CHAPTER 5

Sulphur Isotope Variations in the Atmosphere

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5.1 INTRODUCTION

The measurement of the isotope ratios of sulphur and oxygen can in principal be used to assess sulphur inputs into, transformation within, and removal from, the atmosphere. Major inputs arise from both anthropogenic and biogenic activities (Nakai and Jensen, 1967). Transformations arise from oxidation, neutralization, and other chemical reactions. Advection causes dilution and the main removal processes are dry deposition (governed by gravitation and diffusion) and rain. The admixture of sources can be discerned from their isotopic signatures whereas transformations and removal can be followed from the isotopic fractionation that might occur.

In this chapter, the atmospheric sulphur cycle and the associated chemistry are summarized. Also presented is information on natural isotopic variations and fundamental concepts relating to the use of isotopic data to delineate anthropogenic S in the atmosphere. Examples of successful applications of these concepts are given. These are supplemented by case studies in Sections 8.2, 8.4, and 8.5. Finally, consideration is given to the potential of using isotopically enriched sulphur to study transport and transformation of atmospheric S compounds.

5.2 SULPHUR SPECIES IN THE ATMOSPHERE

5.2.1 Atmospheric S compounds and their concentrations

Sulphur in the atmosphere occurs in the gaseous (H_2S, CH_3SCH_3 (DMS), CH_3SSCH_3 (DMDS), CH_3SH, COS, CS_2, SO_2), liquid (H_2SO_3, SO_4^{2-}, and SO_3^{2-}), and solid (sulphates, S^0) phases. A detailed discussion of these species worldwide is given in Chapter 4 of SCOPE 19 (1983) and will not be repeated here. A summary of pertinent data for some species is given in Table 5.1.

Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment
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Table 5.1 Concentration, residence time, and mixing height of different forms of sulphur in the atmosphere (SCOPE 19, 1983)

Species	Concentration ($\mu g\ S\ m^{-3}$)	Residence time (d)	Mixing height (km)
DMS	0.04	< 1	1.5 ± 0.5
H_2S	0.05	1	1.5 ± 0.5
SO_2	0.2	3	6.5 ± 0.5
SO_4^{2-}	0.5	4	2.5 ± 0.5
CS_2	0.7	70	6.5 ± 1
COS	0.2	500	6.5 ± 1

5.2.2 The atmospheric chemistry of sulphur

The chemistry of sulphur in the atmosphere is complex. The reduced S compounds are subject to direct photochemical oxidation and attack by other photochemically produced species including ozone and the OH radical. Cox and Sheppard (1980) have summarized reaction rates of SO_2, H_2S, and organic sulphides with OH radicals in the troposphere. A simplified summary of oxidative reactions follows.

5.2.2.1 *H_2S oxidation*

Most global balance calculations propose significant emission of H_2S to the atmosphere. There are a variety of possible reactions for the destruction of H_2S. Sprung (1974) gives rates for a variety of homogeneous gas phase reactions. Hydroxyl radical is the most important destroyer of H_2S followed, at a rate three orders of magnitude lower, by ozone.

The reaction of H_2S with the OH radical leads to the formation of HS radical and water;

$$OH + H_2S \rightarrow HS + H_2O$$

The HS radical may react with O_2 to form SO_2, or may proceed directly to sulphuric acid (Thiemens, 1977):

$$\begin{aligned} HS + O_2 &\rightarrow HSO_2 \\ HSO_2 + O_2 &\rightarrow HSO_4 \\ HSO_4 &\rightarrow OH + SO_3 \\ SO_3 + H_2O &\rightarrow H_2SO_4 \end{aligned}$$

It was subsequently shown that the HS radical goes quantitatively to SO_2 by one of two paths:

$$
\begin{array}{ll}
\text{I.} & HS + O_2 \rightarrow SO + OH \\
 & SO + O_2 \rightarrow SO_2 + O \\
\text{II.} & HS + O_2 \rightarrow HSO_2 \\
 & HSO_2 \rightarrow HOSO \\
 & HOSO + O_2 \rightarrow HO_2 + SO_2
\end{array}
$$

In either case, all of the oxygen in the resultant SO_2 comes from atmospheric O_2.

Hales *et al*. (1974) examined the heterogeneous oxidation of H_2S by ozone and concluded that heterogeneous processes on the surface of their reactors were unimportant. Hence, they concluded that heterogeneous oxidation is probably unimportant in the atmosphere. The rates of H_2S oxidation by O_2 in solution at pH values below 6 are also negligible (Chen and Morris, 1972).

5.2.2.2 *S^O dust*

In view of the rapid fallout, oxidation of sulphur dust in the atmosphere is negligible. Upon reaching the ground, it is converted to sulphate by oxidation and hydrolysis reactions which may be mediated by sunlight and sulphur oxidizing bacteria such as *Thiobacillus* sp.

5.2.2.3 *SO_2 chemistry*

Since most of the anthropogenic emissions are in the form of SO_2, and since biogenic sulphides are oxidized to SO_2, the chemistry of SO_2 in the atmosphere is of major importance. Sulphur dioxide may be removed from the atmosphere directly by dry deposition (e.g. Garland, 1978; Platt, 1978; Mayer and Ulrich, 1978). Garland (1978) estimates that about half of the SO_2 emitted to the atmosphere is removed by dry deposition. The remaining half of the SO_2 in the atmosphere is removed by wet deposition, consisting of oxidation, hydration, and condensation. These processes may occur in a variety of sequences. Oxidation may not occur in some droplets before removal from the atmosphere by gravitational settling.

Newman (1980, 1981) reviewed the literature on the atmospheric oxidation of sulphur dioxide in relation to power plant and smelter plume studies. The average rate of oxidation is generally less than 1% h^{-1} in clean air, but in polluted air the rate can easily double (Forrest and Newman, 1977a, 1977b). A diurnal variation in the rate of oxidation is observed that is near zero at night and approximately 3% h^{-1} during mid-day. There is no basis for a choice between the homogeneous or the heterogeneous pathway as the dominant oxidation mechanism.

Eggleton and Cox (1978) reviewed the homogeneous oxidation of SO_2 in the atmosphere. Reactions with free radicals, especially OH, are most important in both polluted and unpolluted air:

$$OH + SO_2 \rightarrow HOSO_2$$

Calvert *et al*. (1978) concluded that the most likely reaction of the $HOSO_2$ radical is with O_2:

$$HOSO_2 + O_2 \rightarrow HOSO_2OO$$

They also noted that the disproportionation reaction forming HO_2 and SO_3 is endothermic and therefore non-competitive with the preceding reaction. The resulting $HOSO_2OO$ radical is extremely reactive. It should eventually gain a H and lose an O atom to become H_2SO_4, or lose both an O and a H atom to become SO_3 which hydrates to H_2SO_4. The H_2SO_4 can then be neutralized by ambient ammonia to form $(NH_4)_2SO_4$. Davis *et al*. (1978) estimated the rates of a variety of reactions involving HSO_3 and HSO_5 radicals. They believe that the dominant processes are the oxidation of HSO_3 to HSO_5 by atmospheric O_2 with a slightly slower rate for the hydration of the HSO_3 radical. The resulting HSO_5 radical is hydrated (probably with several water molecules) at a rate several orders of magnitude greater than any competing reaction. It is not clear at what point the reactions can be considered to change from homogeneous gas phase reactions to heterogeneous solution reactions.

