CHAPTER 6
Hydrosphere


6.1 INTRODUCTION*

Although isotope hydrology is a well-established field, the sulphur isotope systematics of natural waters have not been extensively studied. The isotopic composition of sulphur in sea water is remarkably constant, and that of sulphur in fresh waters so variable that it is difficult to gain fundamental insights of key processes and pathways. With the exception of the pioneering work of Deevey and his collaborators in the early 1960s (see Section 6.4), little was published on the isotope geochemistry of sulphur compounds in unpolluted freshwater ecosystems until the early 1970s.

With the recent development of ‘environmental isotope’ techniques, a number of detailed investigations were undertaken to (a) identify sources of sulphur; (b) determine the pollution component; and (c) trace the fate of sulphur in aquatic ecosystems. Simultaneously, significant advances were made in the use of sulphur and oxygen isotopes as complimentary tools in other areas of applied geochemistry. Of particular interest is the use of isotopic techniques to (a) ‘date’ ground water; (b) identify the recharge area and origin of sulphur; (c) infer groundwater circulation patterns, and (d) evaluate the migration rate, reactions, and extent of equilibration of the sulphur compounds (see Section 6.7).

More recently, interest in sulphur isotope measurements has been heightened by the association of sulphur pollution with acid rain. Acid rain is threatening fisheries’ resources and water quality of many lakes and rivers in Europe and North America. Variations in the isotope abundances of sulphur and oxygen in sulphate and sulphur oxides are ideally suited for acid rain studies. Isotopic compositions can be used for fingerprinting the sources of sulphur pollution as well as monitoring the long-range and transboundary movement of the pollutant sulphur. This chapter includes illustrative case studies pertaining to stable sulphur/oxygen isotopes in relation to lake and river acidification.

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Foremost, this chapter should serve to emphasize the fact that sulphur/oxygen isotopy provides the basis for a powerful but undeveloped tool in the aquatic sciences. Only recently have sulphur isotopes been applied to foodweb studies. Furthermore, the available data are sparse and focus mainly on local areas in Europe and North America. Little has been done on sulphur isotope systematics in the ecosystems of developing countries. With the current data base, it would be premature to attempt even a rudimentary model of sulphur isotope balance on a regional or global scale. An isotopic balance model should constrain current estimates of sources (natural versus anthropogenic) and elucidate sulphur transfer processes and the rates of sulphur turnover in natural waters. In other words, it should provide much needed checks for various models of the global sulphur cycle.

6.2 OCEANS

6.2.1 Dissolved sulphate*

Sulphur is present in the ocean in the form of dissolved sulphates, predominantly NaSO₄⁻, MgSO₄⁰, CaSO₄⁻, KSO₄⁻, and SO₄²⁻ (Garrels and Thompson, 1962; Kester and Pytkowicz, 1969), with an average concentration of 0.904 g S kg⁻¹ (Horn, 1969). Taking the mass of water in the world ocean to be 1.43 × 10¹² Tg gives the total mass of sulphate sulphur as 1.277 × 10⁹ Tg S (Horn, 1969). The flux of sulphur to and from the ocean is ~300 Tg S yr⁻¹ (see below) so that the residence time of sulphur in the ocean is ~1.277 × 10⁹ Tg S ÷ 300 Tg S yr⁻¹ or ~4 × 10⁶ yr.

In contrast to the long residence time of sulphate in the ocean, the relatively short oceanic mixing time of ~1000 years ensures that the sulphur isotopic composition of ocean sulphate is essentially uniform except in regions where local influences such as the mouths of rivers are important.

Measurements of the δ³⁴S values of suites of ocean water samples have been made by Ault and Kulp (1959), Thode et al. (1961), Sasaki (1972), and Rees et al. (1978). The results of these studies are summarized in Table 6.1. The mean values obtained in the first three studies agree very well whereas the decrease in the spreads of δ³⁴S values obtained in successive studies is indicative of the improvement with time of analytical precision.

The mean value of +20.99‰ obtained by Rees et al. (1978) is markedly different from the mean values of around +20.0‰ obtained in the earlier studies. This difference is due to the fact that this latter study was made using sulphur hexafluoride (SF₆) as the gas for isotope analysis whereas the previous studies employed sulphur dioxide (SO₂). Rees (1978, Section 2.1)

* C.E Rees.
points out that results obtained using SF$_6$ are more precise and, more importantly, more accurate than those obtained using SO$_2$.

It is of interest to speculate on whether the sulphur isotope composition of present-day ocean sulphate is constant or if its $\delta^{34}S$ value is increasing or decreasing with time.

The $\delta^{34}S$ value of ocean water sulphate is controlled by the magnitudes of the various fluxes to and from the oceanic sulphate reservoir and by the isotopic compositions of these fluxes. Examination of the $\delta^{34}S$ values of evaporitic sulphates which were derived from the dissolved sulphate in ancient oceans has shown that the isotopic composition of oceanic sulphate has not been constant over geological time (Thode and Monster, 1964, 1965; Nielsen, 1965; Holser and Kaplan, 1966; Schidlowski et al., 1977; Claypool et al., 1980). The implication of these variations in terms of variations of the relative rates of evaporite and sedimentary sulphide formation, as well as of the global atmospheric oxygen budget, has been discussed by the authors cited above and by Rees (1970) and Holland (1973). The topic is covered in detail by Pilot (Section 4.2).

With regard to the present-day ocean, it is important to note that its sulphate content is possibly not in balance. Table 6.2 contains some flux data taken from Table 7.1 of Ivanov (1983). Some of the individual fluxes listed by Ivanov have been combined for the purpose of the calculations developed later in this section. The total flux of sulphur to the ocean ($P_{10} + P_{20}$) is estimated to be $\sim 480$ Tg S yr$^{-1}$ while the total flux of sulphur from the ocean ($P_{10} + P_{19} + P_{21} + P_{22}$) is estimated to be $\sim 7$ Tg S yr$^{-1}$. Thus the estimated input exceeds the estimated output by $\sim 180$ Tg S yr$^{-1}$ or $\sim 60\%$.

Table 6.1 Summary of $\delta^{34}S$ determinations for present-day ocean water sulphate

<table>
<thead>
<tr>
<th>Study</th>
<th>Number of samples</th>
<th>Range of $\delta^{34}S$ values (%)</th>
<th>Spread of $\delta^{34}S$ (%)</th>
<th>Mean $\delta^{34}S$ (%)</th>
<th>$\sigma_{m}^a$ (%)</th>
<th>$\sigma_{i}^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ault and Kulp</td>
<td>25</td>
<td>+18.9 to +20.7</td>
<td>1.8</td>
<td>+20.0</td>
<td>0.1</td>
<td>0.54</td>
</tr>
<tr>
<td>Thode et al.</td>
<td>16</td>
<td>+19.3 to 20.8</td>
<td>1.5</td>
<td>+20.1</td>
<td>0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>Sasaki (1972)</td>
<td>20</td>
<td>20.32 to 20.72</td>
<td>0.70</td>
<td>+20.03</td>
<td>0.05</td>
<td>0.21</td>
</tr>
<tr>
<td>Rees et al. (1978)</td>
<td>25</td>
<td>21.12 to 20.74</td>
<td>0.38</td>
<td>+20.99</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>

$^a$ Standard deviation of the mean.

$^b$ Standard deviation of an individual determination $\sigma_{i} = \sigma_{m} \sqrt{N}$. 

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Hydrosphere
Table 6.2 Calculations of the rate of change of the present-day $\delta^{34}S$ value of ocean water sulphate

<table>
<thead>
<tr>
<th>Fluxes (Ivanov, 1983)</th>
<th>This work</th>
<th>$\delta^{34}S$ value (%o)</th>
<th>Flux values (Tg S yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Continental atmosphere to oceanic atmosphere ($P_8$) and volcanic emissions ($P_{17}$)</td>
<td>$\delta_8 = +5$</td>
<td>110</td>
<td>160</td>
</tr>
<tr>
<td>River ($P_{10}$), underground runoff ($P_{11}$), shore abrasion ($P_{13}$)</td>
<td>$\delta_{10} = +5$</td>
<td>220</td>
<td>270</td>
</tr>
<tr>
<td>Biogenic emission to oceanic atmosphere ($P_{18}$)</td>
<td>$\delta_A - \alpha$</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>Ocean spray sulphate to oceanic atmosphere ($P_{19}$)</td>
<td>$\delta_A$</td>
<td>140</td>
<td>190</td>
</tr>
<tr>
<td>Atmospheric sulphur compounds to ocean ($P_{20}$)</td>
<td>$\delta_{AT}$</td>
<td>260</td>
<td>310</td>
</tr>
<tr>
<td>Removal of reduced sulphur in sediments ($P_{21}$)</td>
<td>$\delta_A - \beta$</td>
<td>110</td>
<td>160</td>
</tr>
<tr>
<td>Removal of sulphate in sediments ($P_{22}$)</td>
<td>$\delta_A$</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>$\alpha$ (%o)</td>
<td>15</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>$\beta$ (%o)</td>
<td>50</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>$\delta^{34}S$ of atmospheric sulphate (%o)</td>
<td>+13.4</td>
<td>+12.1</td>
<td>+13.4</td>
</tr>
<tr>
<td>$\Delta \delta^{34}S$ ocean sulphate (%o per million years)</td>
<td>+0.2</td>
<td>0</td>
<td>-0.4</td>
</tr>
</tbody>
</table>
It is not clear whether this estimated difference between input and output is real or if it is an artefact of the uncertainties in the individual flux estimates. For example, previous estimates of the biogenic emission from the ocean have varied widely—170 Tg S yr\(^{-1}\) (Eriksson, 1960), 30 Tg S yr\(^{-1}\) (Robinson and Robbins, 1970), 48 Tg S yr\(^{-1}\) (Friend, 1973), 27 Tg S yr\(^{-1}\) (Granat et al., 1976). Recently Nguyen et al. (1978) have estimated a marine flux of dimethyl sulphide (DMS) of at least 89 Tg S yr\(^{-1}\), possibly in addition to other biological contributions.

Because there are uncertainties in the various flux estimates, calculations are performed below to determine the rate of change with time of the present-day \(\delta^{34}\text{S}\) value of oceanic sulphate for both the flux estimates presented by Ivanov (1983) and for other possible values.

Let \(A\) represent the present-day value of the sulphate sulphur content of the ocean and let \(I_i, F_j\) \((i = 1,2,...; j = 1,2,...)\) represent the various present-day fluxes of sulphur into \((I)\) and from \((F)\) the ocean. The rate of change of \(A\) with time is

\[
\frac{dA}{dt} = \sum_i I_i - \sum_j F_j
\]

For \(^{32}\text{S}\) and \(^{34}\text{S}\) write

\[
\frac{d^{32}A}{dt} = \sum_i ^{32}I_i - \sum_j ^{32}F_j
\]

and

\[
\frac{d^{34}A}{dt} = \sum_i ^{34}I_i - \sum_j ^{34}F_j
\]

This last equation can be expressed in terms of del values by writing

\[
^{34}A = ^{32}A R_o (1 + \delta_A)
\]

\[
^{34}I_i = ^{32}I_i R_o (1 + \delta_I)
\]

and

\[
^{34}F_j = ^{32}F_j R_o (1 + \delta_F)
\]

where \(R_o\) represents the \(^{34}\text{S}/^{32}\text{S}\) value of the standard reference material (Canyon Diablo troilite) and where \(\delta_A, \delta_I, \delta_F\) represent the fractional del values of \(A, I, F\) relative to the standard reference material. Making these substitutions in the equation for \(\frac{d^{34}A}{dt}\) gives
\[
\frac{d[{}^{32}A \text{R}_0(1 + \delta_A)]}{dt} = \sum_i {}^{32}I_i \text{R}_0(1 + \delta_{I_i}) - \sum_j {}^{32}F_j \text{R}_0(1 + \delta_{F_j})
\]

Cancelling \text{R}_0 throughout and making the assumption that the behaviour of the element, \(A\), and that of the abundant isotope, \(^{32}A\), are essentially identical gives

\[
\frac{d[A(1 + \delta_A)]}{dt} = \sum_i I_i(1 + \delta_{I_i}) - \sum_j F_j(1 + \delta_{F_j})
\]

so that, expanding the differential,

\[
(1 + \delta_A) \frac{dA}{dt} + A \frac{d\delta_A}{dt} = \sum_i I_i(1 + \delta_{I_i}) - \sum_j F_j(1 + \delta_{F_j})
\]

Using

\[
\frac{dA}{dt} = \sum_i I_i - \sum_j F_j
\]

and rearranging the previous equation gives

\[
A \frac{d\delta_A}{dt} = \sum_i I_i(\delta_{I_i} - \delta_A) - \sum_j F_j(\delta_{F_j} - \delta_A)
\]

In Table 6.2, \(\delta^{34}S\) assignments for the various sulphur fluxes are given. The assignment of +5\% for \(P_8\) and \(P_{10}\) may not be exact but will serve for calculation purposes. The \(\delta^{34}S\) value of the flux of atmospheric sulphate to the ocean, \(P_{20}\), is assumed to be equal to the \(\delta^{34}S\) value of atmospheric sulphate and is designated \(\delta_{\text{AT}}\) in the table. It will be assumed that \(\delta_{\text{AT}}\) is determined by the various fluxes to the oceanic atmosphere:

\[
\delta_{\text{AT}} = \frac{\delta_8 P_8 + \delta_9 P_{19} + (\delta_A - \alpha) P_{18}}{P_8 + P_{19} + P_{18}}
\]

This is equivalent to assuming that none of the fluxes from the reservoir of oceanic atmospheric sulphate involves isotope fractionation relative to that reservoir.

The equation for \(d\delta_A/dt\) can now be written as

\[
A \frac{d\delta_A}{dt} = P_{10}(\delta_{10} - \delta_A) + P_{20}(\delta_{\text{AT}} - \delta_A)
\]
\[-P_{18}(\delta_A - \alpha - \delta_A) - P_{19}(\delta_A - \delta_A)\]
\[-P_{21}(\delta_A - \beta - \delta_A) - P_{22}(\delta_A - \delta_A)\]
\[= P_{10}(\delta_{10} - \delta_A) + P_{20}(\delta_{AT} - \delta_A) + \alpha P_{18} + \beta P_{21}\]

In this expression, $\alpha$ represents the difference in $\delta^{34}$S values of ocean water sulphate and the biogenic sulphur flux to the atmosphere, while $\beta$ represents the difference in the $\delta^{34}$S values of ocean water sulphate and sulphide being deposited in the ocean sediments.

Column 1 of Table 6.2 shows the flux values quoted by Ivanov (1983) rounded off to the nearest 10 Tg S yr$^{-1}$. These fluxes, their assigned del values, and values for $\alpha$ (15%) and $\beta$ (50%) were inserted in the equations developed above. The calculated values of $\delta^{34}$S for the atmosphere and the rate of change of $\delta^{34}$S of ocean sulphate are +13.4 and +0.2% per million years respectively. The extent to which these values (tabulated at the bottom of column 1) are realistic depends on the accuracies of the assigned fluxes and del values.

Columns 2 to 10 show the effects of altering the various parameters individually including $\alpha$ and $\beta$. Each flux is increased in turn by 50 Tg S yr$^{-1}$. Thus, for example, column 4 shows that if all the parameters are correct except for the estimate for $P_{18}$ (the biogenic emission of sulphur to the atmosphere should be 70 Tg S yr$^{-1}$ rather than 20 Tg S yr$^{-1}$), then the rate of change of $\delta^{34}$S of ocean sulphate should be +0.6 rather than +0.2% per million years.

Column 11 differs from column 1 in that $P_{19}$ and $P_{20}$ have been altered together. Altering $P_{19}$ alone changes the estimated rate of change of $\delta^{34}$S from +0.2 to +0.5% per million years (column 5). Alteration of $P_{19}$ and $P_{20}$ together gives no net change (compare column 1 with column 11).

The values in Table 6.2 show that it is not possible to state unequivocally whether the $\delta^{34}$S value of ocean sulphate is currently increasing, decreasing, or constant. A clear answer requires estimates of the various important fluxes to a much higher degree of certainty than is presently possible.

### 6.2.2 Sulphur of aquatic organisms*

The hydrosphere is a major habitat which actively influences the distribution of chemical elements, particularly sulphur. The total S in animal and plant tissue varies from less than 1 up to 9% by dry weight. On a dry weight basis, the S content of aquatic plants and animal tissues varies from 0.5 to 5 and 0.1 to 3.3% respectively (Vinogradov, 1953; Kaplan et al., 1963; Mekhtiyeva and Pankina, 1968; Mekhtiyeva et al., 1976; Mekhtiyeva, 1971). (Unless stated otherwise, percent S will be given on a dry weight basis.)

* V.L. Mekhtiyeva.
In order to understand their roles in the hydrospheric sulphur cycle, it is important to know the mass and isotopic composition of sulphur forms in marine organisms and changes in these parameters after their death. The available information is sparse.

Mollusc shells, composed mainly of CaCO₃ (up to 95%), contain sulphate and iron sulphur compounds. The average sulphur content is 1% but certain species contain up to 4%. Vinogradov (1953) concluded that sulphur also occurs in conchiolin, the external epidermic layer of shell composed of scleroprotein.

Cephalopoda are particularly rich in sulphur (Vinogradov, 1953). The S content of shells of molluscs from water bodies of different salinities is in the range of 0.01 to 0.13% (Mekhtiyeva, 1974). Kaplan et al. (1963) found 0.26% S in shells of Chlamis latiaurata. There is no direct correlation between water salinity and sulphate content in mollusc shells due to metabolic factors which are species and age dependent. However, the sulphate content in shells generally increases with increasing \([\text{SO}_4^{2-}]\).

Figure 6.1
The isotopic composition of sulphate in shells of molluscs is practically identical to that of dissolved sulphate in their habitat (Kaplan et al., 1963; Mekhtiyeva, 1974; Figure 6.1). After an organism’s death, the amount of sulphur and $\delta^{34}$S values in skeletons do not change. This fact may be used for palaeohydrochemical reconstructions of sediment accumulation in ancient basins (Mekhtiyeva, 1974).

Trace sulphide and sulphate can be extracted from geological specimens using Kiba reagent under vacuum conditions (Ueda and Sakai, 1983). Using this technique, a Puaua shell from New Zealand was found to have $\delta^{34}$S values for sulphate (490 ppm S) and sulphide (30 ppm S) of +21.4 and +7.7%o respectively (Krouse and Ueda, 1987). The error for the latter is relatively large because of its low concentration.

The chitinic tubes of polychaeta are depleted in $^{34}$S by about 13%o compared to dissolved sulphate. This is apparently due to the presence of pyrite inclusions (Kaplan et al., 1963).

Sulphur is generally supplied to plants in the form of sulphate which is reduced in the course of metabolism to thiol groups reacting with serine. As a result, cysteine is produced which is the precursor of the whole series of sulphur-containing amino acids. Natural thiols and disulphides are readily oxidized to produce numerous derivatives of sulphur oxide compounds.

