CHAPTER 2

Oxygen Isotope Fractionation for Understanding the Sulphur Cycle

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2.1 INTRODUCTION

Oxygen isotope ratio measurements are uniquely applicable to the study of mechanisms of formation of natural or man-made sulphates in the environment because the $^{18}O/^{16}O$ ratios of sulphates that are formed from given supplies of SO_2, water, and oxidants can differ, depending upon the mechanism by which they are formed. Some of the more prominent mechanisms of formation of SO_4^{2-} from SO_2 are aqueous phase air oxidation, aqueous phase H_2O_2 oxidation, and high-temperature oxidation to SO_3 (in combustion sources) accompanied by hydration to H_2SO_4. Once formed, the sulphates of various isotopic ratios are extremely stable with respect to isotopic exchange with water, with which they may be subsequently associated.

Information on mechanisms of formation of sulphates can be very useful in the establishment of limiting criteria for the origins of environmental sulphates and in strategies of pollution control. For example, if the $\delta^{18}O$ (deviation in parts per thousand (‰) of the $^{18}O/^{16}O$ ratio of the sample from that of standard mean ocean water (SMOW)) of atmospheric sulphates at a receptor site of interest is more characteristic of primary sulphates (i.e. sulphates formed within combustion sources before emission into the atmosphere) than of secondary sulphates (i.e. sulphates formed from gaseous sulphur compounds, principally SO_2, by atmospheric conversion processes), it may be suspected that the major source of sulphate pollution at that site is of local rather than distant origin. In such a case, the most effective strategy for control of sulphate pollution and its contribution to acid rain in that area might be more efficient removal of sulphuric acid mist at the local sources of emission.

2.2 BASES FOR THE USE OF OXYGEN ISOTOPY

The concept of determining mechanisms of sulphate formation from oxygen isotope ratio measurements is based on the following phenomena:

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Edited by H.R. Krouse and V.A. Grinenko

(a) The rate of isotopic exchange between sulphate and water is extremely low.
(b) The rate of isotopic exchange between SO_2 and associated water is very high in either aqueous or non-liquid systems.
(c) The difference between $\delta^{18}O$ levels in environmental water and oxidants is usually large.
(d) SO_3 that is formed by high-temperature oxidation of SO_2 hydrates rapidly to form H_2SO_4.

2.2.1 Sulphate–water isotope exchange

Measurements of isotope exchange factors between water and dissolved sulphate, as functions of temperature and pH (Lloyd, 1967; Kusakabe and Robinson, 1977; Chiba and Sakai, 1985), indicate that under typical ambient conditions, the rate of isotope exchange is extremely low. For example, it is evident from kinetic data presented by Lloyd (1967) that, even in a highly acidic rain of pH ~4, the half-time of oxygen atom exchange between sulphate and water is of the order of 1000 years. A significant result of the extremely slow exchange reaction is that, once the sulphate is formed, its $\delta^{18}O$ (which may reflect its mechanism of formation) is preserved. Further, the $\delta^{18}O$ of the sulphate is not appreciably affected by the heat treatments in acidified solutions that are necessary in analytical procedures for the precipitation of $BaSO_4$ (Holt *et al.*, 1978a).

2.2.2 SO_2–water isotope exchange

2.2.2.1 *Aqueous systems*

When SO_2 dissolves in water, it rapidly hydrolyses according to the chemical equilibrium.

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \tag{1}$$

(Eigen *et al.*, 1961; Beilke and Gravenhorst, 1978). Isotopic equilibrium apparently accompanies chemical equilibrium in this reaction, so that, in the atmosphere or hydrosphere, the HSO_3^- isotopically equilibrates with liquid water (in large excess) and upon oxidation the influence of the original $\delta^{18}O$ of the SO_2 on the $\delta^{18}O$ of the sulphate product is effectively lost (Holt *et al.*, 1981a). Correspondingly, because of the overwhelming isotopic influence of the water on the intermediate ion HSO_3^- in the oxidation process, the $\delta^{18}O$ of three of the oxygens in the sulphate product are strongly controlled by the $\delta^{18}O$ of the water oxygens.