The heterogeneous oxidation of SO_2 in solution has been reviewed by Beilke and Gravenhorst (1978) and by Hegg and Hobbs (1978). The primary step in these reactions is the solution of SO_2 in water and its equilibration in the sulphurous acid system to form bisulphite and sulphite:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$$

The dissociation reactions are very fast (order of $10^6\ s^{-1}$). In solution, SO_3^{2-} is present in negligible amounts at pH values less than 6 and HSO_3^- dominates in rain and cloud droplets.

The oxidation of S^{IV} to S^{VI} in droplets may proceed by three mechanisms: oxidation by O_2 without metal catalysts; oxidation by O_2 in the presence of transition metal catalysts; and oxidation by strong oxidants, particularly hydrogen peroxide or ozone. Beilke and Gravenhorst (1978) concluded that the uncatalysed reaction with O_2 is unimportant in droplets. The catalysed reaction may be important where the transition metal component in the solution is extremely high, but oxidation reactions by hydrogen peroxide and ozone are probably the dominant mechanisms. Hegg and Hobbs (1978) suggest that some mixed salt catalysts (equimolar Mn^{2+} and Fe^{3+}) may promote oxidation of SO_2 in urban atmospheres. Newman (1981) suggested that oxidation within cloud droplets is an important means through which air obtains its sulphate and acidity. Recent evidence substantiates this hypothesis (Daum *et al.*, 1982).

5.3 ANALYTICAL TECHNIQUES

5.3.1 Sampling of atmospheric S compounds

The first requisite for sampling sulphur compounds from the atmosphere for isotopic measurements is the preservation of their isotopic composition. Consequently all steps in the procedure should be quantitative to assure that isotopic fractionation does not occur. Concentrations in the atmosphere are usually low (ppb or less). The sampling rate has to be designed to obtain enough material in a time period commensurate with the temporal resolution dictated by the experiment (Forrest and Newman, 1973). About 1 mg of material is required in order to perform a precise isotopic ratio measurement on the mass spectrometer. Further, it is generally desirable to sample and measure the isotopic ratio for each of the sulphur substances present in the atmosphere. A requisite during sampling is the necessity of preventing transformation of one sulphur compound into another, e.g. the conversion of SO_2 to sulphate when it is desired to measure the isotopic ratio of the sulphate particles in the atmosphere.

The flue gas of power plants can be sampled through a quartz wool filter, followed by a heated probe to prevent condensation in the line (Forrest *et al.*, 1973). The SO_3 is then condensed and collected in a coil maintained at a temperature above the dew point of water. Finally the SO_2 is collected and oxidized to sulphate in an impinger containing alkali and hydrogen peroxide.

Huygen (1963) successfully collected SO_2 by forcing air through cellulose filters impregnated with potassium hydroxide plus glycerol or triethanolamine. This procedure was further developed by Forrest and Newman (1973) who collected ambient samples with a filter pack arrangement consisting of a quartz prefilter to trap aerosol sulphate followed by KOH–triethanolamine-impregnated fast-flow cellulose filter paper to absorb SO_2. They achieved air flow rates of 2 $m^3\ min^{-1}$ with 8×10 in filters in high-volume samplers. The filter paper can also be impregnated with silver and mercury salts to collect H_2S (Hitchcock *et al.*, 1978). Another technique to sample SO_2 for sulphur isotope analyses employs adsorption on a molecular sieve (Holt, 1975).

Several procedures for collecting organic sulphur compounds, primarily for final determination by gas chromatography, have been described.

Hydrogen sulphide was absorbed by mercuric-chloride-treated paper (Hockheiser and Elfers, 1970), lead-acetate-soaked membrane filters (Okita *et al.*, 1971), and silver-nitrate-impregnated cellulose filters (Natusch *et al.*, 1972). Nakai *et al.* (Section 8.5.2.1) describe a circulating pumping and chemical trapping system for sampling hydrogen sulphide released by tidal flats. Okita (1970) used glass fibre filters impregnated with mercuric cyanide to adsorb mercaptans and with mercuric chloride to collect mercaptans and DMS. Black *et al.* (1978) used molecular sieve 5A packed in tubes to adsorb SO_2 and H_2S. Cryogenic trapping at liquid nitrogen temperatures enabled Sandalla and Penkett (1977) to concentrate COS and CS_2. Several organic compounds, including H_2S, methyl mercaptan, DMS, and DMDS, were adsorbed on gold-coated beads in a quartz tube by McClenny *et al.* (1979). Although numerous procedures have been described for absorbing specific gases in liquids or solutions by bubblers or impingers, flow rates are generally too low for successfully accumulating sufficient quantities for isotopic analysis.

Particulate sulphur is readily removed from an air stream by filters. By this technique, sulphur isotopic ratios of atmospheric aerosol sulphate have been measured by Forrest and Newman (1973) and by Saltzmann *et al.* (1983). Collected particles may be separated by chemical means. Leahy *et al.* (1975) used benzaldehyde to specifically dissolve and separate H_2SO_4 from other sulphates.

Sulphur isotope analyses can also be carried out on lead-peroxide-treated paper placed on the inner surface of an open cylinder and exposed vertically to the atmosphere, typically for a one-month period. Krouse (unpublished data, 1976; see Section 8.2) found isotope data from these cylinders to be comparable to those obtained by averaging samples collected over shorter time periods with the filter pack of Forrest and Newman (1973).

5.3.2 Further characterization of atmospheric compounds for sulphur isotope analyses

5.3.2.1 *Wind direction*

If concentrations and isotopic compositions of atmospheric S compounds can be characterized according to wind direction, more information might be obtained on sources and mixing phenomena.

Isotopic variations in SO_2 with wind direction were documented near Whitecourt, Alberta, during September 1975 (Krouse *et al.*, 1984). A high-volume sampler was operated on a 16−m high scaffold to study the effects of SO_2 emissions on mid-crown and upper-crown foliage of a mature conifer stand. On 18 September, the wind was north-west and the SO_2 had $\delta^{34}S$ values near +24‰, corresponding to a sour gas plant operation (Section

8.2) in that direction. During the next day, the wind shifted easterly and the $\delta^{34}S$ value decreased to +14‰, testifying to SO_2 arriving from sources other than the dominant industry in the area. During the next two days, the wind swung southerly and then westerly and the $\delta^{34}S$ values increased, reflecting increasing contributions from the industry.