In addition to sulphate, plants may assimilate other sulphur compounds, including hydrogen sulphide (Thomas et al., 1943; Ellis, 1969; Faller, 1972; Brunold and Erisman, 1974, 1975; Fry et al., 1982; see also Chapter 7). The isotopic composition of sulphur in aquatic plants is slightly lighter than that of dissolved sulphate (Figure 6.1). The depletion in $^{34}$S for total sulphur in
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aquatic plants is on the average of 5% for freshwater samples, 1.8% for the Black Sea, 2.3% for the White Sea, 6.5% for the Azov Sea, and 0.8% for the California Gulf. However, one cannot use the average values since species age and season influence metabolic processes and sulphur isotope composition.

The isotope fractionation of sulphur in plant tissue is determined by two factors: diffusion through the cell membrane and biochemical sulphate reduction within the cell. The isotopic effect during $\text{SO}_4^{2-}$ reduction to $\text{H}_2\text{S}$ in plant cells is essentially determined by the relatively slow initial $\text{S-O}$ bond rupture ($\text{SO}_4^{2-}$ to $\text{SO}_3^{2-}$) whereas the $\text{SO}_3^{2-}$ to $\text{H}_2\text{S}$ reduction steps are extremely fast. Further transformations of sulphur without a valency change are not accompanied by significant selectivity.

In most cases, assimilatory sulphate reduction does not lead to significant isotope fractionation. For aquatic organisms, the $k_{32}/k_{34}$ value is usually within the range of 1.000–1.003. Plants in mangrove marshes are unusual in that their total sulphur may be 20% lighter than aqueous sulphate. This is attributed to $\text{H}_2\text{S}$ assimilation by plant roots in the mud (Fry et al., 1982). Another exception is marine grass $\text{Zostera}$ with maximum depletion of 12.7% in $^{34}\text{S}$ as compared to dissolved sulphate.

Comparison of total sulphur content and isotopic data for aquatic plants leads to the following conclusions. The sulphur content falls within the range of 0.2–5%, with the lower values occurring in freshwater species. The sulphur concentration in aquatic plants depends upon their morphology and environmental conditions. Plants with well-developed base tissues (water florals, benthic weeds, macrophytes) contain less sulphur than delicate algae such as $\text{Cladophora}$, $\text{Enteromorpha}$, $\text{Polysiphonia subilifera}$, $\text{Codium vermila}$, etc. (Mekhtiyeva, 1975). In some plants, the sulphur content depends directly upon the sulphate concentration in water. $\text{Enteromorpha}$ is representative of plants with high fractionation factors and low total sulphur contents; $\text{Zostera}$ is quite the opposite with lower fractionation factors and higher sulphur contents (Table 6.3).

In Table 6.3, there is an indication of an inverse relationship between the $\text{S}$ content and the shift in $\delta^{34}\text{S}$ value of aquatic plant tissue with respect to $\text{SO}_4^{2-}$. This is consistent with diffusional fractionation during $\text{SO}_4^{2-}$ transport through the cell membrane.

Higher animals are not capable of reducing sulphate to sulphide and receive reduced sulphur from their food. However, for lower forms in the food chain, the diffusional transport of sulphate through membranes is not excluded. The sulphur content of tissues of aquatic animals is somewhat lower than that of plants. Of all the forms studied, zooplankton from the Indian Ocean proved to be richest in sulphur (3.3%), whereas $\text{Actinia}$ from the Black Sea were the poorest (0.1%). For a variety of similar biotypes, it was found that organisms in basins with higher salinity generally have
Table 6.3 Concentration and isotopic composition of sulphur in *Zostera* and *Enteromorpha* from various basins

<table>
<thead>
<tr>
<th>Sea</th>
<th>Azov Location</th>
<th>Caspian Location</th>
<th>Black Location</th>
<th>White Location</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Zostera</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(percent S)</td>
<td>2.07</td>
<td>2.93</td>
<td>2.57</td>
<td>4.99</td>
</tr>
<tr>
<td>δ¹³⁴S (‰)</td>
<td>-1.9</td>
<td>-0.8</td>
<td>-0.1</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

| *Enteromorpha* (percent S) | 0.29 | 0.38 | -6.2 | 0.81 |
| δ¹³⁴S (‰) | -12.7 | -10.2 | -11.6 | a Compared to dissolved sulphate. |

higher S contents (Mekhtiyeva *et al.*, 1976; Mekhtiyeva, 1975; Mekhtiyeva, 1971; Mekhtiyeva and Pankina, 1968).

Limited data for marine animals show that tissues are depleted in $^{34}$S with respect to sulphate by up to 7‰. Some interesting exceptions are observed. Shrimp from mangrove regions contain sulphur with $\delta^{34}$S = +6‰. The isotope composition of sulphur in animals in hydrothermal ecosystems is close to that of coexisting sulphide minerals with $\delta^{34}$S values ranging from +1 to +4‰ (Fry *et al.*, 1983). Therefore, isotopically light sulphide can obviously be involved in trophic levels of plants and microorganisms.

Fractionation of sulphur isotopes during metabolism in animals is apparently small. Even in tissues of predators such as salmon, seal, and polar bears, which are high in the trophic chain, the isotopic composition of sulphur is close to $\text{SO}_4^{2-}$ assimilated by the lowest numbers (see Section 7.3).

For evaluating the contribution of aquatic organisms to the sulphur pool in sediments, one should know the sulphur isotopic composition of insoluble organic derivatives in living tissues. Mineral and soluble organic compounds are washed away after an organism’s death, whereas insoluble forms are buried in sediments.

Kaplan *et al.* (1963) divided sulphur in marine organisms into organic and mineral forms. Compared to total sulphur, the organic fraction was depleted in $^{34}$S by 1–2‰, whereas the mineral fraction was heavier by 3–4‰.

Mekhtiyeva *et al.* (1976) distinguished three forms of sulphur: (a) soluble organic, represented mainly by glutathione, cystine, cysteine, and coenzyme A, (b) insoluble organic, composed principally of proteins, and (c) mineral sulphur, mainly sulphate.
In both plants and animals, insoluble organic sulphur compounds dominate. The second important form is soluble organic sulphur compounds in animals, but sulphate in plants. In unpolluted environments, the $\delta^{34}S$ of the three sulphur forms are similar for a given specimen with maximum differences of 4.8% for plants and 5.7% for animals. In all organisms, the soluble organic sulphur (compared to total sulphur) is isotopically heavier, whereas the insoluble fraction is lighter. Sulphate in plants is enriched in $^{34}S$, whereas in animals it has a variable composition compared to total sulphur. The comparative $^{34}S$ enrichment in sulphate in plants is consistent with it being the residual of partial metabolism by the cell. Reduced sulphur is concentrated in proteins and thereafter it is transformed into soluble organic compounds which are dominantly oxidized forms. Sulphate in marine animals has a dual origin. It is formed by oxidation of reduced forms and is also supplied from sea water. This conclusion is corroborated by the direct dependence between sulphur contents in animal tissues and $\left[SO_4^{2-}\right]$ in the environment.

Osmotic permeability of cell membranes differs in aquatic organisms. The organisms endowed with high permeability contain high concentrations of sulphate (aspidium, starfish, and sea comb). Animals closely related in classification, e.g. all fish species, and inhabiting similar environments contain nearly equal amounts of various forms of sulphur. Isotopic differences between sulphur in aquatic organisms and the environment are essentially determined by mechanisms of sulphate supply to cells.

The gross production of phytoplankton in oceans is assessed as $2 \times 10^4$ Tg C$_{org}$ yr$^{-1}$ or $3.6 \times 10^4$ Tg of organic matter (dry basis) (Romankevich, 1977). Volkov and Rozanov (1983) assume the average sulphur content in phyto- and zooplankton to be 1%, which suggests that $\sim 360$ Tg S are contributed annually to the oceanic sulphur. Based on Mekhtiyeva (1971), the average sulphur content in oceanic plankton is considerably higher (2.5–3.3%). This suggests that the annual production of planktonic sulphur in the oceans is about $10^3$ Tg. Neither estimate is well founded since there are no sulphur analyses from representative samples of oceanic phytoplankton. Data are available on the content of sulphur in mixed samples of phyto- and zooplankton, and on the variable sulphur content in algae-macrophytes. The higher estimate appears to be more probable as the sulphur content in small plant forms with salt-permeable envelopes is usually higher than in macrophytes.

According to Romankevich (1977), the annual production of phytobenthos in oceans is 300 Tg of dry matter. For an average sulphur content of 2%, this corresponds to 6 Tg of total sulphur or 4.2 Tg of insoluble organic sulphur per annum.

The above estimates suggest that the isotopic composition of total sulphur in aquatic organisms is quite close to that of water sulphate. For planktonic forms, the fractionation factor is 1.0034 (average of three measurements).
Insoluble organic sulphur, which accounts for about 70% of the total sulphur in aquatic organisms, is slightly lighter isotopically (up to 2‰) compared to total sulphur. Decomposition of sulphur organic compounds from dead plankton occurring in the water column may lead to a heavier isotopic composition residual sulphur (by 1–2‰). Thus organic sulphur compounds supplied to the oceans with particulate matter should have \( \delta^{34}S \) values close to +16‰.

For benthic macrophytes, the fractionation factor is lower and in most cases is close to 1.001. The bulk of the benthic biomass is formed by the most distributed oceanic algae Chlorophyta, Phaeophyta, and Rhodophyta, whereas contributions from Zostera and mangroves are insignificant. An average \( \delta^{34}S \) value of +18.5‰ is estimated for the biomass of benthic vegetation, whereas that of their organic sulphur derivatives may be assumed to be +17‰. Dead plants are buried in the proximity of their habitat. Therefore, no significant changes in their mass and isotopic composition occur during the period from their death to burial.

### 6.3 MODERN OCEAN SEDIMENTS*

When preparing SCOPE 19, data reported up to 1980 were used to calculate the isotopic balance of sulphur buried in oceanic sediments. New information on the content of various sulphur forms in sediments, sulphur isotopic composition, and sulphate reduction (Lew, 1981; Lein et al., 1981; Chambers, 1982; Skyring et al., 1983) warranted an updated review. Moreover, the previous SCOPE report did not address fully the geochemical activity of sulphate reducing bacteria in shallow oceanic waters. Interesting ecosystems such as sediments of marshes, tidal flats, and their North European analogues, lidos, were not considered. Intensive sulphate reduction has been studied in these ecosystems in the United Kingdom (MacLeod, 1973; Nedwell and Abram, 1978, 1979; Banat et al., 1981; Nedwell and Banat, 1981), Atlantic USA (Calvert and Ford, 1973; Atkinson and Hall, 1976; Skyring et al., 1979; Shink, 1979; Howarth and Teal, 1979, 1980; Howarth et al., 1983; Stround and Paynter, 1980; King and Wiebe, 1980; Luther et al., 1982; Bouleque et al., 1982; Peterson et al., 1983; Howarth and Giblin, 1983), Pacific USA (Kaplan et al., 1963), and Australia (Chambers, 1982; Skyring et al., 1983).

#### 6.3.1 Intensity of sulphate reduction

Recent investigations showed that microbial sulphate reduction processes are abundant in bottom sediments of continental and marginal seas, various
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geomorphological zones of the ocean to depths of 3000–5000 m, and to limited depths in deep-water trenches. The maximum depth at which sulphate reduction can occur in oceanic sediments has not been established but the process has been documented at a depth of 5–6 m from the silt surface and down to 13 m in Baltic Sea sediments (Lein, 1983).

The intensity of microbial sulphide generation varies from less than 1 μg S kg⁻¹ d⁻¹ in deep-water oceanic sediments to tens of mg S kg⁻¹ d⁻¹ in sediments of the continental Baltic Sea.

However, the highest intensities of sulphide production are found in marshes and tidal flats, including lowland plains along seashores, flooded during high tides or storms. In marshes, soils rich in humus are formed on silt and sand–silt drifts with high Corg content. Such sediments are typical of lowland shores of Great Britain, the Federal Republic of Germany, the Netherlands, and sections of the Atlantic shore of the United States. The total area of such high-tide and low-tide zones is estimated at 6 × 10⁴ km² (Atlas of the Oceans, 1977).

Despite the large number of investigations, the isotopic composition of sulphur has been studied only in sediments of Newport marsh, California, USA (Kaplan et al., 1963) and the Mambray Creek marsh of South Australia (Chambers, 1982).

In marsh sediments, the concentration of sulphate increases with depth. For example, in Newport marsh the sulphate sulphur content in the surface horizon is 0.073% as compared with 0.091% at 30 cm below the surface (Kaplan et al., 1963). Surface water and water squeezed out of green algae had sulphate sulphur concentrations of 0.094 and 0.098% respectively. Therefore, the most active sulphate reduction occurs in the upper (10–20 cm) of marsh sediments. Lower in the column, in the sand underlying the surface silt, reduced sulphur is oxidized due to flushing with O₂-saturated H₂O. Stratified sulphate reduction is characteristic of most marshes. This is also confirmed by changes in Eh values from −300 mV in upper horizons to +100 mV deep in the sediment (Table 6.4). The Corg and Spyrite contents decrease similarly from 1.7 and 0.92% (dry weight basis) in the upper horizon to 0.4 and 0.3% at a depth of 30 cm (Table 6.4). The δ³⁴S values of pyrite change with depth from −20.0‰ (0–5 cm horizon) to −27.7‰ (60–65 cm horizon). Just as in normal sea sediments, free H₂S and acid-soluble sulphides are enriched in ³⁴S by 4–5‰ compared to pyrite sulphur (Table 6.4).

A comprehensive study of the sulphur cycle was carried out from November 1977 to November 1978 in a 10-cm stratum of Mambray Creek marsh sediments (Chambers, 1982). The δ³⁴S values of pyrite varied from −9 to −27‰ (average −17.7‰, 80 determinations at three stations) (Figure 6.3).

Rates of sulphate reduction, measured with ³⁵S-labelled sulphate, ranged from 1.7 to 41 mg S kg⁻¹ d⁻¹ or 100–2400 g S m⁻² yr⁻¹ in sediments of
Table 6.4 Content and isotopic composition of sulphur compounds in Newport marsh sediments and pore water (Kaplan et al., 1963)

<table>
<thead>
<tr>
<th>Horizon (cm)</th>
<th>Eh (mV)</th>
<th>SO₄²⁻ in pore water (%S)*</th>
<th>Pyrite dry sediment (%S)</th>
<th>δ³⁴S (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>0–5</td>
<td>-300</td>
<td>0.073</td>
<td>0.926</td>
<td>+17.0</td>
</tr>
<tr>
<td>30–35</td>
<td>-50</td>
<td>0.077</td>
<td>0.283</td>
<td>+14.3</td>
</tr>
<tr>
<td>60–65</td>
<td>+100</td>
<td>0.091</td>
<td>0.190</td>
<td>+11.6</td>
</tr>
</tbody>
</table>

* Percentage relative to interstitial water content. Other entries on dry weight basis.
Figure 6.3 Values of the $\delta^{34}$S sulphide sulphur from the Mambray Creek deposits (Chambers, 1982)

various marshes (Table 6.5). The annual production of hydrogen sulphide and its derivatives obtained by integrating over high-tide and low-tide zones ranges from $6 \times 10^6$ to $144 \times 10^6$ tonnes of sulphur.

Most of the reduced sulphur formed is oxidized to sulphate, but part of the $\text{H}_2\text{S}$, which is difficult to estimate, evolves to the atmosphere. Evidently only a small fraction of the reduced sulphur is buried in marsh sediments in the form of pyrite with an average $\delta^{34}$S value of about $-17.7\%$.

Table 6.6 summarizes data on the sulphur isotope composition of reduced sulphur compounds and annual intensities of sulphate reduction in sediments of various zones of the ocean.

The data available are insufficient to calculate the reduced sulphur flux in marsh sediments and bottom sediments of shallow water gulf, lagoons,
Table 6.6 Intensity of sulphate reduction, average isotopic composition, production of reduced sulphur, and organic carbon consumption in oceanic sediments

<table>
<thead>
<tr>
<th>Region and depth</th>
<th>Area of sediments (10^6 km²)</th>
<th>Intensity of SO₄²⁻ reduction (μg S kg⁻¹ d⁻¹)</th>
<th>δ³⁴S (%)</th>
<th>Production of reduced sulphur (Tg yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marshes</td>
<td>—</td>
<td>—</td>
<td>−17.7</td>
<td>—</td>
</tr>
<tr>
<td>Gulfs, lagoons, estuaries</td>
<td>—</td>
<td>—</td>
<td>−16.5</td>
<td>—</td>
</tr>
<tr>
<td>Shelf</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–50 m</td>
<td>11 (2)³</td>
<td>55.6</td>
<td>−24.2</td>
<td>79.2</td>
</tr>
<tr>
<td>50–200 m</td>
<td>16 (3)</td>
<td>37.2</td>
<td></td>
<td>53.1</td>
</tr>
<tr>
<td>Continental slope</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200–1000 m</td>
<td>(15)</td>
<td>28.2</td>
<td></td>
<td>201.0</td>
</tr>
<tr>
<td>1000–3000 m</td>
<td>(61)</td>
<td>5.5</td>
<td>−33.2</td>
<td>158.6</td>
</tr>
<tr>
<td>Deep-water sediments</td>
<td>257</td>
<td>1.0</td>
<td>−41.1</td>
<td>—</td>
</tr>
<tr>
<td>Total for the ocean</td>
<td>360 (81)</td>
<td></td>
<td></td>
<td>491.9</td>
</tr>
</tbody>
</table>

³ Data insufficient to calculate average sulphate reduction intensity.
⁴ The figures in parentheses give the areas of biogeochemically active sediments with bacterial sulphate reduction.

and estuaries. It is, however, evident that the total quantity of sulphur buried in these sediments cannot exceed 10–15 Tg S yr⁻¹ globally. Table 6.6 shows a lateral trend in sulphate reduction with the intensity decreasing from littoral towards pelagic sediments.

6.3.2 Rate of bacterial sulphate reduction and other factors influencing the distribution of sulphur compounds and their δ³⁴S values in recent sediments

Analysis of dissolved sulphate in silt and total reduced sulphur in columns of bottom sediments revealed two extreme patterns in sulphur isotope distribution (Figure 6.4). In sediments with intensive pore water sulphate reduction and poor filtering properties (Figure 6.2, st. 655), the isotopic compositions of sulphur of pore-water sulphate and total reduced sulphur approach equality with depth.