In a variety of preparations of sulphate by Fe^{3+} catalysed aqueous air oxidation with water in large excess, Holt *et al.* (1981a) observed that the $\delta^{18}O$ of the sulphate varied with the $\delta^{18}O$ of the water according to regression curves of the general form

$$\delta^{18}O_{SO_4{}^{2-}} = \sim\tfrac{3}{4}\delta^{18}O_{H_2O} + C_1 \qquad (2)$$

The slope of $\sim\frac{3}{4}$ suggests that three of the four oxygens in the sulphate are isotopically controlled by the water. In other experiments in which the $\delta^{18}O$ of the water was held constant, the $\delta^{18}O$ of the sulphate remained constant as the $\delta^{18}O$ of the SO_2 was varied. These results confirmed that the isotopic influence of the SO_2 was erased by hydrolysis in excess water before oxidation.

The effect of the rapid isotopic equilibration between water and dissolved SO_2 was further demonstrated by the $\delta^{18}O_{SO_4{}^{2-}}$ versus $\delta^{18}O_{H_2O}$ relationship obtained when the SO_2 was oxidized by H_2O_2 in aqueous solution. Using reagent-grade H_2O_2 of constant $\delta^{18}O$, the $\delta^{18}O$ of the water was varied, yielding a regression curve of the form

$$\delta^{18}O_{SO_4{}^{-}} = \sim\tfrac{3}{5}\delta^{18}O_{H_2O} + C_2 \qquad (3)$$

The $\frac{3}{5}$ slope suggests that three of the five oxygens in the intermediate adduct HSO_3^-. H_2O_2 were isotopically controlled by the solvent water, two by the oxidant and essentially none by the SO_2. Figure 2.1 gives a comparison of isotopic results from Fe^{3+}-catalysed aqueous air oxidation, charcoal-catalysed aqueous air oxidation, and H_2O_2 aqueous oxidation in curves A, B, and C respectively (Holt *et al.*, 1981a).

2.2.2.2 *Systems with no liquid water*

Experimental results have indicated rapid isotopic equilibration between SO_2 and water vapour in mixtures of SO_2, air, and water vapour (no liquid water), confined to a 3−litre glass container (Holt *et al.*, 1983). Figure 2.2 shows the results of equilibrating SO_2 of constant $\delta^{18}O$ (~14‰) with water vapours of various $\delta^{18}O$ values. Curve A represents experiments in which the equilibrated SO_2 was recovered by evacuating the SO_2–air–water vapour mixture through a dry-ice cold trap (−79 °C) to remove the water vapour and a liquid-nitrogen cold trap to remove the SO_2; curve B represents experiments in which the procedure was the same, except that the water vapour was removed by passing the mixture through magnesium perchlorate for chemical absorption at 22 °C.

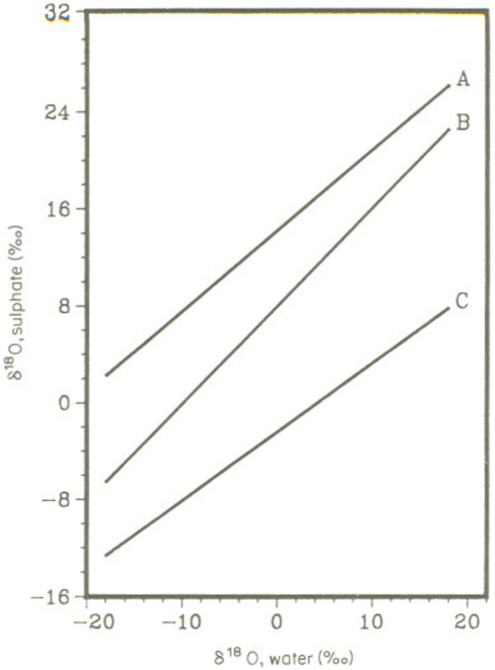

Figure 2.1 Isotopic results of oxidation of SO_2 to sulphate. Curve A, Fe^{3+}-catalysed air oxidation; curve B, charcoal-catalysed air oxidation; curve C, aqueous phase H_2O_2 oxidation