The above event can be depicted on a polar diagram where $\delta^{34}S$ is plotted as the radial coordinate and the angular coordinate corresponds to wind direction (Figure 5.1). It would appear that if the wind direction sector angle could be reduced further during sample collection, such a diagram could pinpoint sources of sulphur emissions very effectively. It must be emphasized that the samples were collected using one sampler with concurrent meteorological data, and interpretations were made later. This procedure is inefficient since the wind direction might change many times during the acquisition of a sample. The construction of Figure 5.1 was possible because the particular major synoptic event was not subject to short-term fluctuations.

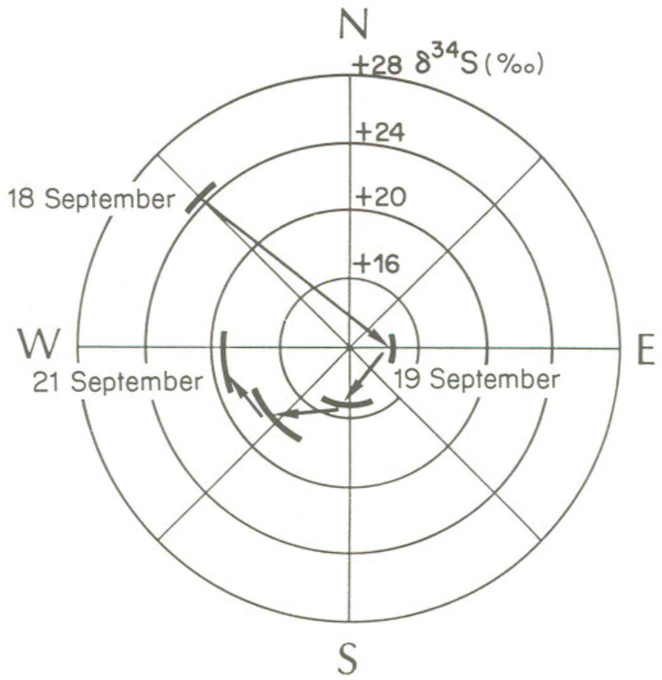

Figure 5.1 Polar plot depicting changes in $\delta^{34}S$ values for atmospheric SO_2 with wind direction near Whitecourt Alberta, 18–21 September 1975 (data from Krouse *et al.*, 1984)

On the basis of the above study, arrays of high-volume samplers, each of which responded to a preselected wind direction, were constructed. An array with four high-volume samplers was tested in 1976 on the same scaffold in the Whitecourt area (Krouse *et al.*, 1984). Since the array was programmed by a simple electrical contact system within the head of the wind vane, some difficulties were experienced at low wind velocities because of internal friction. Nevertheless, the observations were similar to those recorded the previous year during the major synoptic event.

The four-unit sampler array was also used for ground-level sampling in the Teepee Creek area of Alberta (Krouse and Case, 1981). Although there was a minor source of industrial emissions in the area, it was found that the highest SO_2 concentrations were not downwind of the plant. Further, a large component of the SO_2 flux appeared to pass through the study area.

A mobile nine-unit high-volume sampler array was then built and tested (Krouse and Case, 1984). Eight samplers were individually triggered according to preselected wind directions whereas the ninth was directionally independent and operated at wind speeds below a pre-set cutoff. An elapsed time counter on each sampler recorded its accumulated time of operation. Since air flow through each sampler was calibrated and controlled, the amount of air that had passed through the sample could be determined and used in concentration calculations. Filters would not be removed from a sampler that had operated for an insufficient time to provide enough sample for analysis.

A criticism of the mobile array is that winds aloft are seldom in the same direction as those at ground level. Therefore, to avoid false source identification, the elevational dependence of the wind behaviour must be known. The argument can be reversed by stating that the isotope determinations *per se* help to differentiate sources and reduce interpretation errors. It would also seem that concentration and isotope measurements of atmospheric S at ‘nose level’ are justified from the viewpoint of human health.

5.3.2.2 *Particle size*

The size of particles relates to their source, accretion, and transport in the atmosphere. Particles combining lowest density and smallest size arriving at an observation point can potentially come from further distances. Particles may be collected according to aerodynamic size using stacked metal plates with either staggered holes or slots (slotted cascade impactor) (Liu *et al.*, 1980). Commercial units have typically five aerodynamic size classes: >7, 3.3 to 7.0, 2.0 to 3.3, 1.1 to 2.0, and <1.0 μm. These are considered to correspond to particles found on the human skin surface, and in the trachea and primary bronchi, secondary bronchi, terminal bronchi, and alveoli respectively. Aerodynamic sizing with a five-stage slotted cascade impactor was incorporated in the mobile array described above. Data for a study in the midst of three sour gas processing gas plants are given in Table 5.2. It is seen that the smallest particles reaching the non-slotted filter paper are very much depleted in ^{34}S as compared to larger ones and the simultaneously collected SO_2. This suggests that the smallest particles bear little relationship to the nearby industrial operation.

5.3.2.3 *Photographic examination of particles*

If more parameters are examined for particles, more information can be gained about their sources. Simple visual and microscopic techniques are very effective. The diverse nature of particulates is shown in the scanning electron microscope (SEM) photograph of Figure 5.2. which depicts abiological dust particles as well as biological materials such as pollen grains and broken plant debris. The latter should have an isotopic composition representing a mixture of sulphur from the atmosphere and soil (Section 7.2.4). Variations in $\delta^{34}S$ values of the total particles collected at different sampling heights can be explained by different proportions of abiological and biological matter (Krouse *et al.*, 1984).

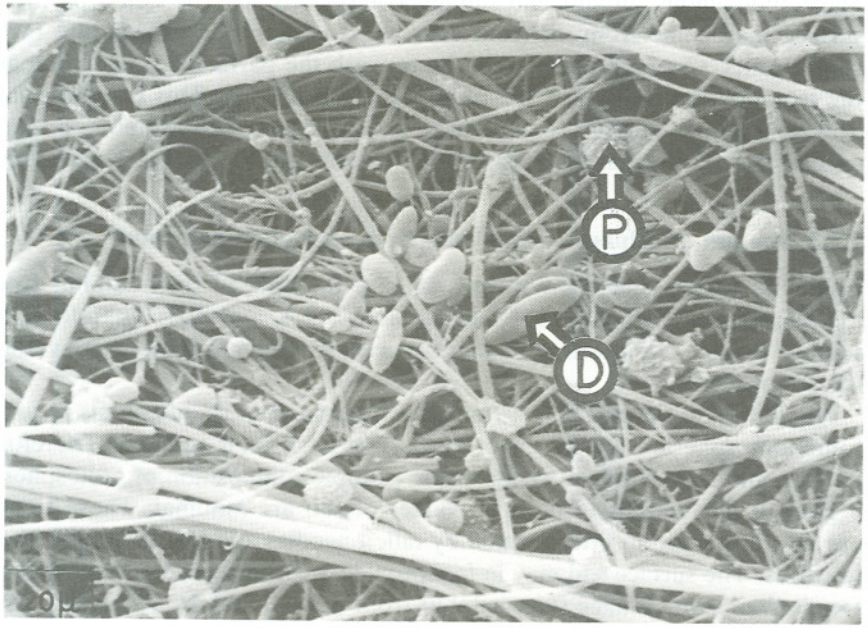

Figure 5.2 Scanning electron photomicrograph of particulates trapped on a filter in a high-volume sampler at 1 m above ground. Selected dust (D) and biological particles (P) are shown