In sediments with a constant high SO₄²⁻ content (Figure 6.2, st. 663), reduced sulphur in lower horizons is appreciably depleted in the heavier δ³⁴S.
Both patterns of the distribution of $\delta^{34}S$ values point to the influence of sulphate reduction on fractionation of isotopes in reduced sediments. In the first case, the isotopic composition of sulphur is shifted by the loss of $^{32}S$ in upper silt horizons. In the second case, production of $H_2S$ with a lighter isotopic composition is explained by slower sulphate reduction rates in silt, resulting in greater isotope fractionation as observed in laboratory
Table 6.7 Average isotopic composition of reduced sulphur, sulphate, and total sulphur in world ocean sediments

<table>
<thead>
<tr>
<th>Morphometric zones and depth</th>
<th>Area ($10^6$km$^2$)</th>
<th>Sulphide</th>
<th>Sulphate</th>
<th>Total sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tg S yr$^{-1}$</td>
<td>$\delta^{34}$S (%)</td>
<td>Tg S yr$^{-1}$</td>
</tr>
<tr>
<td>Shelf, 0–200 m</td>
<td>27</td>
<td>10.4</td>
<td>-24.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Continental slope</td>
<td>76</td>
<td>88.0</td>
<td>-33.2</td>
<td>5.3</td>
</tr>
<tr>
<td>and rise</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Ocean bed</td>
<td>257</td>
<td></td>
<td></td>
<td>19.4$^d$</td>
</tr>
<tr>
<td>Total ocean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>360</td>
<td>98.4</td>
<td>-32.2</td>
<td>27.8</td>
</tr>
</tbody>
</table>

$^a$ Gershanovich et al. (1974).
$^b$ According to Volkov and Rozanov (1983).
$^c$ Sulphate dissolved in pore water.
$^d$ Solid phase sulphate.
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The substantial increase in the fractionation of sulphur isotopes with decreasing intensity of sulphate reduction is expressed in the ranges of $\delta^{34}S$ data for various geomorphological zones of the world ocean system (Table 6.6; Figure 6.5). These data are of primary importance since they suggest that $\delta^{34}S$ values of reduced sulphur in rocks may enable an assessment of the intensity of sulphate reduction in the geological past.

6.3.3 Mass and isotopic balance of sulphur in recent sediments

Table 6.7 contains data necessary for calculating the material and isotopic sulphur balance in modern oceanic sediments. The total sulphur buried annually (other than evaporite formation) is estimated to be 126 Tg, with an average $\delta^{34}S$ value = $-20.5\%$. The major portion of sulphur is buried in reduced forms (primarily pyrite) with an average $\delta^{34}S$ value of $-32.2\%$.

A comparison of data in Tables 6.6 and 6.7 shows that only 20% of newly formed hydrogen sulphide is buried as sulphide minerals in sediments, whereas the remainder is internally cycled. $H_2S$ migrates to the upper

![Image of Figure 6.5](image-url)

Figure 6.5 Variations of $\delta^{34}S$ sulphide and sulphate value in sea and ocean sediments. 1—Baltic Sea, 2—South China Sea, 3—California Bay, 4—Tasman Sea, 5—Pacific Ocean Shelf near Mexico, 6—Western part of the transocean geologic section, 7—the area of the Peru upwelling activity, 8—abiogenic sulphides of the active ocean zones.
hydrosphere horizons and is oxidized there to sulphate. This is confirmed by maxima in pore-water sulphate concentration just below the surface of the sediments. This sulphate is depleted in $^{34}\text{S}$ ($\delta^{34}\text{S} = -15.2$ to $-18.5\%_\text{o}$) as compared with $21\%_\text{o}$ for open-ocean $\text{SO}_4^{2-}$ (Lein et al., 1981). This demonstrates unambiguously the generation of excessive sulphate by the oxidation of biogenic hydrogen sulphide (Figure 6.2, st. 668).

In rare cases where one knows the rate of sedimentation as well as the total sulphur content and sulphate reduction intensity, it is possible to estimate the portion of reduced sulphur buried in the form of pyrite for individual sediment horizons (Table 6.8). Values of buried sulphur for two examples considered (15 and 16%, Table 6.8) are within the limits accepted for global calculations (about 20%, Tables 6.6 and 6.7).

### 6.3.4 Influence of the rate of sulphate reduction on sulphide mineral formation

Sulphide minerals isolated from marine sediments with varying intensities of bacterial sulphate reduction are markedly different in composition and morphology.

Dissolved sulphide and iron sulphide are always present in subcontinental sediments where there is intensive bacterial sulphate reduction. Sulphide ion is easily oxidized chemically and microbiologically (Jannasch et al., 1974; Gorlenko et al., 1977), yielding excess sulphur. Such conditions promote framboidal pyrite formation.

In sediments with low rates of bacterial reduction, free hydrogen sulphide and sulphide ion are practically absent in pore water. These conditions

<table>
<thead>
<tr>
<th>Horizon of silt (cm)</th>
<th>Baltic Sea, st. 2656, depth 46 m$^a$</th>
<th>Pacific ocean shelf near Mexico, depth 140 m$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of the process (years)</td>
<td>35</td>
<td>750</td>
</tr>
<tr>
<td>Intensity (mg kg$^{-1}$ d$^{-1}$)</td>
<td>5.4</td>
<td>0.56</td>
</tr>
<tr>
<td>Calculated content (g kg$^{-1}$)</td>
<td>68.0</td>
<td>37.5</td>
</tr>
<tr>
<td>True content (g kg$^{-1}$)</td>
<td>10.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Buried sulphur (% of calculated value)</td>
<td>15</td>
<td>16</td>
</tr>
</tbody>
</table>

$^a$ Lein et al. (1982).

$^b$ Ivanov et al. (1976).
promote formation of non-framboidal pyrite and pyrite aggregates with sulphide minerals of the mackinawite-greigite group. Therefore, the decrease in sulphate reduction rate evidently inhibits the transformation of unstable sulphide minerals to pyrite.

Sulphides formed from abiogenic hydrogen sulphide in sediments of tectonically active zones of the ocean (Red Sea depressions, East Pacific upwelling, crater lakes, etc.) are represented by individual crystals of cubic, prismatic, and other habits or by drusy and clusterlike aggregates. Such sulphides are characterized by δ³⁴S values in the range -3.0 to +3.0‰, which is radically different from that of sulphides in other regions of the ocean (Lein et al., 1982; Lein, 1983).

6.4 LAKES*

6.4.1 Lakes: water column

Lakes have now been recognized as the critical receptors most susceptible to inputs of acid rain and associated long-range transported pollutants from the atmosphere (Almer et al., 1978; Wright and Snekkvik, 1978). Potentially, measurements of the isotopic composition of both the sulphur and oxygen in the sulphate can be used to identify the sources and ascertain the behaviour and fate of pollutant sulphur in a given lake. The application of stable isotope techniques in acid rain studies has been only partially successful, however.

The δ³⁴SO₄²⁻ data for different types of lakes in many parts of the world are summarized in Table 6.9. The range is fairly wide although most of the data fall between +5 and +15‰. In addition to the source dependence, the isotopic composition of sulphur is also influenced strongly by the trophic conditions in the lake.

6.4.1.1 Isotopic changes due to lake pollution

The diagnostic and prognostic capabilities of δ³⁴SO₄²⁻ measurements can be demonstrated using the data in Table 6.10. The measurements pertain to lakes in the Sudbury basin of Canada and show differing degrees of stress from the inputs of smelter-derived pollutants. On the basis of the observed pH, the lakes can be subdivided into (a) well-buffered lakes unresponsive to the input of acid precipitation and (b) poorly buffered lakes more easily affected by the smelter emissions. The SO₄²⁻ concentration is correlated inversely with distance from the major smelter stack according to the relation

\[ [\text{SO}_4^{2-}] = 55 \text{ (distance)}^{-0.38} \]

* J.O. Nriagu.
Table 6.9 Isotopic composition of dissolved sulphate in selected lakes

<table>
<thead>
<tr>
<th>Lake</th>
<th>Year sampled</th>
<th>([\text{SO}_4^{2-}]) (mg l(^{-1}))</th>
<th>(\delta^{34}\text{S}) (‰)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ontario</td>
<td>1972</td>
<td>29</td>
<td>+5.9</td>
<td>Nriagu (1973)</td>
</tr>
<tr>
<td>Erie</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Western Basin</td>
<td>1972</td>
<td>25</td>
<td>+5.4</td>
<td>Nriagu (1973)</td>
</tr>
<tr>
<td>Eastern Basin</td>
<td>1972</td>
<td>25</td>
<td>+5.2</td>
<td>Nriagu (1973)</td>
</tr>
<tr>
<td>Huron</td>
<td>1972</td>
<td>16</td>
<td>+6.3</td>
<td>Nriagu (1973)</td>
</tr>
<tr>
<td>Michigan</td>
<td>1972</td>
<td>21</td>
<td>+4.6</td>
<td>Nriagu (1973)</td>
</tr>
<tr>
<td>Superior</td>
<td>1985</td>
<td>3.0</td>
<td>+4.4</td>
<td>Nriagu (unpublished results)</td>
</tr>
<tr>
<td>Turkey Lake watershed (four lakes)</td>
<td>1983–85</td>
<td></td>
<td>+4.1</td>
<td>Nriagu (unpublished results)</td>
</tr>
<tr>
<td>Lake WWI, Algoma, Ontario</td>
<td>1982</td>
<td>25</td>
<td>+5.3</td>
<td>Thode and Dickman (1984)</td>
</tr>
<tr>
<td>Lake WWII, Algoma, Ontario</td>
<td>1982</td>
<td>28</td>
<td>+5.5</td>
<td>Thode and Dickman (1984)</td>
</tr>
<tr>
<td>Logger, Algoma, Ontario</td>
<td>1982</td>
<td>6.8</td>
<td>+3.5</td>
<td>Thode and Dickman (1984)</td>
</tr>
<tr>
<td>Ten lakes, Algoma, Ontario</td>
<td>1983</td>
<td>5.3</td>
<td>+4.5</td>
<td>Thode and Dickman (1984)</td>
</tr>
<tr>
<td>Linsley Pond, Connecticut</td>
<td></td>
<td>4.3</td>
<td>+8.6</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Queechy, Connecticut</td>
<td></td>
<td>4.6</td>
<td>+5.8</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Mt. Tom Pond, Connecticut</td>
<td></td>
<td>5.1</td>
<td>+6.1</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Fayetteville Green Lake, New York</td>
<td>1983</td>
<td>0 m (surface), sulphate</td>
<td>+23</td>
<td>Fry (1986)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 m (bottom), sulphate</td>
<td>+28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>18 m, (\text{H}_2\text{S})</td>
<td>−32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 m, (\text{H}_2\text{S})</td>
<td>−27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 m</td>
<td>+35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>68 m</td>
<td>+37</td>
<td></td>
</tr>
</tbody>
</table>
Lake ‘B’, Ellesmere Island, Canada 1983
0 m (surface) 50 +19
20 m 750 +39
40 m 700 +87
Lake Tanganyika
Lake Kinneret 1976
Surface, July 67 +12
Surface, April 63 +16
20 m, July 66 +12
20 m, April 68 +17
42 m, July 90 +15
42 m, April 68 +13
Solar Lake
Sulphate +21
H2S -16
Lake Creteil Chesterikoff et al. (1981)
4 m (mid-column) 590 +32
6 m (bottom) 620 +27
Sernoye (reservoir), USSR +12 to +15
Baikal 1969 5.4 +7.1
Ladoga 1958 +5.9
Onega 1958 +5.2
Onega 1972 +8.8
Balkhash +11

Jeffries and Krouse (1984)
Monster (1973)
Nissenbaum (1978)
Aizenshtat et al. (1981)
Chesterikoff et al. (1981)
Pankina and Mekhitiyeva (1969)
Rabinovich and Grinenko (1979)
Rabinovich and Grinenko (1979)
Rabinovich and Grinenko (1979)
Rabinovich and Grinenko (1979)
<table>
<thead>
<tr>
<th>Lake</th>
<th>Year sampled</th>
<th>$[\text{SO}_4^{2-}]$ (mg l$^{-1}$)</th>
<th>$\delta^{13}$S (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Issyk Kul</td>
<td></td>
<td></td>
<td>+15</td>
<td>Rabinovich and Grinenko (1979)</td>
</tr>
<tr>
<td>Sabundy-Kul</td>
<td></td>
<td></td>
<td>+9.5</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Dzhasybay</td>
<td></td>
<td></td>
<td>+15</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Ul'kenonkol'i</td>
<td></td>
<td></td>
<td>+13</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Pashennoye</td>
<td></td>
<td></td>
<td>+4.4</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Shchuch'ye</td>
<td></td>
<td></td>
<td>+4.4</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Chelbar (brackish)</td>
<td></td>
<td></td>
<td>+10</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Itkol'</td>
<td></td>
<td></td>
<td>+6.2</td>
<td>Chukhrov et al. (1975)</td>
</tr>
<tr>
<td>Sakovo</td>
<td></td>
<td></td>
<td>51</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>2 m, sulphate</td>
<td></td>
<td></td>
<td>+13</td>
<td></td>
</tr>
<tr>
<td>7 m, sulphate</td>
<td></td>
<td></td>
<td>242</td>
<td></td>
</tr>
<tr>
<td>7 m, $H_2$S</td>
<td></td>
<td></td>
<td>-11</td>
<td></td>
</tr>
<tr>
<td>Vanda, Antarctica</td>
<td>1973–3</td>
<td></td>
<td></td>
<td>Nakai et al. (1975)</td>
</tr>
<tr>
<td>4 m</td>
<td></td>
<td>8.7</td>
<td>+15</td>
<td></td>
</tr>
<tr>
<td>40 m</td>
<td></td>
<td>24</td>
<td>+17</td>
<td></td>
</tr>
<tr>
<td>60 m</td>
<td></td>
<td>237</td>
<td>+22</td>
<td></td>
</tr>
<tr>
<td>68 m</td>
<td></td>
<td>611</td>
<td>+46</td>
<td></td>
</tr>
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</table>
Table 6.10 Concentrations and sulphur isotopic compositions of sulphate in lakes around the copper-nickel smelter at Sudbury, Ontario (from Nriagu and Harvey, 1978)

<table>
<thead>
<tr>
<th>Lake</th>
<th>Smelter distance (km)</th>
<th>pH</th>
<th>Sulphate level (ppm)</th>
<th>$\delta^{34}S$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robinson L.</td>
<td>3.2</td>
<td>6.09</td>
<td>30.5</td>
<td>+8.46</td>
</tr>
<tr>
<td>Hannah L.</td>
<td>3.9</td>
<td>3.40</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>St Charles</td>
<td>4.5</td>
<td>4.53</td>
<td>35.4</td>
<td>+3.48</td>
</tr>
<tr>
<td>Nepohwin</td>
<td>5.2</td>
<td>6.15</td>
<td>36.1</td>
<td>+7.32</td>
</tr>
<tr>
<td>'e'</td>
<td>5.2</td>
<td>3.20</td>
<td>23.5</td>
<td>+5.19</td>
</tr>
<tr>
<td>Middle</td>
<td>5.2</td>
<td>5.78</td>
<td>39.5</td>
<td>+2.66</td>
</tr>
<tr>
<td>Silver</td>
<td>6.5</td>
<td>3.20</td>
<td>28.5</td>
<td>+5.19</td>
</tr>
<tr>
<td>Ramsay</td>
<td>7.7</td>
<td>6.61</td>
<td>34.7</td>
<td>+7.34</td>
</tr>
<tr>
<td>Richard</td>
<td>8.4</td>
<td>5.06</td>
<td>25.7</td>
<td>+8.43</td>
</tr>
<tr>
<td>McFarlane</td>
<td>9.7</td>
<td>5.32</td>
<td>27.4</td>
<td>+6.76</td>
</tr>
<tr>
<td>Lohi</td>
<td>10.3</td>
<td>3.80</td>
<td>22.3</td>
<td>+5.31</td>
</tr>
<tr>
<td>Long</td>
<td>11.0</td>
<td>6.45</td>
<td>15.8</td>
<td>+5.23</td>
</tr>
<tr>
<td>Raft</td>
<td>11.6</td>
<td>4.15</td>
<td>20.9</td>
<td>+2.84</td>
</tr>
<tr>
<td>Clearwater</td>
<td>12.9</td>
<td>3.50</td>
<td>24.4</td>
<td>+4.56</td>
</tr>
<tr>
<td>Tilton</td>
<td>13.5</td>
<td>4.20</td>
<td>19.3</td>
<td>+4.50</td>
</tr>
<tr>
<td>Makada</td>
<td>14.8</td>
<td>6.75</td>
<td>21.8</td>
<td>+4.23</td>
</tr>
<tr>
<td>McCharles</td>
<td>20.0</td>
<td>8.95</td>
<td>87.8</td>
<td>+3.57</td>
</tr>
<tr>
<td>Wavy</td>
<td>20.0</td>
<td>3.30</td>
<td>15.8</td>
<td>+5.23</td>
</tr>
<tr>
<td>Little Panache</td>
<td>32.3</td>
<td>8.17</td>
<td>13.7</td>
<td>+6.08</td>
</tr>
<tr>
<td>Panache</td>
<td>32.9</td>
<td>6.70</td>
<td>19.9</td>
<td>+4.70</td>
</tr>
<tr>
<td>Broker</td>
<td>37.4</td>
<td>5.20</td>
<td>7.8</td>
<td>+4.75</td>
</tr>
<tr>
<td>Tyson</td>
<td>39.4</td>
<td>5.70</td>
<td>12.9</td>
<td>+4.84</td>
</tr>
<tr>
<td>Log Boom</td>
<td>41.9</td>
<td>5.19</td>
<td>12.9</td>
<td>+4.80</td>
</tr>
<tr>
<td>J ohinnie</td>
<td>45.2</td>
<td>4.15</td>
<td>11.0</td>
<td>+4.30</td>
</tr>
<tr>
<td>Ruth-Roy</td>
<td>45.2</td>
<td>4.50</td>
<td>12.8</td>
<td>+4.05</td>
</tr>
<tr>
<td>Norway</td>
<td>47.1</td>
<td>4.20</td>
<td>12.3</td>
<td>+4.00</td>
</tr>
<tr>
<td>Perdix</td>
<td>47.7</td>
<td>4.41</td>
<td>14.6</td>
<td>+4.99</td>
</tr>
<tr>
<td>Carlyle</td>
<td>49.0</td>
<td>4.85</td>
<td>11.9</td>
<td>+4.99</td>
</tr>
<tr>
<td>Kakakise</td>
<td>50.3</td>
<td>5.75</td>
<td>13.6</td>
<td>+4.67</td>
</tr>
<tr>
<td>Lang</td>
<td>52.3</td>
<td>6.75</td>
<td>20.3</td>
<td>+4.55</td>
</tr>
<tr>
<td>Acid (Lum II)</td>
<td>57.4</td>
<td>4.39</td>
<td>9.5</td>
<td>+4.48</td>
</tr>
<tr>
<td>Lumsden I</td>
<td>58.1</td>
<td>4.39</td>
<td>8.9</td>
<td>+4.55</td>
</tr>
<tr>
<td>Lumsden III</td>
<td>58.1</td>
<td>4.60</td>
<td>8.9</td>
<td>+5.71</td>
</tr>
<tr>
<td>Apsey</td>
<td>61.3</td>
<td>7.01</td>
<td>10.8</td>
<td>+5.43</td>
</tr>
<tr>
<td>Frood</td>
<td>62.6</td>
<td>6.70</td>
<td>17.6</td>
<td>+4.82</td>
</tr>
<tr>
<td>Grab</td>
<td>67.0</td>
<td>6.25</td>
<td>8.1</td>
<td>+5.26</td>
</tr>
<tr>
<td>Evangeline</td>
<td>73.6</td>
<td>6.42</td>
<td>9.7</td>
<td>+5.36</td>
</tr>
<tr>
<td>Maple</td>
<td>75.5</td>
<td>6.40</td>
<td>12.1</td>
<td>+4.46</td>
</tr>
<tr>
<td>Cutler</td>
<td>76.7</td>
<td>6.79</td>
<td>12.1</td>
<td>+4.22</td>
</tr>
<tr>
<td>La Cloche</td>
<td>83.9</td>
<td>6.68</td>
<td>11.2</td>
<td>+5.03</td>
</tr>
<tr>
<td>Little La Cloche</td>
<td>85.8</td>
<td>6.80</td>
<td>13.2</td>
<td>+4.34</td>
</tr>
<tr>
<td>Owl</td>
<td>90.3</td>
<td>4.75</td>
<td>8.1</td>
<td>+4.73</td>
</tr>
</tbody>
</table>
Table 6.11 Apparent isotopic fractionation factors for sulphate reduction in lakes

