicating a relatively high proportion of biogenic sulphur.

#### 1.5.1 Ocean sulphate in rain water

A number of attempts have been made to determine the fraction of sulphate in rain water (atmosphere) in various regions derived from the oceans, which will have a  $\delta^{34}$ S value of +21‰. The estimates of the so-called excess sulphur, or non-marine sulphate in the atmosphere, are usually based on the ratio of (SO<sub>4</sub><sup>2-</sup>)/(Cl<sup>-</sup>) in the atmospheric samples as compared to the ocean water. If no fractionation of the ions occurs during the transfer from ocean to the atmosphere then (SO<sub>4</sub><sup>2-</sup>)<sub>excess</sub> = (SO<sub>4</sub><sup>2-</sup>)<sub>total</sub> - 0.14 Cl<sup>-</sup>, where the ratio of (SO<sub>4</sub><sup>2-</sup>)/(Cl<sup>-</sup>) in sea water is 0.14. However, there is fractionation of the ions during transfer and according to Korhz (1976) the contribution of marine sulphates to the global atmosphere should be calculated according to the empirical formula:

$$(SO_4^{2-})_{excess} = (SO_4^{2-})_{total} - 0.38Cl^{-}$$

The mechanism of ion fractionation is not known; however, the values for  $(SO_4^{2-})/(Cl^-)$  ratios from 0.14 to ~0.40 seem to relate to carrier particle sizes in the atmosphere. For example, at 6 km inland, the ratio increases by a factor of 2 from that offshore, suggesting that the smaller particles which penetrate deeper in the continent have considerably higher  $(SO_4^{2-})/(Cl^-)$  ratios (Yaalon and Lomas, 1970). Estimates of the fraction of sulphate in the continental atmosphere derived from ocean spray range from 8 to 35%, based on  $(SO_4^{2-})/(Cl^-)$  ratios in precipitation and river runoff samples (Korhz, 1976; Inland Waters Directorate Environment Canada, 1977–79). Early  $\delta^{34}S$  measurements of sulphate in snow and rain samples from remote continental areas gave values between +4.0 and +6‰, or ~15‰ light relative to seawater sulphate (Ostlund, 1959), thus providing evidence for a major component of natural sulphur of biogenic origin in the global atmosphere. Rainwater samples collected from remote areas in the Canadian shield and other similar areas of the world have  $\delta^{34}S$  values ranging from

+2.2 to +4.2‰ (Kramer and Snyder, 1977; Chukhrov *et al.*, 1980; Nriagu and Coker, 1978b). By comparison, rainfall (sulphur) over oceans far offshore have  $\delta^{34}$ S values ranging from +12 to +18‰ (Chukhrov *et al.*, 1980; Rafter and Mizutani, 1967). The  $\delta^{34}$ S values lower than +21‰ are attributed to biogenic sulphur in air masses coming from the continents or from the oceans themselves, perhaps due to methyl sulphide emissions as well as H<sub>2</sub>S.

# 1.6 LAKES AND RIVERS

A wide range of sulphur isotope ratios arise in the environment regardless of man's activities. For example, rivers flowing through a sedimentary rock terrain such as the MacKenzie River in Canada's Northwest Territory exhibit a wide range of  $\delta^{34}$ S values which can be related to the geological strata along its course (Hitchon and Krouse, 1972). Also freshwater lakes with relatively high sulphate contents (karst lakes) which occur widely where evaporite-bearing rocks lie near the surface, will have  $\delta^{34}$ S values reflecting those of the source sulphates enriched in <sup>34</sup>S. Furthermore, considerable fractionation of the sulphur isotopes may occur in these lakes due to the bacterial reduction of sulphate (which may occur either in the shallow sediments or in the anoxic water column). The extent of sulphur isotopic fractionation in these lakes increases with the sulphate concentratinn, rising to a 55‰ spread between sulphide and residual sulphate similar to that in the Black Sea at high sulphate concentrations (Deevey *et al.*, 1963; Matrosov *et al.*, 1975; Vinogradov *et al.*, 1962).

However, in lakes with very low sulphate concentrations (0.5–4.0 mg of  $SO_4^{2-}/litre$ ) in remote areas of continental shield terrain, there is no evidence of sulphur isotopic fractionation due to sulphate reducers and the  $\delta^{34}S$  values of the sulphate reflect that of the rain water in the absence of other natural sources. In the same way, sulphur in the lake sediments, the soil, and vegetation in these areas will have  $\delta^{34}S$  values centered around that of the rain water for that area.

## **1.7 VEGETATION**

Land plants and organic matter in sediments derived from land plants may play an important role in environmental studies. For example, studies of organic matter in lake core sediments as a function of depth provide an opportunity to follow historical changes in the  $\delta^{34}$ S base level values for an area or drainage basin (Nriagu and Coker, 1983; Thode and Dickman, 1983). Plants may absorb and metabolize sulphate from the soil or SO<sub>2</sub> from the atmosphere through the leaves (see Section 7.2.5). The main source of plant sulphur in soils whose parent rock contains little or no sulphides or

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sulphates is atmospheric precipitation. Since there is little or no fractionation of the sulphur isotopes in plant metabolism, plants in these areas will have  $\delta^{34}$ S values reflecting that in the rain water. For example, the  $\delta^{34}$ S values of the total sulphur in plant samples from the remote Kazalehstan steppe area in the Soviet Union centre around +2.0‰, which is consistent with average  $\delta^{34}$ S values of 3.2 and +3.0‰ for the sulphate in rain and soil samples respectively for the same area (Chukhrov *et al.*, 1980).

## 1.8 APPLICATIONS

Stable isotopes of sulphur have been used to trace the movements of sulphur compounds in the atmosphere, rivers, lake water, and ground water. A series of studies originating from the Brookhaven National Laboratories have demonstrated the usefulness of sulphur isotopes in tracing the sulphur emitted from power plants and the oxidation to sulphate of sulphur dioxide present in emission plumes (Newman et al., 1975; Forrest and Newman, 1977a, 1977b). Papers by Forrest and Newman (1977a, 1977b), Kramer and Snyder (1977), Nriagu and Coker (1978a, 1978b), and Nriagu and Harvey (1978) give details of isotopic studies of atmospheric and lake samples downwind from the Sudbury smelter. Holt et al. (1972) showed that sulphur with a unique  $\delta^{34}$ S value could be followed from deep wells through sewage processing and into the effluent. Case and Krouse (1980) have used sulphur isotope ratio studies in the elucidation of sources, mixing and dispersion of sulphur compounds in the atmosphere and hydrosphere. In these studies plots of  $\delta^{34}$ S values versus sulphur content at various distances from a known source proved useful in determining the impact of the source over the area and the fate of sulphur compounds.

The oxygen isotopes used widely as indicators in the study of geological processes have been used along with sulphur isotopes to identify sulphate sources asnd to elucidate mode of formation of sulphate in the atmosphere (Holt *et al.*, 1981; see Chapter 2).

In summary, sulphur isotope studies have already been used extensively in testing regional sulphur flux models, and in identifying and determining the impact of natural and anthropological sources of sulphur on the environment. These studies have been reviewed by a number of authors (Nriagu, 1978; Krouse, 1980; Ivanov, 1981) and will be the subject of later chapters in this book.

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