Table 5.2 The $\delta^{34}S$ values for SO_2 and six aerodynamic class sizes of airborne particulate matter near Crossfield, Alberta, March–April, 1983 (Krouse and Case, 1984)

	Sampler[a]			
Size (μm)	1	2	3	4
>7.0	+18.8	+14.0	+16.6	+19.4
3.3–7.0	+13.2	+12.0	+6.5	+17.1
2.0–3.3	+15.3	+13.6	+14.5	+16.0
1.1–2.0	+13.1	+9.5	+15.5	+15.6
<1.0	+12.3	+13.5	+18.9	+16.6
Non-slotted	−2.0	−3.4	+3.5	+6.1
SO_2	+23.4	+22.4	+15.2	+16.3

[a] Numbers refer to different wind directions.

5.3.2.4 *Endogenous versus adsorbed sulphur*

Since endogenous sulphur and sulphur compounds adsorbed on a particle's surface may come from different sources, it is desirable to separate these components. One approach would be to wash the particulates and compare the isotopic composition of the filtrate and the residue. This is appropriate if water-soluble sulphur compounds are adsorbed to insoluble organic particulates. To date, such investigations have apparently not been attempted.

5.3.3 The use of sulphur isotope data from vegetation and soils

Epiphytic lichens and many mosses acquire the bulk of their sulphur from the atmosphere (Krouse, 1977; see Sections 7.2.3. and 8.2). Therefore the sulphur isotope composition of these species represent a long-term average for atmospheric S.

In addition to upward SO_4^{2-} transport from the soil, rooted plants acquire some atmospheric S by gaseous transport through their stomata. Therefore needles and leaves reflect trends in the isotopic composition of atmospheric S gases if fluctuations in the $\delta^{34}S$ values of soil are minimal. These trends are also preserved in litter formed by fallen needles and leaves in upper soil horizons. The surface soil may in fact provide a better record of atmospheric trends than living foliage since sulphur from wet fall and dry deposition may be incorporated in the litter. The use of vegetation and soil isotope data as indicators of sources of atmospheric sulphur is documented in Chapter 8.

5.4 SULPHUR ISOTOPE ABUNDANCE VARIATIONS IN ATMOSPHERIC COMPOUNDS

5.4.1 Fractionation of sulphur isotopes during transformations of atmospheric sulphur compounds

A critical question is whether the isotope distribution is preserved during chemical transformations in the atmosphere (e.g. SO_2 to SO_4^{2-}). If so, $\delta^{34}S$ and $\delta^{18}O$ values can be used as a label to identify the source of the precursor compounds. Newman and his colleagues assumed that isotope fractionation occurs in the formation of particulate SO_4^{2-} from precursor SO_2 power plant plumes, and that this shift can be employed to estimate the percent conversion of the SO_2 in the plume (Newman *et al.*, 1971; Newman *et al.*, 1975a, 1975b; Forrest and Newman, 1978). They attribute the fractionation to the following isotope exchange reaction in liquid surrounding atmospheric particles:

$$^{32}SO_2\ (g) + {}^{34}SO_3^{2-}\ (l) \xrightarrow{K} {}^{34}SO_2\ (g) + {}^{32}SO_3^{2-}\ (l)$$

Subsequent catalytic oxidation of the HSO_3^- to SO_4^{2-} should yield a $\delta^{34}S$ value for the sulphate that is established by the equilibrium constant K. On the basis of isotope fractionation between SO_2 and HSO_3^- dissolved in water associated with Dowex exchange resins, Eriksen (1972) estimated K to be 1.02. Newman and his colleagues did not observe the anticipated shift of +20‰ in the sulphate relative to the SO_2 which is implied by this scheme. However, this could be due to other factors, including the presence of sulphate derived from other sources. Large shifts in the $\delta^{34}S$ value of SO_2 are also absent in plumes of sour gas processing plants (Figure 5.3). Forrest *et al.* (1973) found that sulphate formed in the combustion process or in stacks at high temperatures was only 1.5‰ enriched in ^{34}S compared to the SO_2. Nriagu and Coker (1978b) found this enrichment to be 2.6‰ in a smelter stack at Sudbury, Canada.

The isotopic composition of SO_2 and sulphate generated by oxidation of biogenic H_2S in natural springs shows considerable variation which may in part be related to sampling problems (van Everdingen *et al.*, 1982, 1985). The average values for H_2SO_4 fallout appear to be similar to the precursor H_2S, whereas the ambient SO_2 is about 5‰ depleted in ^{34}S.

In summary, sulphur isotope fractionation occurs during oxidation of anthropogenic SO_2 and biogenic H_2S. It is smaller than that predicted by equilibrium exchange between SO_2 and SO_3^{2-} In most cases, this fractionation will not preclude identification of sources because of the wide variations in $\delta^{34}S$ values of emissions.

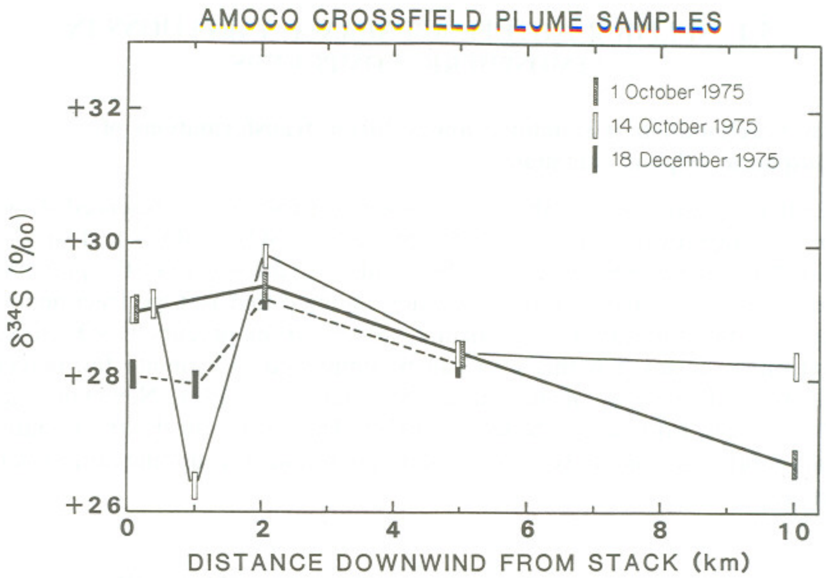

Figure 5.3 Variations in $\delta^{34}S$ values for SO_2 in plume as a function of distance downwind of a sour gas processing plant Crossfield, Alberta, Canada

5.4.2 Natural sources

Sulphur compounds in the atmosphere can originate naturally (volcanic, sea spray, aeolian weathering, biogenic) or anthropogenically (combustion and refining of fossil fuels, gypsum processing, ore smelting). This section summarizes sulphur isotope data pertaining to natural emissions whereas the next section (5.4.3) examines emissions from industrial processing and combustion.