<table>
<thead>
<tr>
<th>Lake</th>
<th>$[\text{SO}_4^{2-}]$ (mg l$^{-1}$)</th>
<th>$[\text{H}_2\text{S}]$ (mg l$^{-1}$)</th>
<th>$(\alpha - 1) \times 10^3$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water column</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake Vanda, Antarctica</td>
<td>608</td>
<td>70</td>
<td>35</td>
<td>Nakai et al. (1975)</td>
</tr>
<tr>
<td>Fayetteville Green Lake, New York</td>
<td>1340</td>
<td>31</td>
<td>56</td>
<td>Deevey et al. (1963); Fry (1986)</td>
</tr>
<tr>
<td>Lake Sakovo</td>
<td>780</td>
<td>9.1</td>
<td>28</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Chernyi Kichiyer</td>
<td>86</td>
<td>50</td>
<td>23</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Bol’shoy Kichiyer</td>
<td>43</td>
<td>8.5</td>
<td>4.1</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Black Sea</td>
<td>2340</td>
<td>7.4</td>
<td>47</td>
<td>Aizenshtat et al. (1981)</td>
</tr>
<tr>
<td>Solar Lake</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sediments (pore water)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linsley Pond, Connecticut</td>
<td>13</td>
<td>10</td>
<td>10</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Queechy Lake, Connecticut</td>
<td>14</td>
<td>5.4</td>
<td>5.4</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Mt Tom Pond, Connecticut</td>
<td>15</td>
<td>9.1</td>
<td>9.1</td>
<td>Nakai and Jensen (1967)</td>
</tr>
<tr>
<td>Chernyi Kichiyer</td>
<td>105</td>
<td>346</td>
<td>7.8</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Bol’shoy Kichiyer</td>
<td>43</td>
<td>155</td>
<td>6.6</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Lake Kononyer</td>
<td>35</td>
<td>608</td>
<td>4.8</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Lake Kuznechikha</td>
<td>36</td>
<td>181</td>
<td>1.6</td>
<td>Matrosov et al. (1975)</td>
</tr>
<tr>
<td>Lake Sakovo</td>
<td>738</td>
<td>200</td>
<td>38</td>
<td>Matrosov et al. (1975)</td>
</tr>
</tbody>
</table>
Stable Isotopes

with \( r = 0.81 \) (Nriagu and Harvey, 1978). There is also a significant correlation between the pH of poorly buffered lakes and the distances from the smelter stack. The \( \delta^{34}\text{SO}_4^{2-} \) for the well-buffered lakes show considerable scatter (see Fig. 3 in Nriagu and Harvey, 1978), suggesting (a) derivation of the sulphur from several sources and/or (b) complex interplay between the point source influence and sulphur transformations either in the watershed or within the lakes. For example, high acid loading may increase the amount of sulphur in these lakes by accelerating the weathering of the bedrock and the overburden. By contrast, the \( \delta^{34}\text{SO}_4^{2-} \) data for the poorly buffered lakes are remarkably uniform, lying mostly between +4 and +5.5\% (Table 6.10). This uniformity clearly suggests that the isotopic composition of these lakes is regulated by the influx of sulphur released from the smelters.

In the Great Lakes system of North America, anthropogenic sources now account for 30\% of the \( \text{SO}_4^{2-} \) in Lakes Superior and Huron and over 70\% in Lake Erie (Nriagu, 1984). There is some suggestion that the industrial inputs are affecting the isotopic composition of \( \text{SO}_4^{2-} \) (Table 6.9), although the inter-lake differences do not seem to be consistent with the levels of pollution. Lake Superior, in particular, has a long water flushing time (about 180 years) and thus contains some sulphur of precolonial age. Like the other Great Lakes, Superior has a small watershed-to-lake area ratio, implying that direct atmospheric deposition accounts for a large fraction of the sulphur input. Its \( \delta^{34}\text{SO}_4^{2-} \) can thus be regarded as being representative of 'unpolluted' waters of the Great Lakes. As can be seen in Table 6.11, the \( \delta^{34}\text{SO}_4^{2-} \) data for the other Great Lakes with more pollutant sulphur deviate from this background value significantly.

The stable isotope technique has been used with some success to assess the contamination of surface waters with sulphur emissions from sour gas processing plants at West Whitecourt, Alberta (Krouse et al., 1984). It was found that the dissolved sulphur became heavier with increasing organosulphur content. The \( \delta^{34}\text{S} \) approached a limiting value of +22\% (Figure 6.6), which corresponded to the isotopic composition of the sulphur released from the sour gas plants. The results of the study suggest that the emission were affecting the biological uptake of sulphur in the boreal forest, which in turn resulted in a marked increase in the flux of isotopically labelled organosulphur compounds into the surface waters (Krouse et al., 1984).

6.4.1.2 Oligotrophic lakes

With the exception of Lake Erie, the Great Lakes of North America possess a characteristic feature of oligotrophic lakes, namely very homogeneous isotopic composition of sulphate. Differences in mean \( \delta^{34}\text{SO}_4^{2-} \) values of the hypolimnion and epilimnion waters were generally less than 0.2\%
(Nriagu, 1973). Temperature (seasonal) changes apparently do not promote significant sulphur isotope fractionation; nor does assimilatory sulphate reduction by biota.

For many hardwater and/or softwater oligotrophic lakes, the $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ values are very close to those of rainfall in their drainage basins, implying a common origin. Good examples are the Algoma Lakes (including those of the Turkey Lakes Watershed) of northern Ontario (Table 6.9). For many hardwater lakes of oligotrophic classification, the $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ values reflect the combined signatures of sulphur from atmospheric fallout and from the weathering of the bedrocks. As noted already, most of the poorly buffered lakes in the Sudbury basin fall into this category.

Recent studies of the isotopic composition of oxygen of the dissolved sulphate in oligotrophic lakes have yielded unexpected results (Caron, 1984; Fritz et al., 1986). The $\delta^{18}\text{O}$ values of $\text{SO}_4^{2-}$ tend to be distinctly different from those of rainfall and often show complex patterns unrelated to the $\delta^{34}\text{S}$ data (Figure 6.7). The oxygen isotopic data thus point to extensive assimilatory reduction of sulphate, and suggest that the turnover of sulphur in oligotrophic lakes may be more rapid than has hitherto been realized.

6.4.1.3 Eutrophic lakes

The $\text{SO}_4^{2-}$, $\text{H}_2\text{S}$, and $\delta^{34}\text{SO}_4^{2-}$ profiles in a typical eutrophic lake that develops an anoxic hypolimnion are shown in Figure 6.8. During the spring
and autumn overturn, any $\text{H}_2\text{S}$ formed in the hypolimnion is oxidized and mixed with the sulphate in the epilimnion, resulting in a fairly homogeneous $\delta^{34}\text{S}$ value throughout the water column (Figure 6.8a). During the period of summer stratification, the $\text{SO}_4^{2-}$ is progressively converted to $\text{H}_2\text{S}$ in the anaerobic hypolimnetic waters.

Ideally, the $\delta^{34}\text{SO}_4^{2-}$ profile for lakes of this class should have three distinctive segments (see Figure 6.8b and c): (a) the epilimnion with a fairly constant $\delta^{34}\text{S}$ profile; (b) the chemocline where the partial reduction of sulphate results in $\delta^{34}\text{SO}_4^{2-}$ values higher than that of the epilimnion—if the hypolimnion is completely anoxic, a maximum in the $\delta^{34}\text{SO}_4^{2-}$ profile should occur at this interface; and (c) the hypolimnion, which may display any profile depending on the oxygen concentration (compare Figure 6.8b
and c). If the system is completely anoxic, there is a severe shortage of sulphate and relatively little fractionation of the sulphur isotopes is expected. If the system is partly anoxic (due to leakage of oxygen across the chemocline), the $\delta^{34}\text{SO}_4^{2-}$ should increase towards the sediment–water interface, in accordance with gradients of declining redox potential and increasing intensity of sulphate reduction. These two may be regarded as the ideal profiles. Many factors, however, can modify the $\delta^{34}\text{SO}_4^{2-}$ profiles in the hypolimnion, such as (a) the thickness of the hypolimnion and the duration of stratification, (b) the sulphate concentration and internal biogeochemical processes in the water column, and (c) the exchange of sulphur isotopes across the sediment–water interface (Nriagu and Soon, 1985). If a large fraction of the product $\text{H}_2\text{S}$ is removed to the sediments by reaction with $\text{Fe}^{2+}$, the $\delta^{34}\text{SO}_4^{2-}$ data in the anoxic hypolimnion may even show measurable seasonal changes.

In view of the many compounding variables, few, if any, good models have been developed to describe the fractionation of sulphur isotopes in this lake type. It should be noted that few studies have included the measurement of the isotopic composition of the oxygen in the sulphate.

6.4.1.4 Meromictic lakes

These differ from the eutrophic lakes in (a) being permanently stratified and (b) generally having a higher concentration of dissolved salts. Typical $\delta^{34}\text{SO}_4^{2-}$ profiles in meromictic lakes can also be expected to show three distinct segments corresponding to the epilimnion, chemocline, and monimolimnion. Representative profiles are shown in Figure 6.9. In Fayetteville Green Lake, State of New York, the $\delta^{34}\text{SO}_4^{2-}$ value is essentially constant near $+23\%_\circ$ in the epilimnion (1–15 m), but increases gradually with depth down the monimolimnion. As expected, the reduced sulphur species were depleted in $^{34}\text{S}$ and the isotopic difference between the $\text{SO}_4^{2-}$ and $\text{HS}^-$ was large and remarkably constant at about $56.6\%_\circ$ (Deevey et al., 1963; Fry, 1986). By contrast, the profile of $\delta^{34}\text{SO}_4^{2-}$ in Lake Vanda, Antarctica, shows a sharp increase at a depth of 60 m below the ice cover where the $\text{H}_2\text{S}$ becomes detectable. The maximum value of $+49\%_\circ$ was attained right at the sediment–water interface (Figure 6.9). The sharp increase in sulphate concentration occurs at about 10 metres above the point of rapid increase in $\delta^{34}\text{SO}_4^{2-}$ values (Nakai et al., 1975).

Figure 6.8(a) $\delta^{34}\text{SO}_4^{2-}$, $\text{SO}_4^{2-}$, and total dissolved sulphide profiles in Lake 223 on 15 June 1979, or following the spring overturn (Cook, 1981). (b) $\delta^{34}\text{SO}_4^{2-}$, $\text{SO}_4^{2-}$, and total dissolved sulphate profiles in Lake 223 on 21 September 1979, or during stratification (Cook, 1981). (c) $\delta^{34}\text{SO}_4^{2-}$, $\text{SO}_4^{2-}$, and total dissolved sulphate profiles in Lake 227 on 1 September 1978, or during stratification (Cook, 1981).
The sulphate concentration in Lake 'A', Ellesmere Island in the Canadian Arctic, increases from about 30 mg l⁻¹ just below the ice cover to well over 1900 mg l⁻¹ in the bottom waters (Jeffries et al., 1984). The $\delta^{34}S$ and $\delta^{18}O$ values of bottomwater $SO_4^{2-}$ also increase with depth from the ice cover although samples closest to the sediments are slightly depleted in $^{34}S$. The isotopic profiles do not depict the freshwater-to-seawater transition zone located at depths of 15–25 metres.

In the case of smaller Lake 'B', which is slightly further inland, Jeffries and Krouse (1984) found the $\delta^{34}S$ values of bottomwater $SO_4^{2-}$ to be as high as $+87\%$ (Figure 6.7). Dissolved carbonate in the bottom waters had $\delta^{13}C$ values of $-21$ and $-27\%$ for Lakes A and B respectively, which is in the range of organic matter. In summary, the sulphur, oxygen, and carbon isotope data collectively provide strong evidence of anaerobic bacterial $SO_4^{2-}$ reduction with attending oxidation of organic nutrients. Because of
preferential $^{32}\text{SO}_4^{2-}$ reduction, the unreacted $\text{SO}_4^{2-}$ became highly enriched in $^{34}\text{S}$ in the bottom waters. For example, the $\delta^{34}\text{S}$ value of $+87\%_0$ in Lake B corresponded to a much lower $[\text{SO}_4^{2-}]$, 700 ppm, i.e. about one-third of that found in the bottom of Lake A.

Insofar as a lake maintains a permanent meromixis, the hypolimnion can be regarded as a closed system. The fractionation of sulphur isotopes during sulphate reduction can hence be approximated by the Rayleigh distillation equation:

$$\left(\frac{R_t}{R_0}\right) = \left(\frac{C_t}{C_0}\right)^{1-\frac{1}{\alpha}}$$

where $R_0$ and $R_t$ are the $^{32}\text{S}/^{34}\text{S}$ ratios at the start and after time $t$, $C_0$ and $C_t$ are the corresponding $\text{SO}_4^{2-}$ concentrations, and $\alpha$ is the instantaneous isotopic fractionation factor. Figure 6.10 shows typical Rayleigh plots for residual $\text{SO}_4^{2-}$ and the $\text{H}_2\text{S}$ produced, assuming $\alpha = 1.005$ and an initial

![Figure 6.10 Rayleigh distillation plots for a closed system undergoing sulphate reduction assuming $\alpha = 1.005$, and initial $\delta$ values of $+10\%_0$. $F$ is the fraction of sulphate remaining in the system.](image-url)
\( \delta^{34}\text{SO}_{4}^{2-} \) of +10%. The patterns of the calculated graphs generally match what have been observed in some meromictic lakes (compare Figures 6.9 and 6.10).

Values of \( \alpha \) for sulphate reduction in lake waters and sediments range from 1.004 to 1.056 (Table 6.11). As to be expected, the lowest \( \alpha \) values are found in lakes with the lowest sulphate concentrations—the sulphate reducers become less discriminating as the available sulphate is depleted. It also means that in lakes with low \( \text{SO}_4^{2-} \) content, the value \( \alpha \) is not constant but will decrease as the available sulphate is biotransformed into reduced species. The available data suggest that when the sulphate concentration is less than 20 mg l\(^{-1}\), the value of \( \alpha \) is generally below 1.01. In contrast, \( \alpha \) is much larger (1.03–1.07) in marine environments with abundant \( \text{SO}_4^{2-} \) (Goldhaber and Kaplan, 1974). It is not surprising that some of the \( \alpha \) values for lakes fall in the marine range, considering their sulphate concentrations (Table 6.11).

### 6.4.2 Lakes: sediments

A detailed review of the distribution and diagenesis of sulphur in lacustrine sediments has already been given in a preceding SCOPE volume (Ivanov and Freney, 1983). The monograph includes a good summary on the use of sulphur isotopes in delineating the critical pathways of sulphur transformations in sediment ecosystems. To avoid duplication, the following section concentrates on the use of stable sulphur isotopes in understanding freshwater sediments as sinks for anthropogenic sulphur, especially in eastern North America. The reduction of anthropogenic sulphate in lake sediments is an important alkalinity-generating process. Measurements of the isotopic composition of sulphur in sediments can thus (a) provide some insight on the self-purification of a lake and its ability to recover from an acid stress and (b) be used for retrospective monitoring of past fluxes of pollutant sulphur into the lake basin. These are key questions relevant to acid rain.

#### 6.4.2.1 Anthropogenic influence on the isotopic composition of sulphur in lake sediments of eastern North America

The role of lake sediments as sinks for pollutant sulphur has received little attention. Several studies have now demonstrated that there has been a significant increase in the sulphur contents of the most recent sediments of lakes in many parts of the world (Table 6.12). For example, the *enrichment factors* (EF) for the Great Lakes vary from about 1.5 in the fairly pristine Lake Superior to over 3 in the most polluted, much shallower, Lake Erie. (EF is the ratio of the average S concentration in surficial sediments to that in the precolonial layers. The difference between the S contents of the two
Table 6.12 Average concentrations and enrichment factors for sulphur in recent (surficial) lake sediments

<table>
<thead>
<tr>
<th>Lake/location (Reference a)</th>
<th>Average [S] (%)</th>
<th>Enrichment factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superior—Great Lakes (1)</td>
<td>0.014</td>
<td>1.8</td>
</tr>
<tr>
<td>Huron—Great Lakes (1)</td>
<td>0.092</td>
<td>1.5</td>
</tr>
<tr>
<td>Michigan—Great Lakes (1)</td>
<td>0.113</td>
<td>2.8</td>
</tr>
<tr>
<td>Erie—Great Lakes (1)</td>
<td>0.150</td>
<td>3.3</td>
</tr>
<tr>
<td>Ontario—Great Lakes (1)</td>
<td>0.210</td>
<td>2.6</td>
</tr>
<tr>
<td>Algonquin Provincial Park, Ontario (2)</td>
<td>0.51</td>
<td>~2.8</td>
</tr>
<tr>
<td>Around Sudbury, Ontario (2)</td>
<td>0.71</td>
<td>4.5</td>
</tr>
<tr>
<td>Wawa, downwind of smelter (3)</td>
<td>0.81</td>
<td>&gt; 3.0</td>
</tr>
<tr>
<td>Wawa, upwind of smelter (3)</td>
<td>0.31</td>
<td>1.7</td>
</tr>
<tr>
<td>Experimental lakes area (4)</td>
<td>0.16</td>
<td>~3.0</td>
</tr>
<tr>
<td>Adirondack Mts, New York (5)</td>
<td>0.13</td>
<td>~2.5</td>
</tr>
<tr>
<td>Swiss lakes (6)</td>
<td>0.67</td>
<td>4.2</td>
</tr>
<tr>
<td>English lakes (7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unproductive</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Moderately productive</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Very productive</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>


Sediment zones will be referred to as excess sulphur.

On the lake sediments near the smelters at Sudbury, which daily release about 2500 tonnes of \( \text{SO}_2 \) into the atmosphere, the EF values typically exceed 4 (see Table 6.12). The observed increase in the S contents of other recent sediments has also been attributed to increased sulphur inputs from anthropogenic sources (Mitchell et al., 1983; Nriagu and Coker, 1983).