Rapid isotopic equilibration between the SO_2 and the water in these systems is indicated by the effect of temperature, at the point of water vapour separation, on the $\delta^{18}O_{SO_2}$ versus $\delta^{18}O_{H_2O}$ relationship. In both sets of experiments, curves A and B, the SO_2–air–water vapour mixtures were allowed to stand at room temperature for about half an hour before recovery of the SO_2. The results, curve A, suggest striking evidence that the isotopic equilibration responded very rapidly to the change in temperature as the gas mixture flowed through the cold trap (−79 °C) in which the water vapour was removed; the difference of ~19‰ between the *y* intercepts of the two curves is in approximate agreement with the difference in the thermodynamic fractionation factors that are calculable from spectroscopic data for the gaseous species, SO_2 and H_2O, at the two temperatures, −79 and 22 °C. In the reaction by which the isotopic equilibration apparently occurs,

$$SO_2(g) + H_2O(h) \rightleftharpoons SO_2 \cdot H_2O \qquad (4)$$

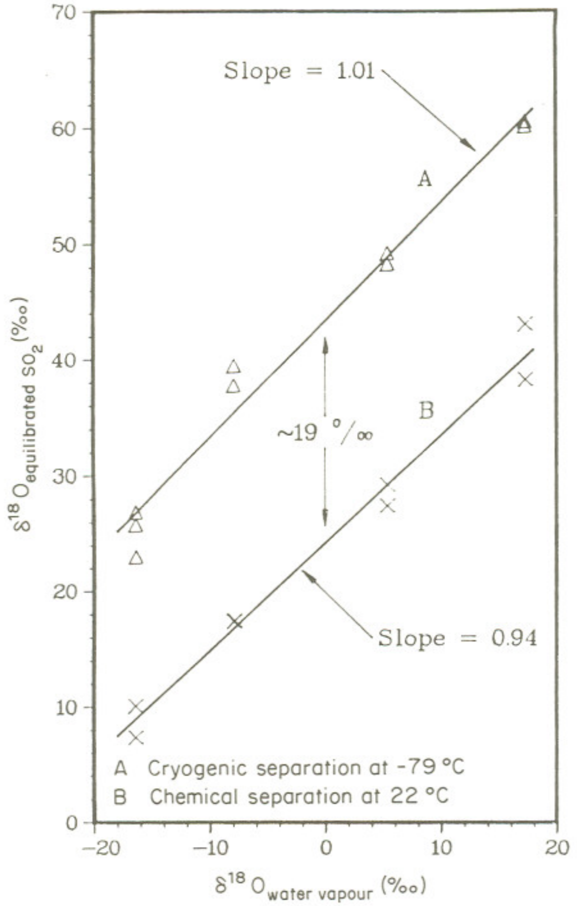

Figure 2.2 Isotopic equilibrations between SO_2 and water vapour at two temperatures (Holt *et al.*, 1983)

the structural form of $SO_2 \cdot H_2O$ (e.g. gas phase or surface adsorbed) is unspecified.

One important consequence of rapid isotopic equilibration between SO_2 and water vapour is that in SO_2–air–water vapour mixtures, in which the water vapour is in large excess (as in the atmosphere), the $\delta^{18}O$ of the SO_2 does not remain unchanged from that at its point of origin; rather, it is dynamically controlled by the $\delta^{18}O$ of the associated water vapour.