5.4.2.1 *Sea spray and marine aerosols*

It is well known that the $\delta^{34}S$ value of seawater SO_4^{2-} is about +21‰ (Rees, 1978). However, lower values are found for marine aerosols. The superficial layer of about 30 μm thickness at the air–sea interface has been found to be highly enriched in organic matter and associated elements such as I, P, and certain heavy metals (McIntyre and Winchester, 1969; McIntyre, 1970; Chesselet *et al.*, 1972; Duce *et al.*, 1975; Morelli, 1977).

It has been estimated that the sea produces between 103 and 104 Tg yr^{-1} of atmospheric sea salt particles with radii less than 20 μm (Eriksson, 1959, 1960; Blanchard, 1963; Petrenchuk, 1980). Most sea salt particles in this size range are produced by whitecap bubbles (Duce, 1981). When a bubble

Table 5.3 Isotopic composition of sulphur in the oceanic atmosphere

Region	Compound	$\delta^{34}S$ (‰) Range	$\delta^{34}S$ (‰) Mean	Remarks	Reference
Central Atlantic Ocean	SO_4^{2-}	2 to +15	+11	Aerosols a few m ASL	Gravenhorst (1978)
New Amsterdam Island, Indian Ocean (37°47′S, 77°32′E)	SO_4^{2-}		+0.9		Nguyen and Cortecci, (unpublished data)
Gulf of Guinea	SO_4^{2-}		+14.7		Nguyen and Cortecci, (unpublished data)
San Francisco Bay, California, USA	SO_4^{2-}	−10.1 to +8.3	−1.3	Wind from sea stratus droplets and particulates	Ludwig (1976)
Waimanolo Bay, Hawaii, USA	Gaseous S	+5.9 to +6.0	+6.0	Two samples of 6 hours duration on separate days	Hitchcock (1976a, 1976b)
	Particulate	+15.0 to +16.2	+15.6		
Chesapeake Bay, Virginia, USA	SO_2	−0.1 to +1.6	0.9	High sulfate concentration	Hitchcock and Black (1984)
		−1.0 to +0.8	−0.1	Low sulfate concentration	
		+0.1 to +1.6	+0.7	High sulfate concentration	
		−9.4 to +0.1	−1.9	Low sulfate concentration	
Atlantic Coast	SO_4^{2-}	+3.3 to +7.3	+4.2		Newman and Forrest (Section 8.4)
Guisseny, Brittany, France	SO_2 SO_4^{2-}	−4.1 to +0.5 +1.5 to +7.3	−3.8 +4.3	Exposed algal beds during low tide	Nguyen and Cortecci (unpublished data)
Mikawa Bay, Japan	H_2S	−21.9 to +12.1	−2.1	H_2S released from sediments	Nakai *et al.* (Section 8.5.2.2)

bursts at the sea–air interface, atmospheric particles are produced both from the microlayer and from the subsurface sea water. Bonsang *et al.* (1980) have found that the SO_4^{2-}/Na^+ ratio of marine aerosols is always higher than that of sea water (0.25) and can reach 1.25. Moreover, they have shown that the marine aerosols with radii less than 1.1 μm are enriched in SO_4^{2-} from oxidation of organic sulphides released by biological activity at the sea surface. This secondary SO_4^{2-} may be depleted in ^{34}S depending on the origin of the organic sulphides (Section 5.4.2.2). Data from a number of studies summarized in Table 5.3 show that the $\delta^{34}S$ value of SO_4^{2-} in marine aerosols ranges from −10 to +16‰. In two studies where gaseous S was also measured, it was on the average 8–10‰ depleted in ^{34}S compared to SO_4^{2-}. Therefore the isotope data provide evidence that the SO_4^{2-} in marine aerosols has lower $\delta^{34}S$ values because of oxidation of biogenic sulphide.

5.4.2.2 *Biogenic emissions*

During dissimilatory SO_4^{2-} reduction by strict anaerobes such as *Desulphovibrio desulphuricans* and *Desulphotomaculum*, copious dissolved sulphide species are produced in either anoxic waters or sediments. Investigators have found that the $\delta^{34}S$ values of sedimentary sulphide vary from 0 to −70‰ with respect to coexisting sulphate (e.g. Vinogradov *et al.*, 1962; Kaplan *et al.*, 1963; Ivanov, 1978; Weyer *et al.*, 1979; Chambers and Trudinger, 1979). Intense emissions of H_2S to the atmosphere occur in oceanic littorals, lagoons, salt marshes, rice-fields, springs, and wet tropical forest soils (Delmas and Servant, 1983; Delmas *et al.*, 1978; see Sections 6.3, 6.7, and 8.5.3). DMS concentrations in the atmosphere in some coastal areas where living algae are exposed at low tide can be much higher than those of H_2S (Paugam *et al.*, 1977).

The isotope fractionation associated with the production of gaseous organic sulphides is more difficult to assess. If they arise from the decomposition of organic S compounds, the isotopic selectivity should be minimal since a given mass of organic debris should all eventually decay. Since the isotopic selectivity during SO_4^{2-} assimilation is small (Section 6.2.2), the organic sulphide should be isotopically similar to the original SO_4^{2-}. Another possibility is that gaseous organic sulphides are generated during SO_4^{2-} reduction. This alternative is not well understood.

In the open ocean, phytoplankton and zooplankton living principally in the euphotic layer assimilate seawater SO_4^{2-} and generate sulphides such as DMS, DMDS, CH_3SH, and H_2S (Lovelock *et al.*, 1972; Nguyen *et al.*, 1978; Barnard *et al.*, 1982; Maroulis *et al.*, 1977; Andreae and Raemdonck, 1983). These sulphides are released to the atmosphere and oxidized to SO_2 and ultimately SO_4^{2-}. Nguyen *et al.* (1974, 1983) observed open ocean atmospheric concentrations of 0.1 and 1 $\mu g/m^3$ for SO_2 and sulphate respectively in the sub-Antarctic and Antarctic.

In laboratory experiments, Nguyen and Cortecci (unpublished data) found that SO_2 generated above algae under restricted air flow had a $\delta^{34}S$ value of −14.9‰, which was considerably lower than the value of −3.8‰ observed *in situ*. Data for gaseous S compounds in oceanic atmospheres are summarized in Table 5.3. The H_2S released, in Mikawa Bay, Japan, had the largest range of $\delta^{34}S$ values (−22 to +12‰) with the minimum value recorded in the coldest month.