The suggestion that the input determines the sulphur concentration is inconsistent with the presumed general mobility of sulphur in sediments. As a matter of fact, the near-quantitative interconversion of one form of sulphur into the other at a given horizon (cf. Goldhaber and Kaplan, 1974; Altschuler et al., 1983) suggests that sulphur may not be as mobile as is generally believed. Most lake sediments are deficient in S and any sulphate ions transferred into them are quickly reduced to sulphide below the oxidized microzone. Furthermore, typical lake sediments contain a large excess of reduced iron which quickly precipitates sulphide ions (Volkov, 1961; Berner, 1971; Nriagu, 1975). Further, recent studies (Smith and Klug, 1981; Mitchell et al., 1981; Nriagu and Coker, 1983) show that a large percentage of the S in many lake sediments is bound to organic material, and consequently also rendered immobile. The immobilization of sulphur can explain why the S contents of the sediments tend to chronicle the S flux into the lake.
The influence of inputs on sedimentary sulphur is further demonstrated by the strong correlation between the S contents of recent sediments and the sulphate concentrations in the overlying waters (Gorham et al., 1974; Nriagu, 1984). It should be emphasized that the source influence can best be seen in lakes with aerobic hypolimnion. Any development of bottom anoxia increases the transfer of S to the sediments, thereby confusing the relationship between sulphur input and accumulation in the sediments.

In fact, the pollution component of $\text{SO}_4^{2-}$ in the Great Lakes can be estimated using the shift in the S contents of the sediments. Such data for Lake Erie sediments suggest that anthropogenic sources account for about 70% (18 mg l$^{-1}$) of $\text{SO}_4^{2-}$ (Nriagu, 1984). The extrapolation of the historical graph of changes in $\text{SO}_4^{2-}$ concentrations (in the overlying water) to precolonial times shows a similar pollution input (Beeton, 1965; Pringle et al., 1981). A mass balance of the inputs from the weathering of the bedrocks and the glacial overburdens likewise suggests that 60–70% of the $\text{SO}_4^{2-}$ in Lake Erie comes from pollution sources (Nriagu, 1975). On the basis of the excess sulphur values, it has also been estimated that anthropogenic sources now account for about 30–40% of the $\text{SO}_4^{2-}$ in the waters of Lakes Huron and Superior, and about 60% in Lake Ontario and southern Lake Michigan. These percentages are in good agreement with the estimated background of precolonial $\text{SO}_4^{2-}$ concentrations of 14 mg l$^{-1}$ in Lake Ontario, 5 mg l$^{-1}$ in Lake Michigan, 8 mg l$^{-1}$ in Lake Huron, and 2 mg l$^{-1}$ in Lake Superior (Beeton, 1965; Pringle et al., 1981).

Potentially, the isotopic technique should provide a confirmation as to whether the sources of S in the recent lake sediments have indeed changed. In one of the first detailed studies, Nriagu and Coker (1976) showed that the surficial sediments of Lake Ontario are depleted in $^{34}$S compared to the older sediments. They interpreted the $\delta^{34}$S profiles in terms of sulphur diagenesis and preferential loss of $^{32}$S to the overlying water; the interpretation was adapted from diagenetic models for S in marine sediments. A recent study of sediments as sinks for S in the Great Lakes (Nriagu, 1984) suggests, in fact, that the observed $\delta^{34}$S profiles are more likely to be a reflection of increasing input of pollutant sulphur into Lake Ontario.

Subsequently, the isotopic composition of S in the humic acids (HA) from Lake Ontario has been determined (Figure 6.11). What is remarkable is the depletion of $^{34}$S in the surficial samples and the close similarity with the $\delta^{34}$S profiles of the other forms of sulphur in these sediments (see Nriagu and Coker, 1976). The $\delta^{34}$S of the HA presumably includes the isotopic signature of the precursor organic matter, the isotopic imprints of the subsequent diagenetic changes, and the isotopic effects of any secondary enrichment reactions (Nissenbaum and Kaplan, 1972; Dinur et al., 1980). It is impossible to establish the relative influence of each of these three processes. In view of the little that is currently known about the fractionation
of S isotopes in organic material, it would be ill advised to attribute the shift in isotopic composition solely to a change in the source of the sulphur in the humic acids. Nevertheless, the profile observed is very suggestive of a strong source influence. It may be noted that the HA is depleted in $^{34}$S in relation to the acid volatile sulphides and the total S in the same sediment horizons.

A more recent study dealt with the concentration and isotopic composition of S in lake sediments located in two contrasting regions with respect to sulphur pollution. The first group of lakes is located near Sudbury, Ontario, and derives most of the sulphur from the big nickel–copper smelting complex nearby (Nriagu and Coker, 1978a; Nriagu and Harvey, 1978). This point source has a fairly constant isotopic signature and the sedimentary record of sulphur pollution in these lakes should be related to the local history of smelting activities. The strong influence of smelter emissions is manifested by the fact that many of the lakes in this area have become acidic (OME, 1981). The second group of lakes are located in the more remote Algonquin Provincial Park with no known major local sources of sulphur. The historical records and isotopic profiles in the sediments should

![Figure 6.11 The $\delta^{34}$S profiles for humic acid sulphur from Lake Ontario](image)
presumably reflect the flux of long-range transported sulphur into the lake basins.

Representative profiles of total sulphur and $\delta^{34}$S in lake sediments in the two areas are shown in Figure 6.12. A prominent feature of the profiles is the spectacular enrichment of sulphur in the surficial sediments. For the lakes around Sudbury, the dramatic increase in the flux of excess sulphur began around 1890, coinciding with the initiation of smelting operations (Nriagu et al., 1982). It is interesting that the pronounced increase in the accumulation of S in Windy Lake sediments, located about 20 km from Sudbury, dates to roughly 45 years BP, and hence coincides with the installation of the taller 170 m stack at Copper Cliff in 1923. The accumulation of excess S in lake sediments in the Algonquin Park generally began around 1860–70, and may be related to the beginning of extensive industrialization of the Great Lakes basin. These data thus suggest that lake sediments are sensitive to the influx of pollutant sulphur from both local and distant sources.

The changes in the $\delta^{34}$S profiles closely parallel the input of excess sulphur into the lake sediments (Figure 6.12). Typically, the most recently deposited sulphur is isotopically lighter than the sulphur in the older sediments. More importantly, the shift in $\delta^{34}$S coincides with the onset of excess S in every case (Figure 6.12). The sulphur in the surficial sediments near Sudbury tends to be lighter (average $\delta^{34}$S value, $\sim -8$‰) than in Algonquin Park sediments of comparable age (mean $\delta^{34}$S value $\sim -0.5$‰). The apparent difference may be related to the disparity in the isotopic signature of sulphur from local versus regional sources (Nriagu and Coker, 1983). The highly contaminated sediments of Kelly Lake (a recipient of both domestic and industrial effluents) contain over 3% sulphur with very negative $\delta^{34}$S values of $-20$ to $-30$‰ (Figure 6.12).

Various diagenetic models, conceivably, can be invoked to account for the total S or $\delta^{34}$S profiles. The time frame for the onset of excess sulphur accumulation in these lakes, however, lends support to their interpretation in terms of input control. The results do suggest that sedimentary sulphur can be used as a time tracer for acid rain deposition in these lakes. The quantification of the historical changes in the flux of acidic sulphur compounds into lakes would require a careful assessment of principal pathways of sulphur flux into the sediments. There are currently few reliable indices of past changes in the buffering capacity of lakes which can be attributed to acidic precipitation, and the sulphur isotopic technique does seem to provide the much-needed clues.

A few other studies have addressed the $\delta^{34}$S profiles in recent lake sediments. The total S content and $\delta^{34}$S profiles which Cook (1981) reported in the Experimental Lakes Area of northern Ontario are very similar to those in Figure 6.12. The total S profiles in two lakes in the Adirondack
Figure 6.12 Profiles of total sulphur and $\delta^{34}$S in sediments of representative lakes of Northern Ontario (Nriagu and Coker, 1983)
Mountains of New York likewise show an increasing flux of excess sulphur beginning around 1850 (Mitchell et al., 1983); the preliminary data furthermore show a depletion of $^{34}$S in the surficial sediments samples (M.J. Mitchell, personal communication, 1983). Thode and Dickman (1983) found the difference in $\delta^{34}$S values between the recent and the underlying older sediments to be about 3$\%$ and 9–11$\%$ in lakes located downwind and upwind respectively of the smelters at Wawa, Ontario. In each instance, the $\delta^{34}$S was shifted to a lower value in the surficial sediments. These available data, all from lakes in eastern North America, show a very diagnostic pattern which needs to be confirmed in lakes in the other parts of the world.

6.5 ISOTOPIC COMPOSITION OF SULPHUR IN CONTINENTAL SEAS*

In contrast to the world’s oceans, concentration and $\delta^{34}$S values of sulphate in continental seas vary widely. Isotopic data for different sulphur forms in water and sediments of continental seas are rather sparse even for the largest, the Mediterranean Sea. The Black Sea has been studied comprehensively; less information has been obtained for the Azov, Caspian, Baltic, and Red Seas.

From the environmental viewpoint, inland seas may serve as the recipients of anthropogenic sulphur. Alternatively, non-sulphur-containing pollutants might alter the sulphur cycle in these waters, perhaps affecting biota and emission of S compounds to the atmosphere.

6.5.1 The Black Sea

The Black Sea is a unique water basin. Its surface layers (150–200 m) contain oxygen, whereas the bulk of its water body (about 87$\%$) contains hydrogen sulphide with concentrations as high as 9.6 mg $l^{-1}$ (average 7.6 mg $l^{-1}$).

The water exchange between the Black Sea and the Mediterranean and Azov Seas via the Bosphorus and Kerch Straits was investigated by Scopintsev (1975). The contents of different sulphur forms in Black Sea sediments have been studied in detail (Ostroumov et al., 1961; Ostroumov and Volkov, 1964). The isotopic composition of sulphur in water and sediments of the Black Sea was first studied by Vinogradov et al. (1962) and later by Migdisov et al. (1974).

All the reduced S forms in recent sediments, as well as hydrogen sulphide in the water column, are enriched in the lighter isotope with $\delta^{34}$S values as low as $-42\%$. The isotopic composition of $SO_4^{2-}$ ($+19.4\%$) approximates the oceanic value and is rather homogeneous throughout the total depth.

* V.L. Mekhtiyeva.
Some variations in the isotopic composition of $\text{SO}_4^{2-}$ (from +16.7 to +21.2%) are observed in the littoral zone (Mekhtiyeva and Pankina, 1968; Chukhrov et al., 1975). The isotopic composition of sulphate in the river system of the Black Sea Basin was investigated by Rabinovich and Grinenko (1979).

From data on the contents of different sulphur forms in sediments and the annual sediment deposition rate on the shelf (145 Tg yr$^{-1}$), the annual reduced sulphur flux to the Black Sea sediments has been estimated to be 2.4 Tg, of which 1.4 Tg reaches the shelf (Lein and Ivanov, 1983). Lein et al. (1983) have calculated the mass isotopic balance for sediments in the hydrogen sulphide zone of the sea.

On the basis of the above data, a mass isotopic balance calculation for sulphur in the entire Black Sea has been attempted (Tables 6.13 and 6.14).

As seen from Table 6.13, the isotopically light sulphur is buried in sediments. Despite the fact that this flux is relatively small, it establishes

Table 6.13 Flux of sulphur in the Black Sea sediments

<table>
<thead>
<tr>
<th>Zone</th>
<th>Sediment deposition ($10^6$ tonnes yr$^{-1}$)</th>
<th>Average S content (%)</th>
<th>$\delta^{34}$S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulphide</td>
<td>75</td>
<td>1.35 0.03</td>
<td>-23.9 25.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>145</td>
<td>1.01 0.05</td>
<td>20.0 23.0</td>
</tr>
</tbody>
</table>

Table 6.14 Mass isotopic balance of sulphur in the Black Sea

<table>
<thead>
<tr>
<th>Inputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}$S (%)</th>
<th>Outputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}$S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River runoff</td>
<td>3.8</td>
<td>+4.5</td>
<td>Efflux to Azov Sea</td>
<td>14.98</td>
<td>+19.0</td>
</tr>
<tr>
<td>Flux from the Azov Sea</td>
<td>16.5</td>
<td>+17.0</td>
<td>Efflux to Bosporus</td>
<td>159.9</td>
<td>+19.4</td>
</tr>
<tr>
<td>Flux from Bosphorus</td>
<td>158.7</td>
<td>+19.8</td>
<td>Burial in sediments</td>
<td>2.47</td>
<td>-20.0</td>
</tr>
<tr>
<td>Total</td>
<td>179</td>
<td>+19.2</td>
<td></td>
<td>177</td>
<td>-18.8</td>
</tr>
</tbody>
</table>
that the isotopic composition for the total efflux from the Black Sea is somewhat lighter than that of the influx. Therefore, the calculated mass balance (Table 6.14) predicts that the $\delta^{34}S$ value of sulphate is gradually increasing in the Black Sea.

6.5.2 The Azov Sea

The Azov Sea is a huge, shallow gulf of the Black Sea. Its salinity is as high as 13% in the south and 10–12% in the remainder, decreasing to 2–4% near river mouths. The sulphate flux to the Azov Sea includes river runoff, precipitation, fluxes via the Kerch Strait, and a small-scale water exchange with Sivash (Tsurikova and Shulgina, 1964). On the average, 27.5 Tg of sediments with a sulphur content of 1.1% reach the sea bottom annually (SCOPE 19, 1983).

The isotopic compositions of water-insoluble sulphate and other sulphur forms in sediments of this water basin have been thoroughly studied (Rabinovich, 1971; Migdisov et al., 1974; Rabinovich and Veselovskiy, 1974; Mekhtiyeva, 1975; Chukhrov et al., 1975). The $\delta^{34}S$ values for $SO_4^{2-}$ correlate with the salinity and directions of currents (Figure 6.13). The

![Figure 6.13 Map of the Azov Sea with currents (arrows), sampling sites, and $\delta^{34}S$ values of $SO_4^{2-}$]
influence of river runoff is clearly evident in zones adjacent to mouths. The admixture with Black Sea water is observed in the south and central parts of the basin. The $\delta^{34}S$ values of sulphate vary from $+12.8\%_0$ in the middle of the Taganrog Gulf to $+18.5\%_0$ in the open, southern part of the sea.

The reduced S forms in sediments become gradually depleted in $^{34}S$ in going from freshwater lagoon to normal sea sediments. These variations in the isotopic composition of sulphur are not related to the distribution of organic carbon in the sediments. On the contrary, they correspond to changes in salinity and sedimentation conditions. Data obtained by Migdisov et al. (1974) show that sulphur with a $\delta^{34}S$ value of $+9.2\%_0$ is buried in sediments over most of the sea area. In the Kerch region, the $\delta^{34}S$ value is $-22\%_0$. If sulphur with isotopic composition similar to the Kerch region is assumed to constitute only 10% of the bulk of the sulphur, then sulphur buried in the Azov Sea sediments has a $\delta^{34}S$ value of about 6%.

The mass isotopic balance of sulphur from the Azov Sea shows that the expenditure of sulphur exceeds its income, with a net loss of $^{34}S$-depleted sulphur (Table 6.15). Therefore, $SO_4^{2-}$ in the Azov Sea is becoming progressively enriched in $^{34}S$.

### 6.5.3 The Caspian Sea

The present isolation of the Caspian Sea from the world ocean system is a short period in its long history. This basin is one of the links in the

<table>
<thead>
<tr>
<th>Inputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (%)</th>
<th>Outputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River runoff</td>
<td>1.15</td>
<td>+5.4</td>
<td>Efflux to the Black Sea</td>
<td>16.50</td>
<td>+17.0</td>
</tr>
<tr>
<td>Precipitation</td>
<td>0.07</td>
<td>7.1</td>
<td>Efflux to Sivash</td>
<td>0.42</td>
<td>+16.0</td>
</tr>
<tr>
<td>Flux from Sivash</td>
<td>0.16</td>
<td>+19.0</td>
<td>Burial in sediment</td>
<td>0.30</td>
<td>+9.0</td>
</tr>
<tr>
<td>Flux from the Black Sea</td>
<td>14.98</td>
<td>+19.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>16.36</td>
<td>+18.0</td>
<td><strong>Total</strong></td>
<td>17.22</td>
<td>+16.8</td>
</tr>
</tbody>
</table>

*Note: Flux data from Tsurikova and Shulgina (1964), Migdisov et al. (1974), Rabinovich and Veselovsky (1974), Scopintsev (1975); isotopic data from Mekhtiyeva (1975), Rabinovich and Grinenko (1979), Lein and Ivanov (1983).*
Mediterranean Sea system, known in palaeogeography as the Thetis Ocean. Ocean waters last penetrated into the Caspian depression about 10 million years ago. Since that time, the Caspian Sea has undergone repeated salination and desalination.

The present salinity ranges from 0.03‰ in the northern part to 13.5‰ in the south-east (Figure 6.14). As the salinity increases, the sulphur isotopic composition also changes. The northern part is influenced by river runoff ($\delta^{34}$S value of sulphate, $+8.7\%$). The $\delta^{34}$S value increases to $+10.5\%$ in the middle and to $+13.3\%$ in the southern regions.

The content and isotopic composition of sulphur forms in the Caspian sediments were studied by Mekhtiyeva (1974, 1980). Mekhtiyeva and Rabinovich (1975) calculated the isotopic balance of sulphur for 1973 (Table 6.16).

Figure 6.14 Map of the Caspian Sea with currents (arrows), sampling sites, and $\delta^{34}$S values of $\text{SO}_4^{2-}$. For Kara-Bogaz-Gol, the average $\delta^{34}$S is based on 15 determinations.
Table 6.16 Mass isotopic balance of sulphur in the Caspian Sea

<table>
<thead>
<tr>
<th>Inputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (‰)</th>
<th>Outputs</th>
<th>$10^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River runoff</td>
<td>6.682</td>
<td>+6.6</td>
<td>Efflux to Kara-Bogaz-Gol</td>
<td>10.0</td>
<td>+13.0</td>
</tr>
<tr>
<td>Precipitation</td>
<td>0.364</td>
<td>+6.2</td>
<td>Burial in sediments</td>
<td>2.49</td>
<td>-22.3</td>
</tr>
<tr>
<td>Ground water</td>
<td>0.833</td>
<td>+4.0</td>
<td>Wind</td>
<td>0.07</td>
<td>+11.8</td>
</tr>
<tr>
<td>Total</td>
<td>7.879</td>
<td>+6.0</td>
<td></td>
<td>12.56</td>
<td>+6.0</td>
</tr>
</tbody>
</table>

The data show that the sulphur balance in the Caspian Sea is very dependent on the water supply to the Gulf of Kara-Bogaz-Gol, the largest gulf in this area. Kara-Bogaz-Gol is a huge lagoon to which water arrives over high rapids. Due to intensive evaporation, large amounts of salt are precipitated, making this gulf the largest salt deposit in the world. The annual water flux from the Caspian Sea to the gulf changed from 25 km$^3$ in 1930 to 5.39 km$^3$ in 1976. Calculations show that at a water flux to Kara-Bogaz-Gol of 10–11 km$^3$ yr$^{-1}$, a balance is established both in the concentration of sulphates in the Caspian Sea and the isotope composition of sulphur. At a water flux of 25 km$^3$ yr$^{-1}$, the sulphate content in the Caspian Sea would decrease in one year by 30 Tg or 13%, and its $\delta^{34}S$ value would increase by 0.13‰ as the result of biogenic sulphide production.