Another consequence of rapid isotopic equilibration is that oxidation of SO_2 in humidified air yields sulphate, three oxygens of which are isotopically controlled by the $\delta^{18}O$ of the associated water vapour. Thus, a three-quarters control of sulphate oxygens by associated water is possible in both aqueous and non-liquid systems, although the mechanisms responsible for the two transformation processes are entirely different.

2.2.3 $\delta^{18}O$ values of SO_2 oxidants and of associated water

A potential advantage to the use of $\delta^{18}O$ measurements in the study of mechanisms of sulphate formation is the relatively large difference between the $\delta^{18}O$ of oxygen in air and the $\delta^{18}O$ of waters of the atmosphere and the hydrosphere. A mechanism by which the $\delta^{18}O$ of the sulphate is dominated by the $\delta^{18}O$ of the water (0.0‰ for sea water, down to −50‰ for atmospheric water) is expected to yield a sulphate that is generally lower in $\delta^{18}O$ than one by which the $\delta^{18}O$ of the sulphate is dominated by the $\delta^{18}O$ of air (~23‰; Horibe *et al.*, 1973).

2.2.4 Rapid hydration of SO_3

Sulphur trioxide is formed at high temperatures in SO_2–O_2–SO_3 systems in exhaust gases from smelters, power plants, combustion engines, etc., and is continuously emitted into the atmosphere. As the exhausted gases cool, the SO_3 rapidly reacts with combustion-produced water vapour, and, since the combustion-produced water vapour is relatively high in $\delta^{18}O$ (because of its prior high-temperature isotopic equilibration with air oxygen), the hydrated sulphuric acid that is formed has a relatively high $\delta^{18}O$. This relatively high $\delta^{18}O$ of H_2SO_4 of high-temperature SO_3 origin thereby characterizes its mechanism of formation (Holt and Kumar, 1984).

2.2.5 Sulphide oxidation

On the basis of experiments bubbling O_2 through Na_2S solutions, Lloyd (1967) suggested that the inorganic oxidation of sulphide to sulphate takes place in two steps:

$$S^{2-} + H_2O + O_2 \rightarrow SO_3^{2-} \tag{5}$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-} \tag{6}$$

He concluded that there is no oxygen isotope selectivity during the incorporation of water oxygen. For reaction (6), he attributed a kinetic isotope effect of 8.7‰ favouring the lighter isotope during incorporation of O_2. Lloyd calculated that two-thirds of the oxygen comes from water and one-third from molecular oxygen. This ratio is influenced by oxygen exchange between SO_3^{2-} and water (Section 2.2.2.1).

Taylor *et al*. (1984) cited three reactions involved in the oxidation of FeS_2:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4{}^{2-} + 16\ H^+ \qquad (7)$$

$$Fe^{2+} + \tfrac{1}{4}\,O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\,H_2O \qquad (8)$$

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4{}^{2-} + 2\ H^+ \qquad (9)$$

In reaction (7), all sulphate oxygen is derived from water molecules, whereas in reaction (9), stoichiometrically, 87.5% of the sulphate oxygen is derived from molecular oxygen and 12.5% from water molecules. Taylor *et al*. (1984) plotted $\delta^{18}O$ values for $SO_4{}^{2-}$ in acid mine waters against those of associated H_2O and, on the basis of theoretical lines, estimated the relative contributions of the above reactions. These theoretical lines were revised by van Everdingen and Krouse (1985).

2.2.6 Bacterial $SO_4{}^{2-}$ reduction

Bacteria preferentially metabolize ^{16}O during the reduction of $SO_4{}^{2-}$ to H_2S. This leaves the remaining $SO_4{}^{2-}$ enriched in ^{18}O according to the relationship

$$\delta^{18}O - \delta^{18}O_0 = 1000\ (1 - \alpha)\ \ln F$$

where F is the fraction reacted; $\delta^{18}O$ and $\delta^{18}O_0$ refer to remaining and initial sulphate respectively. Lloyd (1967) found that $1000\ (1 - \alpha) = -4.6‰$.