The oceanic influence should decrease in going from near shore to continental environments. Saltzman *et al*. (1983) examined atmospheric SO_2 and SO_4^{2-} at the Hubbard Brook Experimental Forest Station, New Hampshire, USA. The $\delta^{34}S$ values of SO_2 and aerosol SO_4^{2-} ranged from −1.1 to +2.3‰ (11 samples) and from +0.8 to +3.5‰ (14 samples) respectively. It is noted that these data are not significantly different from those at Chesapeake Bay (Table 5.3). However, one should not conclude that marine aerosol is the sole source or even the major component at Hubbard Brook in view of the industrial emissions in the northeastern USA which have a similar average $\delta^{34}S$ value (Section 8.4).

Grey and Jensen (1972) found that $\delta^{34}S$ values from biogenic H_2S at the margins of Great Salt Lake ranged from 0 to +10‰. Since the maximum value is close to that of SO_4^{2-} in the lake, it might correspond to H_2S generated during plant decay.

Biogenic H_2S from cold and warm springs appears to arise almost entirely from SO_4^{2-} reduction because of its significant depletion in ^{34}S. For example, springs near Paige Mountain, Northwest Territories, Canada, have SO_4^{2-} with a $\delta^{34}S$ value near +16‰. In contrast, the intense biogenic emissions contain H_2S and SO_2 with $\delta^{34}S$ values of −32 and −38‰ respectively. Aerosol H_2SO_4 is similarly depleted in ^{34}S (Krouse and van Everdingen, 1983).

The isotopically selective generation of gaseous reduced S compounds is not unique to bacteria. Living vascular plants under severe S stress emit H_2S which is depleted in ^{34}S in comparison to the foliar S (Section 7.2.6).

5.4.2.3 *Volcanic activity*

Flux and isotope data for different volcanic emanations have been compiled in Section 4.6. Whereas the isotope composition of individual gases and particulates may vary widely at a given site, the weighted average for total sulphur has a much smaller spread. Lein (Section 4.6.1) estimates that 28×10^6 tonnes S are emitted annually from volcanoes with an average $\delta^{34}S$ value of +4.7‰.

Volcanic activity influences the sulphur isotope composition of aerosols in the stratosphere. Extreme variations after the eruption of Mt Agung were reported by Castleman *et al*. (1974). At heights near 19 km in the Southern

Hemisphere, the $\delta^{34}S$ value of sulphate increased to +16‰ during 1963 and then decreased to −24‰ by 1965. The variation was much less at the same altitude in the Northern Hemisphere and at 15 km height in the Southern Hemisphere. During several years without major eruptions, the $\delta^{34}S$ values were found to be quite uniform (+2.6 ± 0.3‰).

5.4.3 Anthropogenic sources

5.4.3.1 *Combustion of coal*

The $\delta^{34}S$ values of coal range from −30 to +30‰ (Section 4.5.2). Since much of this spread is due to coexistent pyrite, the isotopic composition of emissions from coal burning depend upon pretreatment for mineral sulphide and sulphate removal.

The $\delta^{34}S$ values of flue gas from coal combustion can range from −0.5 to +20‰ with −1 to +3‰ being most common (Nielsen, 1974). Newman *et al.* (1975b) measured $\delta^{34}S$ values in the range +1.3 to +3.6‰ (average, +2.8‰) for SO_2 emitted from a coal-fired power plant at Keystone, Pennsylvania, USA. Buzek *et al.* (Section 8.9) found $\delta^{34}S$ values in the flue gas of the Chwaletice coal-fired power plant near Prague to range from −1.4 to +0.1‰ with an average of −0.7‰. Combustion of coal can also produce fly ash, the $\delta^{34}S$ values of which represent S-containing minerals in the coal with perhaps contributions from oxidation of organic sulphur compounds (see also Sections 8.3, 8.4, and 8.9).

5.4.3.2 *Combustion and refining of oil and gas*

The $\delta^{34}S$ values of oils and H_2S in gas–oil associations can range from −5 to +30‰. A large number of data was compiled by Pankina (Sections 4.5.3 and 4.5.4). She concluded that the majority of $\delta^{34}S$ values for oil fall between 0 and +10‰. The range for H_2S is wider, with an estimated average of +10‰. Nielsen (1974) found $\delta^{34}S$ values in the range +4.8 to +5.4‰ in flue gas of oil-fired power plants. Newman and Forrest (Section 8.4) found that fuel oils used in power plants of the north-eastern USA ranged in $\delta^{34}S$ value from −5 to +14‰ (see also Section 8.2).

5.4.3.3 *Sulphide ores*

Roasting of sulphide ores is a major source of SO_2 in the atmosphere. The $\delta^{34}S$ values of sulphide ores are highly variable (−25 to +25‰) but the most common values are in the vicinity of 0 to +5‰. The average calculated by Grinenko and Grinenko was +3.4‰ (Section 4.3).

5.4.3.4 *Gypsum mining and processing*

Gypsum mining and wall board manufacturing introduces sulphate particulates into the atmosphere with positive $\delta^{34}S$ values in the range found for evaporites (Section 4.2).

5.4.4 Summary

Data for $\delta^{34}S$ values of precipitation, gases, and particulates are summarized in Tables 5.4 and 5.5 and Figure 5.4. On average, the marine atmosphere is between 5 and 10‰ enriched in ^{34}S as compared to the continental atmosphere. The wide range of sulphur isotope ratios arise in response to different natural and anthropogenic sulphur emissions. On the global scale, the statistics are inadequate to conclude whether the average isotopic composition of the total industrial area differs significantly from that of the total rural area. However, on the local scale, large differences in $\delta^{34}S$ values are found over short distances near dominant industrial and natural emitters. It is in these situations that stable isotope studies prove most successful (Section 5.5 and Chapter 8).