6.5.4 The Baltic Sea

The Baltic Sea is almost surrounded by land. The limited water exchange with the North Sea and significant runoff established its low salinity, which decreases drastically from west to east and from bottom layers to the surface. The Baltic Sea has a constant bilayer structure. Its southern and central parts are covered by a water layer with a salinity of 7–8‰. At the mouth of the Gulf of Finland, it decreases to 6.2‰; in Neva Bay, it drops to 0.5‰. The bottom water salinity ranges from 8 to 19‰, increasing towards the Danish Straits. Between the surface and bottom layers, there is an intermediate mixing zone (Chernovskaya et al., 1965; Mikulsky, 1974).

The distribution of $\delta^{34}S$ values in silt sediment cores of Kiel Bay, over the depth interval from 0 to 40 cm, was studied by Hartman and Nielsen (1969). The sediments in the central, eastern and southeastern parts of the Baltic Sea were studied by Lein et al. (1982) and Migdisov et al. (1983).
The mass balance of sulphur calculated from these data (Lein and Ivanov, 1983) shows that 0.44 Tg of reduced sulphur with an average $\delta^{34}S$ value of $-17.2\%$ and $-0.616$ Tg of sulphate sulphur with a $\delta^{34}S$ value of $+24.3\%$ enter the reduced fine-grained sediments over the entire area of the sea annually. The total annual sulphur flux to the sediment of 0.46 Tg has an average $\delta^{34}S$ value of $-15.7\%$.

A sulphur mass balance for the Baltic Sea is given in Table 6.17; since information is limited these calculations are tentative.

Because of the lack of data on the isotopic composition of waters flowing through the Danish Straits, analogous information from the Azov and Black Seas has been used. The flux from the North Sea, varying in salinity from 10 to 12\%, consists of water from the Baltic Sea which mixes with ocean water in Kattegat. The salinity of the latter waters is lower than that of ocean water (15–25\%; Mikulsky, 1974).

Preliminary calculations show that the average isotopic composition of sulphates in the Baltic Sea is strongly influenced by the ocean. Lesser effects are produced by continental runoff, sulphur burial in sediments, and fluxes from the atmosphere.

### 6.5.5 The Red Sea

The Red Sea depression was formed as a result of complex rift processes beyond the limits of the continental shelf. The depth increases steeply down to 500–700 m. On the long axis, there is a crack with depths as much as 200–2600 m. It is a zone of young fractures, characterized by tectonic and volcanic activity. Strong thermal currents and the evolution of hot brines

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**Table 6.17 Approximate mass isotopic balance of sulphur in the Baltic Sea**

<table>
<thead>
<tr>
<th>Input</th>
<th>10$^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (%)</th>
<th>Outputs</th>
<th>10$^6$ tonnes yr$^{-1}$</th>
<th>$\delta^{34}S$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux via straits</td>
<td>914</td>
<td>+19.5</td>
<td>Efflux via straits</td>
<td>915</td>
<td>+18.0</td>
</tr>
<tr>
<td>Precipitation and dry deposition</td>
<td>0.7</td>
<td>+4.8</td>
<td>Burial in sediments</td>
<td>0.6</td>
<td>-15.7</td>
</tr>
<tr>
<td>River runoff</td>
<td>1.0</td>
<td>+6.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>915.7</td>
<td>+19.5</td>
<td>915.6</td>
<td>+18.0</td>
<td></td>
</tr>
</tbody>
</table>

* Precipitation and dry deposition, Jensen and Nakai (1961) and Chukhrov et al. (1977); river runoff, Rabinovich and Grinenko (1979); sediments, Lein and Ivanov (1983).
have formed metal-bearing sediments. Sixteen underwater brine ‘basins’ have been discovered so far.

The salinity is substantially higher than that of the ocean due to intense evaporation. It is 36.7‰ in the southern and 40.5‰ in the northern parts of the sea. The salinity of thermal waters filling the depressions is much higher (up to 319‰ in Atlantis II).

This unusual hydrothermal regime of the Red Sea is reflected in the isotopic composition of sulphur in the sediments (Hartman and Nielsen, 1966; Kaplan et al., 1969).

The isotopic composition of sulphate from pore waters in metal-bearing sediments in the Atlantis depression is the same as those of brine and seawater sulphates. On this basis and other evidence, it is concluded that bacterial sulphate reduction does not occur in these sediments (temperature about 60 °C and salinity about 300‰). The sediments in this depression differ from those normally found in the deep ocean. There are abnormally high concentrations of sulphides, mainly sphalerite and to a lesser extent pyrite, whereas in normal sediments, pyrite prevails. In Atlantis II, there is also gypsum, anhydrite, and elemental sulphur.

On the basis of δ³⁴S values, sulphur of the Red Sea may be separated into four groups: sulphates of pore waters in normal sediments (+23‰); sulphates of brines, sulphate minerals, and some pore waters (+15 to +23‰); sulphides, sulphate minerals, and elemental sulphur of metal-bearing sediments with temperatures higher than 50 °C (+12 to +15‰); and sulphides from normal sea sediments and depressions with brine temperatures of less than 50 °C (−20 to −37‰).

The sulphur isotope data demonstrate the existence of two sulphur cycles in the Red Sea sediments. One is the normal type found in the water basins and includes both abiogenic and biogenic reactions. The second is only biogenic and typical of thermal waters and highly mineralized sediments. Both systems and their interactions have not been adequately studied and it is impossible to calculate a mass isotopic balance. Sulphate in the body of the Red Sea is isotopically homogeneous and similar to that of ocean water.

6.5.6 Conclusion

The isotopic composition of sulphur has been summarized for five inland seas. With the exception of the Red Sea, they are distinguished by low salinities.

Many factors determine the isotopic composition of SO₄²⁻ in continental seas. The most important is water exchange with the World oceans, via straits. The Azov, Baltic, and Caspian Seas are strongly influenced by river runoff bearing SO₄²⁻ that is isotopically lighter than that of the ocean.
Sulphate in the Caspian Sea is also affected isotopically by efflux to Kara-Bogaz-Gol. An important factor for all the basins is bacterial sulphate reduction in bottom silt, resulting in the enrichment of heavy isotopes in \( \text{SO}_4^{2-} \).

The isotopic systematics of sulphur in sediments of continental seas is similar to those of the ocean. The distinction is that the initial concentration and isotopic composition of dissolved sulphate may be different.

### 6.6 RIVERS*

A comprehensive review of the isotopic composition of sulphur in rivers has already been published (Ivanov et al., 1983). This section therefore, will focus primarily on more recent reports.

The \( \delta^{34}\text{S}\text{SO}_4^{2-} \) in any river represents a mixture of the sulphur derived from the soil, bedrock, and the atmosphere. It can be modified by biotic processes in the river and its watershed. In principle, the \( \delta^{34}\text{S} \) measurements can be used (a) to fingerprint the sources of sulphur and (b) as a natural tag on the key pathways of sulphur transformation in riverine ecosystems. Combined measurements of the isotopic compositions of sulphur and oxygen in sulphate further constrains the possible sources, key processes, and pathways. So far, however, relatively little work has been done on sulphur isotope systematics in the watersheds of the major rivers of the world.

In an ambitious study, Longinelli and Edmond (1983) found fairly uniform \( \delta^{34}\text{S} \) values in the Amazon basin (Figure 6.15). The sulphur isotope data suggest that a large fraction (over 60%) of the sulphate load of the river originates from the Permian evaporites (\( \delta^{34}\text{S}, +10\%_o \)) in the Andes source region. About 35% of the dissolved sulphate was attributed to oxidative weathering of sulphides in bedrocks downstream in the drainage basin. The contribution of cyclic sulphate from rainfall was believed to be only 5%. The \( \text{SO}_4^{2-} \) concentration in the Amazon River is only 3 mg \( \ell^{-1} \), which is similar to the level one finds in many remote (unpolluted) headwater streams dominated by atmospheric inputs. The conclusion that little of the sulphate in the Amazon is derived from the atmosphere is thus surprising considering the high frequency of volcanic activities in South America.

The \( \delta^{18}\text{O} \) values of sulphate in the Amazon basin hover around +7.5\%o upstream of the Tefe confluence (Figure 6.15). Below this point, a divergence develops with downstream \( \delta^{34}\text{S} \) values becoming less than +3\% in 1976, but increasing to +9\% in 1977. These values presumably reflect yearly differences in rates of \( \text{SO}_4^{2-} \) uptake (assimilatory sulphate reduction) by the local fauna and flora. The absence of discernable parallel effects in the
$\delta^{34}S$ values supports this conclusion and argues against extensive dissimilatory sulphate reduction in the river basin.

The histogram of $\delta^{34}SO_4^{2-}$ for the Amazon basin is compared against similar plots of the data for Mackenzie River, Canada, and the major rivers of the Soviet Union (Figure 6.16). The very tight clustering of data from the Amazon strongly suggests that most of the sulphur is derived from one dominant source. The Mackenzie data show two minor clusters in the range of $-1$ to $+4\%$ and $+8$ to $10\%$. The faint bimodality and the wide spread in $\delta^{34}S$ values (which spans the isotopic range for the bedrocks) suggest that

Figure 6.15 $\delta^{34}S$ and $\delta^{18}O$ values for dissolved sulphate as a function of location along the main channel of the Amazon River (Longinelli and Edmond, 1983)
Figure 6.16 δ³⁴S⁰⁻ histograms for the Amazon, Mackenzie, and the major rivers of the Soviet Union (data from Longinelli and Edmond, 1983; Hitchon and Krouse, 1972; Rabinovich and Grinenko, 1979)

The sulphur load in different segments of the river is controlled primarily by inputs from small streams draining geological terrains with isotopically distinct signatures (see Hitchon and Krouse, 1972). The data for the Soviet rivers show a slightly skewed normal distribution about +6‰, although the discharge weighted average was +8‰ (Rabinovich and Grinenko, 1979). The sulphur brought in by individual rivers, however, has distinctive isotopic imprints acquired from the bedrocks. The δ³⁴S⁰⁻ values of Soviet rivers often show pronounced seasonal changes which can result from (a) input of groundwater sulphate (the sole component during the base flow regime) and (b) the additional isotopically lighter sulphur from surface runoff.

Figure 6.17 shows the distribution of sulphur concentrations in the major rivers of the world. The lowest mean SO₄²⁻ concentration in a major river is about 0.6 mg L⁻¹ in River Niger (Nriagu, 1986), whereas the arid Colorado
River has the highest average concentration of over 100 mg l⁻¹. Other rivers with over 50 mg l⁻¹ SO₄²⁻ include the Rhine, Vistula and Oder, Mississippi, Shatt al Arab, and Huang He (see Husar and Husar, 1985).

The average SO₄²⁻ concentration in African rivers is less than 3.0 mg l⁻¹ (Nriagu, 1986). The sulphur load is derived mostly from the weathering of bedrocks dominated by Precambrian shield formations. The mean δ³⁴SO₄²⁻ for African rivers is therefore believed to be +2‰. Sulphate concentrations in South American rivers also average under 3 mg l⁻¹. Since the Amazon is responsible for about 75% of the sulphur flux from the continent, its mean δ³⁴SO₄²⁻ of +7‰ can be regarded as the continental average.

Sulphate concentrations in Asian rivers range from 4 mg l⁻¹ (Brahmaputra and Mekong) to over 70 mg l⁻¹ (Huang He, Indus, and Shatt al Arab). Most of the sulphur burden comes from the weathering of carbonates and evaporites with only minor contributions from the degradation of aluminosilicates (Ming-Hui et al., 1982; Sarin and Krishnaswami, 1984). As expected, the isotopic composition of sulphate in Asian rivers should be highly variable. The δ³⁴SO₄²⁻ value of +10‰ can be considered a realistic average for these rivers.

On the basis of published isotopic data for surface waters of Japan and New Zealand, a δ³⁴SO₄²⁻ average value of +5‰ is proposed for rivers and streams of the Pacific Islands. A large fraction of the dissolved sulphur in Australian rivers is derived from evaporites and from weathering of
sulphide minerals in bedrocks. On the basis of the few published data, the $\delta^{34}\text{SO}_4^{2-}$ for Australian rivers can be assigned a provisional mean value of $+12\%$.

Sulphate concentrations in many rivers of Europe and central North America now exceed 20 mg $\ell^{-1}$, the average values for the two continents being 28 and 26 mg $\ell^{-1}$ respectively (Husar and Husar, 1985). Most of the sulphur burden is of anthropogenic origin, derived primarily from the burning of fossil fuels and smelting operations. On the basis of the available data in the literature, mean $\delta^{34}\text{SO}_4^{2-}$ values for Europe and North America have been estimated to be $+6$ and $+4\%$ respectively.

From available data, a global average for $\delta^{34}\text{SO}_4^{2-}$ in rivers is estimated to be $+7\%$. This must be regarded as a very tentative value pending further studies on the isotopic composition of sulphur in the major rivers of the world.

### 6.7 GROUND WATER*

#### 6.7.1. Introduction

The concentration and isotopic composition of aqueous sulphur compounds in ground waters is determined by a variety of inputs and reactions (Figure 6.18). In some areas, wet and/or dry fallout with subsequent evaporative enrichment at ground surface is the dominant source. In other areas, any or all of dissolution or precipitation of sulphate minerals, the oxidation of pyrite or organic matter, bacterial reductions, and sulphide mineralization may be important. Thus, the use of environmental isotopes for the recognition of anthropogenic sulphur in ground waters is a difficult task. Difficulties in interpreting such data is one reason why, until recently, only a relatively small number of papers on the subject have been published. However, recent investigations clearly show that the $^{34}\text{S}$ and $^{18}\text{O}$ contents of inorganic, aqueous sulphur compounds (primarily $\text{SO}_4^{2-}$, $\text{H}_2\text{S}$, or $\text{HS}^-$) can provide information on

(a) the origin of sulphur;
(b) biogeochemistry, evolution of ground waters; and
(c) groundwater residence flow paths.

The geochemistry of many young and economically important groundwater systems is controlled by the recharge environment, i.e. climatic conditions, precipitation and dry fallout, vegetation cover, soil and bedrock compositions, and depth to the water table. This environment determines how much and

*P. Fritz and R.J. Drimmie.*
what kind of sulphur species enter the groundwater regime and it is here that the magnitude of man’s influence on the aqueous sulphur system is determined.

Rock–water interactions within aquifers subsequently can add considerably more sulphate (or sulphide) than the amounts released in the unsaturated zone. Such ‘aquifer’ sulphur will reflect the isotopic composition of dissolving aquifer minerals or, where sulphide oxidation has occurred, the environment in which sulphate was formed. These additions may mask recharge input, but can yield information about flow paths and the geochemical evolution of a groundwater body.

In the following discussion, recharge environment and ground waters 
\textit{sensu stricto} are discussed separately in an attempt to describe the complexities of the sulphur system in the hydrosphere and to summarize the observations that can be derived from isotope analyses on aqueous sulphur compounds.

\textbf{6.7.2 The recharge environment}

Where groundwater recharge takes place, man’s influence on the sulphate/sulphide concentrations and isotopic compositions occurs at several levels:
Figure 6.19 The oxygen and sulphur isotopic composition of aqueous sulphate in fallout, soil leachate and shallow ground waters in two small watersheds on the crystalline rocks of the Canadian Shield
(a) Fallout in precipitation or as particulate matter, from reservoirs that are approximately equal in size (Kramer, 1975)
(b) Surface ‘contamination’ from waste disposal or fertilizer
(c) Geochemical or biological reactions initiated through land cultivation, irrigation, or drainage

Fallout and its isotopic composition has been described in Chapter 5. The $\delta^{18}O$ and $\delta^{34}S$ values of fallout are strongly dependent on the sulphur source and the meteorologic environment in which the oxidation to sulphate occurred. Thus, in coastal environments, marine sulphate tends to dominate ($\delta^{18}O = +9.5\%$ SMOW and $\delta^{34}S = +20\%$). At inland stations, industrial or bacterial sulphur released from soils and open waters determines isotopic compositions (Nriagu and Coker, 1978b). Terrestrial sources can be variable with $\delta^{18}O$ and $\delta^{34}S$ values as high as $+20\%$ (Holt et al., 1978; Krouse, 1980). In general, anthropogenic sulphate has $\delta^{34}S$ values between 0 and $+10\%$ and $\delta^{18}O$ values between $+5$ and $+15\%$.

In the upper soil zone, fallout participates in a number of biochemical reactions. The nature of these is not yet fully understood, but the effects of such transformations are clearly seen at two small watersheds in northern Ontario, Canada.

Fallout in Ontario is strongly influenced by industrial emissions and typical $\delta^{18}O$ values vary between $+7$ and $+15\%$ with extreme values as high as $+25\%$. The $\delta^{34}S$ values vary between 0 and $+10\%$ (Novicki, 1976; Holt et al., 1978; Feenstra, 1980). Shallow ground waters, however, show much lower $\delta$ values. This is shown in Figure 6.19 for the Perch Lake basin (Chalk River) and Plastic Lake watershed (Dorset).

Both basins are heavily forested. In the Perch Lake basin, the unsaturated zone and the shallow aquifers overlying crystalline bedrock consist of up to 20 m of uniform sand with simple mineralogies. No measurable amounts of sulphate, sulphides, or carbonates are found in the unsaturated zone (2 m to water table). In the Plastic Lake basin, only a thin veneer of glacial till overlies the bedrock.

The $\delta^{34}S$ values of fallout in both watersheds are very similar and typical for industrial pollution in southwestern Ontario. Unfortunately, in both studies, the sampling periods were too short to record seasonal variations similar to those noted by Nriagu and Coker (1978a, 1978b). The $\delta^{18}O$ values for the fallout sulphate differ somewhat between the two basins, possibly because of differences in source and meteorological conditions.

Remarkably similar $\delta^{34}S$ values were found for sulphate in fallout, soil zone (water soluble), and shallow ground waters (Figure 6.20). This contrasts sharply with the $\delta^{18}O$ values in the different compartments, where significant depletions in $^{18}O$ between fallout and ground water/runoff are recognized.
The limited number of samples from soils from the Plastic and Perch Lake basins strongly suggests that the $^{18}O$ depletion occurs already in the uppermost soil horizons, most probably in the organic rich and biologically very active ‘A’ horizons. If, then, the $^{34}S$ values are ‘inherited’ from the fallout, this would suggest that the sulphur is in steady state, i.e. no significant sources or permanent sinks exist in the soil zone as well as the shallow ground waters of those systems.

However, for the sulphur budget of recharge areas, the release of biogenic, including bacteriogenic, sulphur may be important. Nriagu and Coker (1978b) provide data which suggest that 10–30% of fallout sulphur in the Great Lakes basin has such an origin. Reduced sulphur compounds emitted by vegetation are most probably depleted in $^{34}S$ (Winner et al., 1981) and it is believed, but not fully documented, that bacterial activities in soils, wetlands, and open-water bodies are mainly responsible for their production and release to the atmosphere. Thus, many detailed studies are required before the role of wetlands versus normal forest vegetation and soils in this cycle is fully described and understood.