Mizutani and Rafter (1969b) reported that the ratio of $\delta^{18}O$ to $\delta^{34}S$ of the remaining $SO_4{}^{2-}$ was approximately 1:4. This observation is interesting because of the one sulphur atom to four oxygen atoms in the $SO_4{}^{2-}$ structure. However, the same authors (1973) found departures from this ratio when waters of different $\delta^{18}O$ values were used in the reduction medium. The $\delta^{18}O$ value of the remaining sulphate was a function of that of the water. Since it is known that the rate of exchange between $SO_4{}^{2-}$ and H_2O is extremely low under the conditions of their experiments, it was concluded that the isotopic composition of $SO_4{}^{2-}$ was influenced by backreaction of intermediates that had exchanged oxygen with water.

2.2.7 Sulphate crystallization

During crystallization of $CaSO_4{\cdot}2H_2O$ in natural evaporation pans, the precipitates were found to be enriched in ^{18}O by 3.6 ± 0.9‰ compared to dissolved sulphate (Lloyd, 1967). It is not certain whether this represents equilibrium isotope fractionation or a kinetic effect.

2.3 APPLICATIONS OF ^{18}O STUDIES TO ENVIRONMENTAL SULPHATES

Oxygen isotope ratio measurements have been applied to studies of mechanisms of sulphate formation in the atmosphere, particularly in relation to acid rain and to studies of formation mechanisms and isotope thermometry (Mizutani and Rafter, 1969a) in the hydrosphere and the lithosphere.

2.3.1 Atmosphere

2.3.1.1 *Precipitation sulphates*

Isotopic analyses of sulphates in precipitation have led to at least three significant observations. Firstly, the $\delta^{18}O$ of the sulphate varies seasonally and in phase with corresponding isotopic variations of the precipitation water (Cortecci and Longinelli, 1970; Longinelli and Bartelloni, 1978; Holt *et al.*, 1981b; see Figure 5.8). Holt *et al.* (1979a) noted that in samples collected at Argonne, Illinois, the amplitude of the seasonal variation of $\delta^{18}O$ in precipitation sulphate was $\sim\frac{3}{4}$ of that of the precipitation water. In view of results from laboratory experiments discussed in Section 2.2.2.1, this suggests that the isotopy of three of the four oxygens in precipitation sulphate is controlled by the precipitation water, and therefore that essentially complete isotopic equilibration occurs between the precipitation water and dissolved HSO_3^-, prior to significant oxidation to sulphate.

A second observation is that the $\delta^{18}O$ of precipitation sulphates is higher, in relation to the associated precipitation water, than that of sulphates prepared in the laboratory by a variety of methods to simulate secondary sulphate formation and lower than that of sulphates prepared in the laboratory by high-temperature SO_3 formation to simulate primary sulphate formation. (Primary and secondary sulphates are defined in Section 2.1). This is illustrated by experimental results in Figure 2.3 (Holt *et al.*, 1982). The rain and snow data represent samples collected at Argonne, Illinois, during the period October 1976 to March 1978. Curves 1 to 3 represent $\delta^{18}O_{SO_4^{2-}}$ versus $\delta^{18}O_{H_2O}$ relationships for sulphates prepared in the laboratory by aqueous phase reactons (Holt *et al.*, 1981a), corresponding to secondary sulphate formation in the atmosphere; curves 4 to 7, sulphates prepared by non-liquid phase reactions (Holt *et al.*, 1983), also corresponding to secondary sulphates; and curve 8, sulphate prepared by high-temperature reactions (Holt and Kumar, 1984), corresponding to primary sulphates in the atmosphere. Specifically, curve 1 was by Fe^{3+}-catalysed aqueous air oxidation; curve 2, charcoal-catalysed aqueous air oxidation; curve 3, aqueous H_2O_2 oxidation; curve 4, non-liquid air oxidation in the presence of an electric spark (simulating lightning in the atmosphere); curve 5, non-