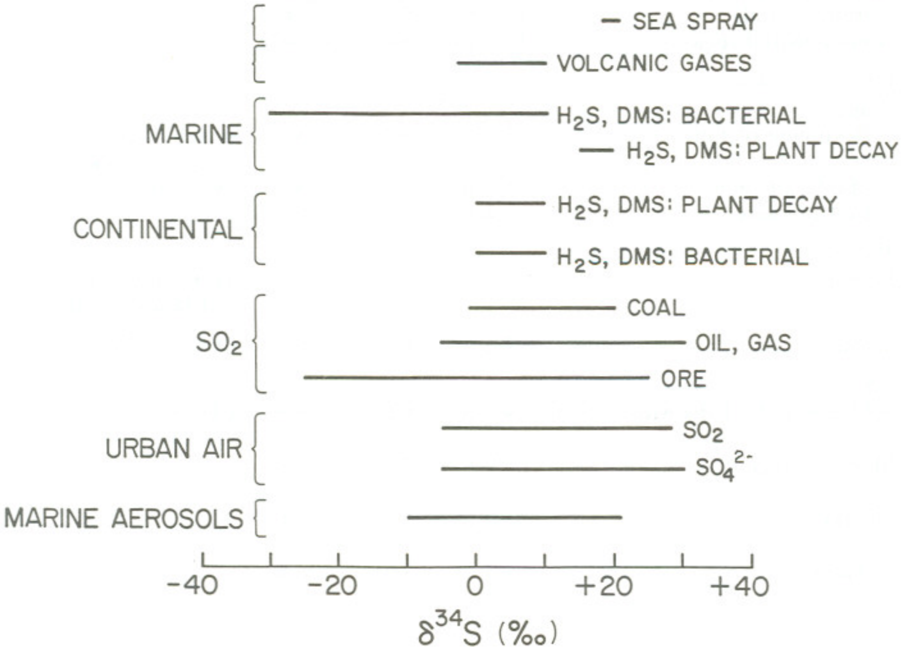

Figure 5.4 Variations of $\delta^{34}S$ values for different sources of atmospheric sulphur compounds

Table 5.4 Isotopic composition of SO_4^{2-} in precipitation

	$\delta^{34}S$ (‰)		
Region	Range	Mean	Reference
Italy			
Pisa	−2.5 to +7.1	+1.1	Cortecci and Longinelli (1970)
Venice	−0.2 to +8.3	+3.0	Longinelli and Bartelloni (1978)
Israel			
Mediterranean Coast	+5.3 to +14.3	+8.9	Wakshal and Nielsen (1982)
Central Galilee	+4.5 to +5.9	+5.3	
Jordan Rift Valley	+5.2 to +5.4	+5.3	
Japan			
Tokyo (1971–79)	−1.3 to +5.5	+1.7(1)	Nakai *et al.* Section 5.4.3 (1)
Nagoya (1971–79)	−1.1 to +5.1	+1.9(1)	Jensen and Nakai (1961) (2)
Industrial regions	+3.2 to +7.3	+6.0(1)	
Kurume (rural)	+11.7 to +15.6	+12.8(1)	
Non-industrial regions	+12.3 to +15.6	+14.0(2)	
Czechoslovakia			
Prague			
Beginning of rains	+4.1 to +8.4	+5.8	Busek, Cerny, and Sramek (Section 8.9)
Middle of rains	+2.2 to +8.9	+5.4	
End of rains	+0.4 to +9.7	+6.9	
Poland			
Lublin	+2 to +8	+3.7	Trembaczowski, and Halas (contributed data
Sweden	+3.2 to +8.2	+5.9	Ostlund (1959)
USSR			
Sakhalin and Vladivostok region	+4.2 to +8.6	+5.9	Chukhrov *et al.* (1977)
Magadan region	+3.9 to +7.6	+5.8	” ”
Siberia	+3.0 to +21.6	+10.6	” ”
Yakutia[a]	+4.9 to +8.5	+6.6	” ”

	$\delta^{34}S$ (‰)		
Region	Range	Mean	Reference
USSR			
Kazakhstan			
Steppes	+2.1 to +3.7	+3.2	Chukhrov *et al.* (1977)
Mountains[a]	+3.6 to +4.6	+4.1	" "
Kirgizia mountains	+5.6 to +8.6	+6.9	" "
Tadzhikistan mountains[a]	+3.8 to +12.9	+7.2	" "
Caucasus			
Mountains[a]	+0.7 to +2.4	+0.7	" "
Near Elbrus[a]		+10.0	
Kola Peninsula	+3.8 to +5.9	+4.0	" "
Moscow and Novgorod regions	+1.6 to +5.9	+4.0	" "
Urals	+5.1 to +5.7	+5.4	" "
Rostov region	+2.8 to +11.3	+7.1	Gavrishin and Rabinovich (1971) Rabinovich (1971)
USA			
Utah, Salt Lake City			
Urban	−1.5 to +5.3	+2.2	Grey and Jensen (1972)
Rural	+8.0 to +0.2	+9.0	
New Zealand			
Gracefield	0 to +19.4	+10.9	Mizutani and Rafter (1969)
Canada			
Sudbury, Ontario, within 90 km of smelters	+2.0 to +6.8	+4.7	Nriagu and Coker (1978a)
Great Lakes Basin			
Urban	+3 to +9.4[b]	+6	" "
Remote and Rural	+2 to +6.5[b]	+4	" "
Arctic			
Severnaya Zemlya, USSR[a]	+9.2 to +11.9	+10.7	M. Astratov *et al.* (1986)

Table 5.4 *Continued*

Region	$\delta^{34}S$ (‰) Range	Mean	Reference
Antarctica			
George-von-Neumeyer Station[a]	+9 to +22	+17	H. Nielsen (contributed data)
Atlantic Ocean	+12.1 to +15.0	+13.7	Chukhrov *et al.* (1978)
Pacific Ocean			
Coco Island, River[a]	+9.4 to +16.3	+13.1	Chukhrov *et al.* (1978)

[a] Measurements in accumulated snow and ice.
[b] $\delta^{34}S$ values higher in winter.
[c] River draining igneous rocks. Sulphate should have originated from precipitation.

5.5 DELINEATION OF ANTHROPOGENIC AND NATURAL FLUXES OF ATMOSPHERIC S COMPOUNDS

5.5.1 Use of $\delta^{34}S$ and concentration data to identify sources of atmospheric gases

Plots of $\delta^{34}S$ values versus various functions of concentration can prove effective for identifying sources and monitoring the fate of atmospheric sulphur pollutants. A number of hypothetical source combinations were examined by Krouse (1980). The conceptual and mathematical analyses assumed complete mixing without any isotope fractionation. In principle, the conclusions are valid for gases, ions, and fine particulates in fluids. It is noted that the approach fails in rivers where the flow is lamellar but has been successfully applied in some cases to soil and vegetation (Chapter 7).