Minor enrichment in $^{34}S$ in soils and, more importantly, in aqueous environments are most likely due to bacterial reduction which would cause
a preferential enrichment in $^{34}\text{S}$ and $^{18}\text{O}$ in the residual sulphate (Mizutani and Rafter, 1969). Uptake of sulphur by vegetation or bacterial activities and the mineralization of organic sulphur are expected to be important. This would involve reduction and oxidation reactions, which would cause a 'readjustment' of the $\delta^{18}\text{O}$ value of sulphate. The origin of oxygen in 'secondary' sulphate depends on the environment in which oxidation takes place. Under aerobic conditions, about two-thirds of the oxygen will come from the water and one-third from atmospheric oxygen (Lloyd, 1968; see Chapter 2), but in oxygen-poor environments, the $\delta^{18}\text{O}$ value of the sulphate can be very close to that of the water. In both cases, the observed depletion of $^{18}\text{O}$ in soils and the unsaturated zone can be explained (Taylor et al., 1984; van Everdingen and Krouse, 1985).

Land cultivation, irrigation, and possibly fertilizers (Chesterikoff et al., 1981) contribute to salinization problems in many parts of the world, and as sulphate is often a major dissolved constituent in the saline waters, isotopic studies might reveal important information about its source. For example, on the prairies of southern Alberta, Canada, saline soils and ground waters threaten large areas of agricultural land. Sulphate is a major constituent of these salts.

Canadian prairie soils in Alberta are largely developed on tills which since deglaciation have been subject to weathering to a depth of several metres. Organic carbon in the form of coal chips (Cretaceous) is abundant in many areas. During weathering, this organic matter becomes oxidized and is believed to be the source of the sulphate. Isotope analyses on sulphate found in shallow ground waters in recharge environments support this interpretation (Wallick, 1981; Wallick and Huemmert, 1983; Hendry et al., 1986). However, locally and in deeper strata, reduction does take place. Since bacterial or inorganic reduction will cause enrichments in both $^{18}\text{O}$ and $^{34}\text{S}$, a wide spectrum of isotopic compositions in the aqueous sulphate is found. The $\delta^{34}\text{S}$ values measured in this till aquifer vary between $+10$ and $-30$ permil% (Shakur, 1982), with the more negative values being attributed to the oxidation of reduced and isotopically depleted sulphur. On the other hand, where reduction is important, pyrite may precipitate a $\delta^{34}\text{S}$ value similar to this dissolved sulphide. Overall, this can result in a depth gradient with more positive $\delta^{34}\text{S}$ values in sulphur found at depth within partially reducing environments and lower $\delta^{34}\text{S}$ values near the top, where oxidation of reduced sulphur becomes important.

Till deposits are typically very tight with very low hydraulic conductivities. Thus, it can take many weeks before piezometers yield enough water for chemical and isotopic analyses. Hendry et al. (1986) present, therefore, isotope data extracted directly from the tills of southern Alberta (Canada) by an aqueous extraction technique. Their findings (Figure 6.20) are strikingly similar to the data shown in Figure 6.19. In both cases, the $\delta^{34}\text{S}$
values of sulphate in weathered and unweathered tills are very similar, but the secondary sulphates of the weathered till have considerably lower $\delta^{18}O$ values. Contrary to the Chalk River-Dorset data, the weathered tills are characterized by substantially higher sulphate contents than seen in the unweathered material. Thus, although the physical settings and geochemical environments are different, the data indicate that secondary processes in soils and ground water can produce sulphate with negative $^{18}O$ values approaching those of the local ground water.

The oxidation of reduced sulphur can proceed via inorganic reactions or can be bacterially mediated. Of special interest is a denitrification reaction proposed by Kolle et al. (1983) on the basis of field data. The reduction (loss) of $NO_3^-$ (often formed by oxidation of $NH_4^+$) can proceed with the help of *Thiobacillus denitrificans* by the reaction:

$$5 FeS_2 + 14 NO_3^- + 4 H^+ \rightarrow 7 N_2 + 10 SO_4^{2-} + 5 Fe^{2+} + 2 H_2O$$

The pyrite is thought to be microcrystalline and may have an organic matter precursor. The reaction suggests that all oxygen in the sulphate originates in the nitrate. However, a limited number of data from shallow ground water in a small watershed in northern Germany where this process appears to be operative indicates that the $\delta^{18}O$ values are close to those expected by normal aerobic pyrite oxidation (Kolle et al., 1983; Dr O. Strebel, personal communication). Whether this is due to kinetic isotope effects or the participation of atmospheric oxygen is not yet decided.

In conclusion, it is seen that recharge environments are characterized by very intense biological and geochemical processes which have a profound influence on the distribution of environmental isotopes. Thus, the $\delta^{18}O$ and $\delta^{34}S$ values in aqueous sulphate and sulphide reflect the environmental conditions of the recharge environment and do not necessarily correspond to the fallout sulphate values. It is important to note that oxygen isotope analyses clearly point to the upper soil horizons as the loci where the transformation of fallout sulphur takes place.

In deeper horizons of the unsaturated zone and shallow ground waters, addition of sulphate from pyrite and/or organic matter oxidation is potentially important. Such sulphate will reflect the isotopic composition of its precursor and the $\delta^{18}O$ value will be determined by the environment in which the oxidation occurred. The highest $\delta^{18}O$ values are typically found in sulphate formed in systems open to atmospheric oxygen, whereas the lowest will form in oxygen-poor environments and approach the $\delta^{18}O$ value of the water in which they are generated.
6.7.3 Ground water

As discussed above, the geochemistry of many young and active groundwater systems is dominated by processes in the recharge environment. Evaporites are usually not important in recharge areas. Exceptions are evaporative environments such as those found in arid zones (Robinson and Ruwaih, 1985; see Section 8.6).

In deeper aquifers, sedimentary strata are often important. The dissolution of gypsum and/or anhydrite proceeds with isotope selectivity and the sulphate in solution preserves the evaporite δ values unless reducing conditions cause a partial loss and heavy isotope enrichments in the residual $\text{SO}_4^{2-}$.

The ranges of $\delta^{18}O$ and $\delta^{34}S$ values of marine evaporites as they were deposited through geologic time are shown in Figure 6.21 which also depicts the typical range of ‘terrestrial’ sulphates as they form through the oxidation of organic matter sulphur, biogenic/diagenetic pyrite, or fallout. The trend for isotope effects associated with bacterial reduction is indicated by the maximum and minimum relative enrichment trends. A summary of isotope analyses on sulphur compounds in groundwater systems has been presented by Pearson and Rightmire (1980).

Figure 6.21 Range of isotopic compositions in terrestrial and marine sulphates. Trend lines expected for bacterial reductions and isotope exchange between sulphate and water are also indicated.
A practical application was presented by Frank (1974) at the Asse salt dome in Germany where a nuclear waste disposal programme is in progress. Sulphur isotope analyses were used to identify flow paths of ground waters that had passed through different evaporitic sequences. Permian and Lower and Middle Triassic gypsum occur in various horizons. Since the $\delta^{34}S$ values of oceanic $SO_4^{2-}$ were different during each period, the origin of groundwater sulphate can be determined. Similar studies based on the observation that dissolved, marine sulphates behave conservatively in many aquifers and preserve the signatures of their evaporative precursors have been undertaken elsewhere in Germany (e.g. Nielsen and Rambow, 1969; Geyh and Michel, 1977; Michel and Nielsen, 1977; Nielsen, 1979). Correlations with evaporative sequences permitted determinations of flow paths and also recognized where marine sulphate was mixed with sulphate originating from the oxidation of pyrite.

The dissolution of marine gypsum is often accompanied by a dramatic increase in $[SO_4^{2-}]$. Figure 6.22 summarizes isotope data collected from a major aquifer in south-west Ontario where good-quality ground water is found in glacial deposits, whereas the underlying bedrock yields more saline water. Well installations have to be kept above these strata, a task that is rather difficult because of a very irregular bedrock topography.

The isotope results from this Ontario aquifer show that the shallow ground waters are considerably depleted in heavy isotopes and have lower $\delta$ values than precipitation fallout. This observation was discussed above and appears to be valid for many recharge areas with a biogeochemically active, unsaturated zone. The addition of Salina sulphate, i.e. gypsum from Silurian sequences, is clearly recognized and sulphur isotope data can be used to quantify bedrock water contributions to the water supply wells (Woeller, 1982). This could not be done with the techniques of physical hydrology or other geochemical techniques.

In a somewhat different environment, Fontes and Zuppi (1976) studied sulphate sources in springs and ground waters of central Italy and recognized two sources for the dissolved sulphate, one being evaporites enriched in heavy isotopes and the other a $^{34}S$-depleted source of reduced sulphur associated with volcanic rocks.

It is evident that in groundwater systems in which reduction becomes important such simple considerations are not possible. An interesting example for this is the Edwards aquifer described by Rightmire et al. (1974) and Rye et al. (1981). The latter report that:

The $\delta^{34}S$ values of dissolved sulfide and the sulfur isotope fractionation between dissolved sulfide and sulfate species in Floridan groundwater generally correlate with dissolved sulfate concentrations which are related to flow patterns and residence time within the aquifer. The dissolved sulfide derives from the slow in situ biogenic reduction of sulphate dissolved from sedimentary gypsum in
the aquifer. In areas where the water is oldest, the dissolved sulfide has apparently attained isotopic equilibrium with the dissolved sulfate ($\delta^{34}S = +65\%$) at the temperature (28°C) of the system. This approach to equilibrium reflects an extremely slow reduction rate of the dissolved sulfate by bacteria; this slow rate probably results from very low concentrations of organic matter in the aquifer.
In the reducing part of the Edwards aquifer, Texas, there is a general down-gradient increase in both dissolved sulfide and sulfate concentrations, but neither the $\delta^{34}\text{S}$ values of sulfide nor the sulfide–sulfate isotope fractionation correlates with the groundwater flow pattern. The dissolved sulfide species appear to be derived primarily from biogenic reduction of sulfate ions whose source is gypsum dissolution although up-gradient diffusion of $\text{H}_2\text{S}$ gas from deeper oil field brines may be important in places. The sulfur isotope fractionation for sulfide–sulfate ($\sim 38\%_\circ$) is similar to that observed for modern oceanic sediments and probably reflects moderate sulfate reduction in the reducing part of the aquifer owing to the higher temperature and significant amount of organic matter present; contributions of isotopically heavy $\text{H}_2\text{S}$ from oil field brines are also possible.

A Cambro–Ordovician system in the North Central USA was studied by Gilkeson et al. (1981). They present sulphur and oxygen isotope analyses on sulphate from an aquifer in which the recharge aqueous sulphate changes in $\delta^{34}\text{S}$ value from between 0 and $+7\%_\circ$ up to as high as $+30\%_\circ$, whereas $\delta^{18}\text{O}$ values increase from between 0 and $+5\%_\circ$ to about $+17\%_\circ$. Interesting, however, is the fact that ‘ahead’ of the reduced zone is an oxidized zone in which the dissolution of marine carbonates is recognized. The authors explain this somewhat unusual phenomenon as being due to recharge during earlier, but still postglacial, times during which the reducing barrier had not yet been established. They also were able to document that excessively high barium concentrations in these waters could be directly linked to sulphur geochemistry.

It has been proposed that oxygen atoms in aqueous sulphate can exchange with those of water (Figure 6.21). Lloyd (1968) presented experimental data which suggested half-times of between $10^4$ and $10^5$ years for this exchange. Thus, in very old groundwater sulphate, one might have expected a $\delta^{18}\text{O}$ value in equilibrium with that of the water. Recently, however, on the basis of extrapolation from elevated temperature experiments, Chiba and Sakai (1985) argued that the exchange is much slower with a half-time of the order of $10^7$ years.

A comparison of published oxygen isotope data for groundwater sulphates and associated water strongly suggests that equilibration has not been significant. As indicated in Figure 6.21, it would cause an enrichment in $^{18}\text{O}$ only and none of the aquifers analysed shows such phenomena.

However, oxygen isotope exchange between sulphate and water apparently occurs during sulphate reduction. As indicated above (Figure 6.21), bacterial reduction causes both $^{18}\text{O}$ and $^{34}\text{S}$ enrichments. As the product, i.e. reduced sulphur, is removed from the system, often as Fe–S minerals, both isotopes should show Rayleigh behaviour. A $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ plot should thus be a straight line, usually with a slope of 0.25–0.4. This, however, is not maintained in all systems and both laboratory (Mizutani and Rafter, 1973; Fritz et al., in preparation) as well as field data (Basharmal, 1983; Fontes
et al., 1985) strongly suggest that the initial Rayleigh behaviour of the $^{18}$O enrichments does change and asymptotically approaches a constant value which is at least close to the expected value of the sulphate water equilibrium. This is shown in Figure 6.23.

The reaction sequence which permits such 'exchange' is not clear but is possibly approximated by the following reaction paths:

$$
egin{align*}
&\text{H}_2\text{O} \\
\downarrow \\
\text{SO}_4^{2-} + \text{enzyme} \rightleftharpoons \text{SO}_4^{2-} \text{enzyme complex} \rightleftharpoons \text{SO}_3^{2-} \rightarrow \text{H}_2\text{S} \\
\downarrow \\
\text{H}_2\text{O}
\end{align*}
$$

Overall $\text{SO}_4^{2-} \rightleftharpoons \text{SO}_3^{2-}$ equilibration

$$\alpha \approx 1.049$$

$$\text{SO}_3^{2-} \rightarrow \text{H}_2\text{O}$$

$$\alpha \approx ?$$

This shows the enzyme complexing of sulphate and its reduction to sulphite and sulphide. Also indicated are possibilities for isotope exchange as proposed by Mizutani and Rafter (1973). This behaviour is shown in Figure 6.24 which also summarized unpublished data by Fritz et al. (in preparation).

The laboratory data document that a $\delta^{18}$O difference between sulphates and water of about $+30\%_o$ is approached if this difference is plotted against the residual sulphate of a reducing system. This is close, if not identical, to the isotopic difference expected for isotopic equilibrium between water and sulphate.

The field data (Figure 6.24) come from a study in central Sweden and the 'asymptotic' behaviour of $\delta^{18}$O, if compared to $\delta^{34}$S, can be recognized. Again, the isotopic difference between sulphate and water is close to $30\%_o$.

The isotope geochemistry of sulphur compounds in ground waters depends strongly on existing redox regimes. When oxidizing conditions prevail, the oxygen and sulphur isotopic compositions of sulphate in ground waters are diagnostic of the origin of the sulphate. It is usually possible to distinguish between sulphates added through the oxidation of reduced sulphur and contributions from marine evaporites. The variable isotopic composition of evaporites deposited during different geologic periods often permits rather detailed analyses of flow paths. Under favourable circumstances, isotope data can be used in mass balance calculations that attempt to unravel mixing relationships of different ground waters.

Bacterial reduction of sulphate causes both $^{18}$O and $^{34}$S enrichments. However, whereas the sulphur isotopic composition of the residual sulphate shows Rayleigh behaviour, the $\delta^{18}$O values approach those expected for
Figure 6.23 The isotopic composition of sulphate in ground waters in Central Sweden.
Figure 6.24 The isotopic difference in $^{18}$O contents between water and sulphate in a reducing system is plotted against the residual fraction (% residual SO$_4^{2-}$). Open squares are data from Mizutani and Rafter (1973), solid circles are unpublished data from Fritz et al. (in preparation). The figure shows convergence of the experimental data at $\delta^{18}$O$_{\text{water}} - \delta^{18}$O$_{\text{sulphate}} = +30\%$.

sulphate–water equilibria. This bacterially mediated 'exchange' does occur in ground waters, but strict inorganic exchange as proposed by Lloyd (1968) does not play a significant role. Therefore $\delta^{18}$O values of sulphate cannot be used as an indirect dating tool to assess groundwater ages.

6.8 ISOTOPIC COMPOSITION OF SULPHATE IN GAS- AND OILFIELD FORMATION WATERS*

The isotopic composition of SO$_4^{2-}$ in 'formation waters' of oil and gas deposits is appropriate to study for the following reasons:

(a) During exploration and exploitation of oil and gas deposits, formation water comes to the earth's surface together with hydrocarbons. Sulphur isotopes can be used to detect its presence and trace its migration in shallow groundwater systems.

(b) Formation waters may be contaminated by drilling fluids or water to enhance oil recovery.

*R.G. Pankina.
(c) Sulphate in formation waters can be biologically and thermochemically reduced to H_2S. Oil and gas may be involved in the reduction process.

Thode et al. (1958) were the first to report on the isotope composition of SO_4^{2-} in formation waters of the Devonian Leduc field of Alberta, Canada (Table 6.18). The range in \( \delta^{34}S \) values of 10\% can be explained by variations in the isotope composition of Devonian evaporites (see Section 4.3).

Data obtained by the author on the sulphur isotopic composition of formation water SO_4^{2-} in gas- and oil-bearing strata of Devonian, Carboniferous, and Permian reservoir rocks in the Middle Volga region are shown in Figure 6.25. Waters in terrigenic deposits of the Middle and Upper Devonian are CaCl_2 brines with very low [SO_4^{2-}]. The gas does not contain H_2S and the \( \delta^{34}S \) values of SO_4^{2-} vary from +9.7 to +16.8\% over the region. Since these values are lower than those of Devonian evaporites, there is a significant contribution of secondary sulphate.

The mineralization in waters in Lower Carboniferous deposits varies from several milligrams to 280 g \( \ell^{-1} \). However, the Na^+/Cl^- coefficient is rather stable (0.72–0.85). The [SO_4^{2-}] content usually varies from 100 to 2680 mg \( \ell^{-1} \). Most samples are enriched in \(^{34}S\) whereas some approach the Carboniferous evaporite value (+14.0\%). The enrichments in \(^{34}S\) result from intensive SO_4^{2-} reduction, as shown by the presence of \(^{34}S\)-depleted H_2S and the existence of sulphate reducing bacteria. Since the minimum \( \delta^{34}S \) values were only slightly lower than those for evaporites, contributions from secondary sulphates leached from clays and sands prevailing in the region are minor. In some cases, the lower \( \delta^{34}S \) values might reflect an incursion of Lower Permian waters.

Waters from Middle Carboniferous deposits (mostly carbonate) are less mineralized with higher SO_4^{2-} contents (up to 1560 mg \( \ell^{-1} \)). However, there are regions where waters are more metamorphosed and contain less SO_4^{2-}. H_2S is found in all dissolved gases. The isotopic composition of

<table>
<thead>
<tr>
<th>Well</th>
<th>SO_4^{2-}, ppm</th>
<th>( \delta^{34}S ), (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>314</td>
<td>743</td>
<td>+19.5</td>
</tr>
<tr>
<td>527</td>
<td>541</td>
<td>+19.9</td>
</tr>
<tr>
<td>308</td>
<td>550</td>
<td>+13.2</td>
</tr>
<tr>
<td>271</td>
<td>676</td>
<td>+22.6</td>
</tr>
<tr>
<td>153</td>
<td>625</td>
<td>+18.8</td>
</tr>
<tr>
<td>Okalta Ireton 4</td>
<td>572</td>
<td>+12.6</td>
</tr>
</tbody>
</table>
Figure 6.25 Sulphur isotope composition of $\text{SO}_4^{2-}$ in formation waters of gas- and oilfields in the Middle Volga region. Vertical dashed lines are estimated mean $\delta^{34}\text{S}$ for contemporaneous oceanic $\text{SO}_4^{2-}$.