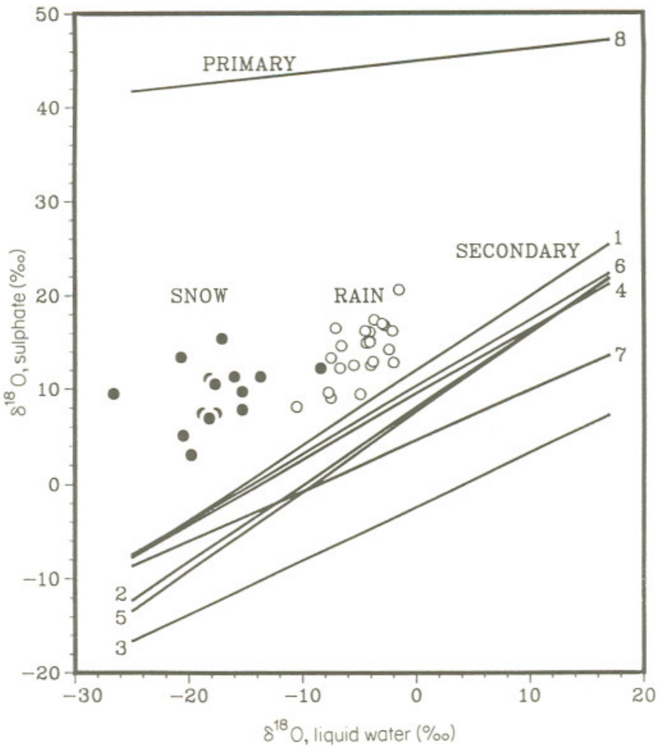

Figure 2.3 Isotopic comparison of atmospheric sulphates to laboratory-prepared sulphates (see text for identification of curves)

liquid air oxidation in the presence of NO_2 (simulating NO_x pollution in the atmosphere); curve 6, non-liquid air oxidation in the presence of gamma irradiation (simulating OH radicals in the atmosphere); curve 7, non-liquid oxidation after adsorption of SO_2 on charcoal in air (simulating SO_2 adsorption on soot particles in the atmosphere); curve 8, air oxidation of SO_2 to SO_3 at high temperature (catalytic surface at ~450–500 °C), accompanied by hydration of the SO_3 to H_2SO_4.

The experimental results in Figure 2.3 illustrate that the $\delta^{18}O$ of the 'primary' sulphate (derived from high-temperature SO_3) is much higher and less dependent on the $\delta^{18}O$ of the associated water than the group of 'secondary' sulphates. The results also illustrate that the $\delta^{18}O$ data for precipitation sulphates fall in between the expected values for primary and secondary sulphates, suggesting that they comprise a mixture of the two types.

A third observation about precipitation sulphates is that, at receptor sites near sea coasts, the $\delta^{18}O$ may be significantly affected by sea spray (Mizutani and Rafter, 1969c; Cortecci and Longinelli, 1970).

2.3.1.2 *Aerosol sulphates*

During the same period of collection of precipitation samples of Figure 2.4 (December 1976 to March 1978), Holt *et al.* (1981b) collected consecutive 7–day samples of aerosol sulphates and water vapour at the Argonne site. A comparison of the month-averaged $\delta^{18}O$ values for both precipitation sulphates and aerosol sulphates is shown in Figure 2.4. As substantiated by isotopic results on other samples that had been collected intermittently during 1975 and 1976, the oxygen isotopies of precipitation sulphate and aerosol sulphate indicate that the respective mechanisms of formation are not identical throughout the year. Heterogeneous, aqueous phase oxidation appears to be the predominant mechanism of precipitation sulphates at all times. In contrast, although aerosol sulphates may also be formed by the same mechanism during late autumn, winter, and early spring, a competing mechanism that tends to lower the $\delta^{18}O$ may be present during the summer months.