$\text{SO}_4^{2-}$ in these waters varies from +2.6 to +19.7%. The significant depletions of $^{34}\text{S}$ identify secondary sulphates as the dominant source. Even intensive $\text{SO}_4^{2-}$ can result in insignificant $^{34}\text{S}$ enrichment if the $\text{SO}_4^{2-}$ concentrations are so high that the actual percentage of reduction is low.

In general, Permian waters are highly mineralized with concentrations of $\text{SO}_4^{2-}$ up to 9400 mg $\ell^{-1}$ and $\text{H}_2\text{S}$ up to 601 mg $\ell^{-1}$. The isotopic composition of $\text{SO}_4^{2-}$ approximates that of Permian evaporites (+8.2 to +10.0%).

Belyi and Vinogradov (1972) reported that $\text{SO}_4^{2-}$ in formation waters of Cretaceous and Jurassic deposits of the Amu-Daria syncline had $\delta^{34}\text{S}$ values of +10.4 to +15.0% and +10.1 to +21.4% respectively.

Vredenburg and Cheney (1971) reported $\delta^{34}\text{S}$ values for $\text{SO}_4^{2-}$ in formation waters in the Wind River basin. In reservoir rocks of different ages, they found +9.1 to +26.7% for Mississippian, +9.5 to +36.6% for Pennsylvanian, +14.5 to +23.4% for Permian, +12.4 to +28.5% for Triassic, +10.4 to +32.7% for Jurassic, and +6.4 to +14.3% for Cretaceous.

In the Big Horn basin, Orr (1974) reported $\delta^{34}\text{S}$ values for $\text{SO}_4^{2-}$ from +8.3 to +25.3% and +10.7 to +27.6% in formation waters contacting Carboniferous (Tensleep) and Permian (Phosphoria) deposits respectively.

The diversity of the isotopic composition of $\text{SO}_4^{2-}$ in formation waters is explained by the combination of water-rock interactions and biological
activity. There may be a SO₄²⁻ remnant from the original water in sediments. Additional SO₄²⁻ may arise from the dissolution of evaporites (enriched in ³⁴S) or secondary sulphate minerals (often depleted in ³⁴S). Surface or near-surface SO₄²⁻ transported downwards by meteoric water intrusion tends to have lower δ³⁴S values than deeper evaporites.

6.9 GEOTHERMAL AREAS*

In volcanic and geothermal areas where fluids are derived from basic magmas at high temperatures, H₂S is the dominant S-bearing gas and its isotopic composition reflects a magmatic source in the upper mantle. Typical δ³⁴S values are around 0‰: Kilauea +0.6 ± 0.2‰, Krafla (Iceland) +0.6 ± 0.3‰ (Robinson, 1986), and Yellowstone 0 ± 3‰ (Truesdell et al., 1978). Acidic melts have higher SO₂/H₂S ratios, but as the temperature decreases H₂S becomes the dominant S-bearing gas in low-temperature fumaroles (< 300 °C) and geothermal systems. Its isotopic composition often still reflects the magmatic source, but in this case there may have been an involvement of crustal rocks and crustal sulphur. The δ³⁴S values of net sulphur discharged from andesite volcanoes in Japan vary from +2.0 to +12‰ as a consequence of crustal contamination (Sakai and Matsubaya, 1977). Average δ³⁴S values for H₂S in New Zealand geothermal systems range from +3.3 to +7.9‰, dominantly due to their setting in rhyolites/andesites (Robinson, 1986).

In the near-surface environment, the H₂S oxidizes rapidly to [SO₄²⁻] in surface waters. Under the extreme conditions in volcanic crater lakes and fumaroles (S concentration 5-10 g kg⁻¹; pH 1), such sulphate may have δ³⁴S values up to +20‰ which can be interpreted as approaching isotopic equilibrium with the H₂S (Robinson, 1978, in New Zealand; Sakai and Matsubaya, 1977, in Japan). Normally, however, the sulphate represents complete or partial oxidation of H₂S without any isotopic fractionation; e.g. Ketetahi hot springs in Mt Tongariro, New Zealand, have δ³⁴S values of +2.6 ± 0.7‰ for sulphate which represents complete oxidation of H₂S.

Sulphate is also present deep in geothermal systems but in much lower concentrations (30 mg kg⁻¹ at Wairakei, New Zealand). This primary sulphate has much higher δ³⁴S values (up to +24‰), representing an approach to or attainment of isotopic equilibrium with H₂S at temperatures around 350–370 °C. Due to the slow rates of isotopic exchange, the high-temperature value is frozen in. If exchange rates are known, residence times in the geothermal system can be calculated (Sakai, 1983). In contrast, oxygen isotopes in the sulphate exchange with water in the geothermal reservoir and can be used as a geothermometer (McKenzie and Truesdell, 1977). The

*B.W. Robinson.
deep geothermal fluids are characterized by high chloride and low sulphate concentrations with high δ\(^{34}\)S values. However, near-surface sulphate produced by H\(_2\)S oxidation characterizes waters that have low chloride and high sulphate concentration with low δ\(^{34}\)S values. Geothermal waters in many parts of the world (United States, New Zealand, and the Philippines) represent mixing between these two end numbers and data scatter about mixing lines as shown in Figure 6.24.

In some coastal geothermal areas of Japan, sulphate δ\(^{34}\)S values of around +20‰ have been used as evidence for present-day sea water contaminating the geothermal fluids (Sakai and Matsubaya, 1977). Also in Iceland, δ\(^{34}\)S values up to +8‰ have been interpreted by Sakai et al. (1980) as due to some seawater interaction. Thermal waters of the Green Tuff type in Japan represent Miocene oceanic sulphate, which in some areas has undergone bacterial reduction, and sulphate δ\(^{34}\)S values range from +20 to +34‰. Similar high δ\(^{34}\)S values have been found in some New Zealand warm springs (< 50 °C) where bacterial reduction may have taken place.

Figure 6.26 Mixing of deep and shallow sulphate in geothermal systems. Data scatter about the mixing lines for Yellowstone (Truesdell et al., 1978) and New Zealand (Robinson and Sheppard, 1986)
Continental geothermal areas in India have sulphate with a wide range in $\delta^{34}$S values: +6.5 to +37.5% (Giggenbach et al., 1983). The oxygen isotopic composition of this sulphate has equilibrated with the thermal water down to 100 °C. Little alteration in the near-surface environment appears to have taken place and the sulphate is thought to originate from sedimentary material at depth.

### 6.10 WARM AND COLD SPRINGS*

#### 6.10.1 Introduction

Sulphur isotope compositions have been measured for sulphur-containing components in a number of springs throughout the world. To a lesser extent, $\delta^{18}$O values for dissolved and related mineral sulphates have also been determined. The isotope data have proved useful in identifying strata with which these waters have interacted and elucidating associated physical, chemical, and biological processes.

Processes occurring in springs are site specific. Two subsurface sulphur source extremes can be considered: sulphide minerals and sedimentary sulphate (Muller et al., 1966; Pankina et al., 1966). It is highly likely that the dissolved S-containing ions are subsequently redistributed in response to redox reactions and pH changes.

Sulphur isotope variations in thermal and cold springs of the world have been reviewed by Krouse (1974). For this volume, the sulphur isotope geochemistry of a few springs where either sulphide or sulphate minerals were primarily dissolved will be examined.

#### 6.10.2 Springs containing primarily dissolved sulphate

In western Canada and probably world wide, the majority of dissolved sulphur in warm and cold springs has originated from the solution of sulphate minerals. In many cases, this sulphate is in evaporites deposited in ancient ocean basins. Such springs often precipitate travertine.

The isotope geochemistry of these springs is essentially that of ground water (Section 6.7) and its modification upon emergence. The concentration of the dissolved ions are altered by pressure reduction, more aerobic conditions, and escape of gases to the atmosphere.

A dominant feature of these waters is that the dissolved sulphate often undergoes bacterial reduction and the sulphide product is markedly depleted in $^{34}$S. Data illustrating this isotopic selectivity for wells, boreholes, and springs south of Great Slave Lake, Canada, are shown in Figure 6.27.

* H.R. Krouse.
Upon approaching the orifice, the sulphide tends to be reoxidized, although significant quantities of H₂S are usually found escaping to the atmosphere. The extent of this reoxidation can seldom be determined from the sulphur isotope composition of SO₄²⁻. However, since oxygen is introduced from O₂ and H₂O during oxidation (Section 2.2.5), the δ¹⁸O value of SO₄²⁻ can be used effectively to assess the sulphide reoxidation. This technique is particularly effective at higher latitudes where meteoric water is more depleted in ¹⁸O. For example, in spring waters near Paige Mountain, NWT, Canada, van Everdingen et al. (1982) demonstrated that up to 30% of the SO₄²⁻ was reoxidized sulphide.

Part of the oxidized sulphide may be precipitated as elemental sulphur and secondary sulphate, often in algal mats, near the spring orifice. These precipitates have δ³⁴S values near that of the dissolved sulphide, as shown for a few springs of western Canada in Figure 6.28. Some secondary sulphate may arise by oxidation of evolved H₂S to SO₂ and H₂SO₄ which subsequently attacks carbonate minerals. This mechanism has been invoked to explain cave development in travertine deposits (van Everdingen et al., 1985). The secondary sulphates are depleted in both ³⁴S and ¹⁸O as compared to the primary sulphate source.

In some hydrological systems, secondary sulphate depleted in ³⁴S and ¹⁸O may be subsequently reduced again to render dissolved sulphide extremely depleted in ³⁴S. This appears to be the case for some Flysch waters in Czechoslovakia (Smejkal et al., 1971).
6.10.3 Springs containing primarily dissolved sulphide

In volcanic and geothermal areas, $\text{H}_2\text{~S}$ is usually the dominant S-bearing species in the fluids and often has $\delta^{34}\text{S}$ values near 0‰, reflecting its magmatic source (see Section 6.9). There are, however, rare occurrences of warm and cold springs where dissolution of mineral sulphides constitutes the main source of sulphur. Such springs often form colourful surface deposits of sulphate minerals such as jarosite. The ultimate origin of the sulphate from deeper mineral sulphide deposits is deduced from metal ion content, variable $\delta^{34}\text{S}$ values of the sulphate that are close to those of the deep sulphide deposit, and $\delta^{18}\text{O}$ values of the sulphate that may be highly negative at high latitudes. A few such springs in western Canada were studied by Shakur (1982).

Barite sinter deposits at Flybye Springs, NWT, Canada, were investigated by Cecile et al. (1984). Although the $\delta^{34}\text{S}$ values ranged from $+15$ to $+23$‰, they were not as positive as barites in vugs of nearby Early to Middle Devonian carbonate units ($+29$ to $+32$‰). Further, the $\delta^{18}\text{O}$ values of the sinter barite were in the range $-11$ to $-17$‰, in contrast to the vug barite values of $+17$ to $+26$‰. The isotope data clearly show that the sinter deposits did not result from simple dissolution of barite, transport, and
precipitation. Rather, sulphate reduction occurred after dissolution, and the sinter sulphate constitutes oxidized sulphide from that reduction.

6.10.4 Sulphur geochemistry of springs in relation to anthropogenic sulphur

From the viewpoint of this volume, the sulphur isotope geochemistry of springs is relevant to many aspects of anthropogenic sulphur in the environment. Emissions of gaseous sulphur compounds from certain springs are substantial, even to the point that high H2S concentrations threaten life. Emission rates have seldom been measured for individual springs and the contributions to the atmospheric sulphur reservoir from springs world wide is not well known. There is the further complication that biogenic emissions from some springs may vary with the seasons. Parameters that may change seasonally include flow rate, temperature, pH, and E_H. These in turn influence the concentrations of S-containing ions and microbiological conversions. Consequently, the emissions may change in rate and isotope composition.

In local situations, seasonally dependent emissions from springs could conceivably complicate assessments of anthropogenic contributions of S compounds to the atmosphere. Concentration measurements alone would prove inadequate. However, it is highly likely that the 834S values of the natural and industrial emissions will differ sufficiently so that, in combination with concentration measurements, sources could be duly apportioned.

Another issue is the extent to which anthropogenic activities might alter the S content and/or microbiological conversions in springs. It is noted that anthropogenic perturbations need not be limited to the addition of sulphur compounds. Introduction of other chemicals, such as nitrogen compounds from fertilizer applications or organic nutrients, might upset physical chemical parameters and microbial balances. Such effects are potentially more likely in springs associated with shallow groundwater systems.

6.11 SUMMARY AND KEY AREAS FOR FURTHER RESEARCH*

The principal sulphur reservoirs in the ocean are shown in Figure 6.29. With the exception of the SO4_2^- pool, reliable data on the sizes and isotopic compositions of these reservoirs are currently not available. The transfer of sulphur between the reservoirs involves physical, chemical, and biological processes, many of which are isotopically selective. Among the transformations, dissimilatory SO4_2^- reduction has been recognized as being the most dramatic in terms of S isotope fractionation, and typically results in

* J.O. Nriagu.
accumulation of the lighter $^{32}$S in the reduced sulphide reservoirs. Isotopic differentiation associated with $\text{SO}_4^{2-}$ assimilation is usually small under natural conditions. Little is known about the isotopic effects of the biologically mediated production of dissolved and volatile organic sulphur compounds. It is conceivable that the production of volatile sulphur compounds is an important pathway in the enrichment of ocean waters with $^{34}$S and the transfer of the lighter $^{32}$S to the continents.

The isotopic composition of present-day sea water is uninspiring in that it deviates but little from a constant value of $+21\%$ (Section 6.2.1). The surprising feature, however, is that oceanic $\delta^{34}\text{SO}_4^{2-}$ had pronounced secular trends (see Section 4.2). The available data in the literature suggest that the mean oceanic $\delta^{34}$S value was similar to the present-day value in late Proterozoic, became heavier in Cambrian through Devonian, declined to a minimum in the Permian, rose again sharply during the Triassic, and has been increasing gradually since the mid-Cretaceous (Figure 6.30).
Furthermore, the mean of $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{13}\text{C}_{\text{carbonate}}$ for the geological periods are negatively correlated ($r = 0.839$), with the linear regression,

$$\delta^{34}\text{C} = 3.074 - 0.131\delta^{34}\text{S} \quad (\text{Veizer et al., 1980})$$

When examined in greater detail, however, cyclical patterns with clockwise and counterclockwise excursions can be discerned (Klump and Garrels, 1986).

This relationship stems from the fact that bacterial $\text{SO}_4^{2-}$ reduction is a major pathway for organic matter decay in marine sediments. It implies that there is a close coupling of the sulphur and carbon cycles which in turn has controlled the levels of $\text{O}_2$ in the atmosphere. The covariance of $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ through time indicates that, during periods of organic carbon burial, oxygen derived from photosynthesis is partly consumed by the oxidation of pyrite to sulphate: carbon is translocated from the inorganic to the organic pool. On the other hand, during periods of intensive sulphate reduction, pyrite is generated and organic carbon is oxidized with the concurrent...
regeneration of the inorganic carbon pool. The linkage of the marine sulphur–carbon–oxygen cycles can be expressed by the following reactions:

$$8 \text{SO}_4^{2-} + 2 \text{Fe}_2\text{O}_3 + 15 \text{CH}_2\text{O} + 16 \text{H}^+ \rightleftharpoons 4 \text{FeS}_2 + 15 \text{CO}_2 + 23 \text{H}_2\text{O}$$

or

$$2 \text{Fe}_2\text{O}_3 + \text{SO}_4^{2-} + 16 \text{CO}_2 + 8 \text{H}_2\text{O} \rightleftharpoons 4 \text{FeS}_2 + 16 \text{HCO}_3^- + 15 \text{O}_2$$

The $\text{SO}_4^{2-}$ includes seawater sulphate or evaporitic gypsum and anhydrite, and $\text{CH}_2\text{O}$ represents organic carbon.

The use of sulphur isotopes in deciphering the linkages between the sulphur cycle and the biogeochemical cycles of the other key elements (N, P, Si, Fe, O, and C) remains a fruitful area for future research. In this respect, it should be noted that in a model in which the burial rate of organic carbon increased by about 30%, the response of the oceanic $\delta^{13}\text{C}$ was nearly instantaneous whereas the $\delta^{34}\text{S}$ value of $\text{SO}_4^{2-}$ changed at a much slower rate, reflecting the long turnover time of the oceanic sulphate reservoir. Oxygen levels are predicted to respond fairly quickly in comparison to the transfer of material between the oxidized and reduced reservoirs of C and S. The latter approach their new steady-state masses and isotopic compositions over several millions of years (Klump and Garrels, 1986).

The present-day biosphere shows a discernable dichotomy in the distribution of sulphur isotopes: $^{32}\text{S}$ tends to accumulate in terrestrial ecosystems whereas the marine environment is enriched with the heavier $^{34}\text{S}$. The available data are clearly inadequate to ascertain the implications of this arrangement on the $\delta^{34}\text{S}$ of the oceans (see Section 6.2.1). There is need for isotopic measurements on the sulphur transported by the major rivers of the world. Even less is known about the isotopic composition of the groundwater sulphur reservoir (Section 6.7). Without these data, it will be impossible to determine the overall isotopic balance which is necessary to evaluate published models of the global sulphur cycle.

Lakes and rivers constitute a tiny sulphur pool in comparison to oceans. Small inputs of sulphur from anthropogenic sources can thus significantly change the concentrations and isotopic composition of the sulphur in many freshwater ecosystems. Indeed, lakes and rivers have become the critical target ecosystems most susceptible to stress from acid rain (Section 6.4.1).

The reservoirs and principal transport pathways for sulphur in freshwater ecosystems are depicted in Figure 6.31. Since lacustrine environments are mostly sulphur deficient, the biota are less discriminating in their metabolism of sulphur isotopes and the fractionation by the various biogeochemical processes generally tends to be small (compare Figure 6.29 and 6.31).

Sulphate reduction (equations above) has now been recognized as a major source of alkalinity in poorly buffered lakes (Kelly and Rudd, 1984; Carignan,
The sulphur cycle therefore plays an indirect key role in determining the response of a susceptible lake to acid rain inputs and the rate of recovery of an acid-stressed lake. The reaction pathway for reduced sulphur in freshwater ecosystems differs from that of the marine cycle in one fundamental way: the \( \text{H}_2\text{S} \) formed is tied up primarily by organic matter and, to a lesser extent, as 'FeS' (Nriagu and Soon, 1985; David and Mitchell, 1985). Formation of pyrite, typical of marine environments, is very much a minor process and presumably occurs by a radically different pathway involving the reaction of organic sulphur compounds with iron:

\[
\text{S-(L)} + \text{S}^0 + \text{Fe}^{2+} \rightarrow \text{FeS}_2 + \text{L}^2^-
\]
\[
\text{S-(L)} + \text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS}_2 + \text{HL}^-
\]

where (L) is any organic ligand. Evidence for the above reaction comes from the isotopic compositions of pyrite in lake sediments which are usually very close to that of the organic sulphur fraction (Nriagu and Soon, 1985). Alternatively, organic S and FeS\(_2\) might arise from the same dissolved sulphide. The actual process of organosulphur formation and the role of these compounds in the lacustrine sulphur cycle remains an important area for research.
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Hydrosphere


Hydrosphere