Despite these apparent differences in the seasonal variation of $\delta^{18}O$ in precipitation and aerosol sulphates, both types fall between the primary and

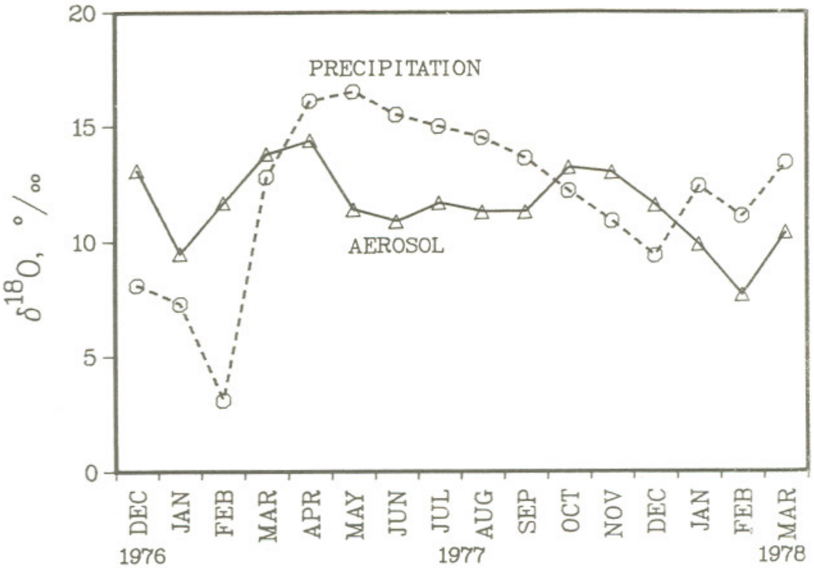

Figure 2.4 Comparison of $\delta^{18}O$ in precipitation sulphates and aerosol sulphates at Argonne, Illinois, USA (Holt *et al.*, 1981b)

secondary sulphate curves in Figure 2.3. This suggests that both types may contain appreciable amounts (10–30%) of primary sulphate at Argonne, Illinois (Holt *et al.*, 1982).

In other studies results indicated that, depending on meteorological conditions, the $\delta^{18}O$ of aerosol sulphates often varies inversely with barometric pressure (Holt et al., 1981b) and that it can vary diurnally and in conjunction with varying origins of sulphur emissions, as determined by backtrajectories of air-mass movements (Holt *et al.*, 1978b).

2.3.1.3 *Sulphur dioxide*

As suggested in Section 2.2.2, the rapid isotopic equilibration that occurs between SO_2 and either liquid water or water vapour has important implications regarding the $\delta^{18}O$ of SO_2 in the atmosphere. One is that atmospheric SO_2 is very probably in dynamic isotopic equilibrium with the water vapour with which it is associated; consequently, any change in $\delta^{18}O$ of water vapour (e.g. by precipitation, evaporation of ground water, etc.) probably causes an immediate corresponding change in the $\delta^{18}O$ of the SO_2 in the same air mass. For this reason, the $\delta^{18}O$ of SO_2 in the atmosphere cannot be used as a fingerprint of its origin (combustion source; volcano; product of oxidation of H_2S, S, or other sulphur compounds in the atmosphere; etc.).

Another implication is that the $\delta^{18}O$ of SO_2 in the atmosphere cannot be sampled and converted to CO_2 for mass spectrometric analysis without concurrent association with water with which it can immediately undergo isotopic exchange (Holt *et al.*, 1979b).

2.3.2 Hydrosphere (see also Chapter 6)

Measurements of oxygen isotope ratios in water and in dissolved sulphates afford a unique method of studying important bacterial, chemical, and physical processes that occur in the oceans, lakes, streams, and ground waters (Longinelli and Craig, 1967; Rafter and Mizutani, 1967).

2.3.2.1 *Oceans*

It has been observed that the $\delta^{18}O$ of ocean sulphate (~9.5‰) apparently does not correspond to isotopic equilibrium between ocean sulphate and ocean water ($\delta^{18}O = 0.0‰$) (Lloyd, 1967, 1968; Holser *et al.*, 1979; Claypool *et al.*, 1980). The complete explanation of this apparent lack of isotopic equilibrium is still debatable. Some of the possible causes which have been proposed are: (a) oxygen isotope fractionation in bacterial reduction of SO_4^{2-} to lower-valence species of sulphur compounds, (b) oxygen isotope exchange between sulphur compounds of intermediate valence states and ocean water, (c) oxygen isotope fractionation in bacterial and/or chemical oxidation of reduced species to SO_4^{2-}, (d) a steady-state ratio of sulphate inputs and outputs of the sea, and (e) oxygen isotope fractionation in the physical processes of crystallization of sulphate minerals (to form evaporites) and oxidative weathering of pyrites.

2.3.2.2 *Streams and lakes*

The $\delta^{18}O$ of sulphates in streams and lakes can be quite varied, depending on natural and anthropogenic inputs and on bacterial activity. For example, results obtained by Longinelli and Cortecci (1970) on the Serchio River in Italy showed that the $\delta^{18}O$, $\delta^{34}S$, and concentration of the sulphates generally increased downstream along the course of the river.

A $\delta^{34}S/\delta^{18}O$ ratio of 4:1 has been found for SO_4^{2-} obtained from different depths in Lake Vanda, Antarctica (Rafter and Mizutani, 1967). In contrast, for a stratified ice-covered lake on Ellesmere Island in the Canadian Arctic, the $\delta^{34}S/\delta^{18}O$ ratio was highly variable with an average value near unity (Jeffries *et al.*, 1984).

2.3.2.3 *Ground waters*

Oxygen-18 analyses of ground waters have been effectively used in determining whether the sulphates in the ground waters are from solution of evaporites or from aqueous air oxidation of sulphides. Longinelli (1968) found no relation among $\delta^{18}O$ of sulphate, $\delta^{18}O$ of water, and water temperature in thermal springs in Tuscany, Italy. This was interpreted as evidence that the sulphates in the thermal waters came from dissolution of Upper Triassic evaporites. Shakur (1982) also used $\delta^{18}O$ and $\delta^{34}S$ data to study sulphate geochemistry of freshwater wells, springs, and associated deposits (see Section 6.7.3). In one such study, very negative $\delta^{18}O$ values of radioactive barite sinters proved that HS^- was being oxidized in the water before precipitation as $Ba(Ra)SO_4$ (Cecile *et al.*, 1984).

2.3.3 Lithosphere (see also Chapter 4)

Shakur (1982) used $\delta^{18}O$ data to identify secondary alteration of primary deposits of marine evaporites (gypsum and anhydrite). The significant difference in the δ values of Upper Cambrian and Lower Devonian evaporites (see Section 4.2) was used to locate the position of a thrust-fault in Palaeozoic strata in the Norman Range, Northwest Territory, Canada (van Everdingen *et al.*, 1982). This represents a direct application of stable isotope data in subsurface mapping.

2.4 CONCLUSIONS

Oxygen isotope analysis of atmospheric sulphates and atmospheric water has potential use in the estimation of the fractions of primary and secondary sulphates at any given receptor site. A relatively large fraction of primary sulphate corresponds to local sources of SO_x emissions and a relatively small fraction to distant sources. The fractions of the two types of sulphates multiplied by the total loadings of sulphate, as a function of time, correspond to the respective temporal variations in loadings at a receptor site.

Measurements of $\delta^{18}O$ of sulphates and of associated waters can be applied to the study of bacterial, chemical, and physical processes that regulate the steady-state balance of the sulphur–oxygen system in the oceans. Similarly, $\delta^{18}O$ measurements can be made to determine whether the sulphates in certain ground waters originate from solution of evaporite sulphates or from aqueous air oxidation of sulphides. Such information is important to geological subsurface mapping.

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