In the atmosphere, a frequently encountered situation is a source 'A' which is relatively constant in its emission rate and $\delta^{34}S$ value for a few hours or days, but upon which is superimposed a source 'B' varying in emission rate at a different fixed $\delta^{34}S$ value. The former might be the 'background' and the latter an industrial stack. The lowest concentration corresponds to contributions from source A only. With increasing concentration, the contribution from B increases so that the δ value approaches that of B at very high concentrations (Figure 5.5a). It can be readily shown in this case that a plot of $\delta^{34}S$ versus the reciprocal of concentration is

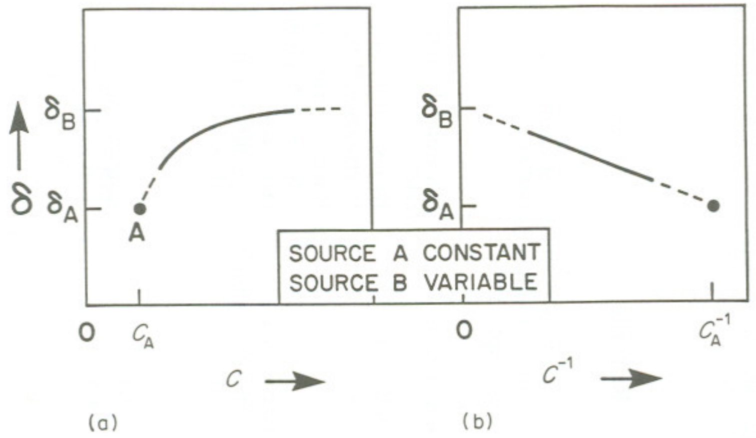

Figure 5.5 $\delta^{34}S$ values versus (a) concentration and (b) concentration^{-1} for mixtures of sulphur from two sources. Source A with δ_A has a constant emission rate. Source B with δ_B varies in its emission rate

linear, the *y* intercept corresponding to the $\delta^{34}S$ value of the variable emitter B (Krouse, 1980; Figure 5.5b). This model applies over short periods of time since generally the background conditions do not remain constant due to factors such as changing wind direction and fluctuations in biological emissions.

The case of a constant background and two variable sources is shown in Figure 5.6. In this case, data obtained by plotting δ values versus the inverse of concentration fall within a triangular area. Data falling near either edge of the triangle correspond to a mixture of the background and one of the variable sources. Suppose that there is a third variable source. Its line on the δ value versus concentration^{-1} plot will either fall within or outside the triangle of Figure 5.6b. In the latter case, a larger triangle results. Therefore it is difficult to delineate as to whether there are two or more variable emitters. Nevertheless, the plotting of δ versus concentration^{-1} is a logical exercise that indicates the complexity of the situation. If the data do not fall within a triangle, then there was not a source emitting at a constant rate and δ value during the observation period.

If there is a basic uniform background $\delta^{34}S$ value for the global atmosphere or a large area thereof, then the model Figure 5.6 should apply. The value 'A' corresponding to the lowest concentration is the background. As additional sources contribute, the concentration increases as well as the range in $\delta^{34}S$ values. There should be a lower and upper limit to the atmospheric $\delta^{34}S$ value. These are at least −40‰ (biogenic emissions from a spring; van Everdingen *et al.*, 1982) and +30‰ (SO_2 emissions from a

Table 5.5 Isotopic composition of selected atmospheric sulphur gases and particulates

Type of atmosphere	Region	Compound	$\delta^{34}S$ (‰) Range	$\delta^{34}S$ (‰) Mean	Remarks	References
Stratosphere	0–43°S 18.3–19.8 km	SO_4^{2-}	+2.3 to +2.9 +20 declining to −24	+2.6	No (major) volcanic eruption following the eruption of Mt Agung	Castleman *et al.* (1974)
Continental, biogenic	Great Salt Lake, Utah, USA	H_2S	0 to +10.0		Lake margin	Grey and Jensen (1972)
	Paige Mountain, NWT, Canada	H_2S	−9 to −6		Cold springs	Krouse and van Everdingen (1983)
Urban	Prague, Czechoslovakia	SO_4^{2-}	+3.6 to +9.0	+5.8		Buzek, Cerny, and Sramek (Section 8.9)
		SO_2	+0.6 to +5.7	+2.3		
	Calgary, Canada	SO_2	+7.5 to +14.0	+10.9	Lead peroxide exposure cylinders 1971	H.R. Krouse (contributed data)
	Edmonton, Canada	SO_2	+10.5 to +10.6	+10.6		
	Red Deer, Canada	SO_2	+14.0 to 20.9	+19.0		
	New Haven, Conn., USA	SO_4^{2-}	+1.1 to +6.9	+4.2	1969–70	Newman and Forrest (Section 8.4)
		SO_2	−2.1 to +8.7	+2.6	1968–70	

	Long Island, N.Y., USA	SO_4^{2-}	+1.9 to +9.8	+5.3	1970–75	
		SO_2	+2.o to +4.7	+2.1	1970–75	
	New York CIty, USA	SO_4^{2-}	+3.2 to +13.7	+8.5	1971–72	
		SO_2	−1.9 to +3.9	+1.5	1968–72	
Power plants						
Oil	Northport, USA	SO_2	+4.1 to +5.4	+4.8	Fluegas	Forrest and Newman (1977a) (see Section 8.4)
Coal	Keystone, USA	SO_2	+1.3 to +3.7	+2.9	" "	
Coal	Labadie, USA		−5.0 to +3.6	−2.7	" "	
Coal	Akansk-Achinsk, USSR		+3.4 to +5.0	+4.1		Grinenko and Grinenko (see Section 8.3)
Coal	Chvaletice, Czechoslovakia	SO_2	+1.4 to +0.1	−0.7	Flue gas	Busek *et al.* (see Section 8.9)
Sour gas	Balzac, Alberta, Canada	SO_2	+6 to +21	+15		Krouse and Case (1982)
processing plants, (see Section 8.2)	Whitecourt, Alberta, Canada	SO_2	+12 to +25	+20	Downwind	Krouse *et al.* (1984)
		SO_2	+5 to +9	+7	Upwind	
		SO_4^{2-}	+12 to +30	+21	Downwind	
		SO_4^{2-}	+6 to +11	+9	Upwind	
Smelter	Sudbury, Ontario, Canada	SO_4^{2-}		+3.7	Three-stack samples	Nriagu and Coker (1978b)
		SO_4^{2-}	+4.2 to +7.6	+5.7	Plume	
		SO_2	+0.9 to +2.6	+1.3	Stack and plume	Forrest and Newman (1977b)
		SO_2	+1.1 to +1.8	+1.4	Downwind	

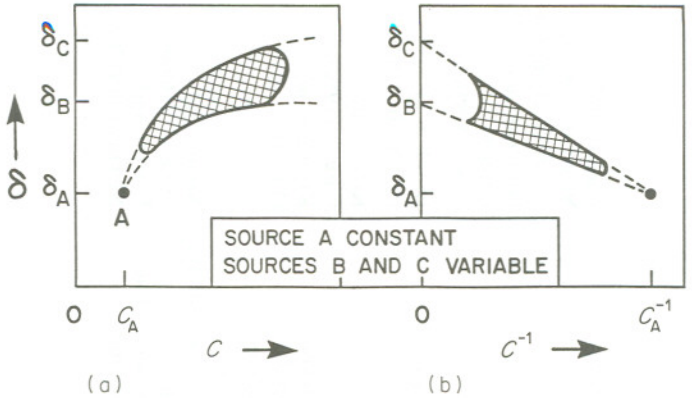

Figure 5.6 The $\delta^{34}S$ values versus (a) concentration and (b) concentration^{-1} for one source A with δ_A and a constant emission rate and two sources B and C with different δ values and varying in their emission rates

sour gas plant; Krouse, 1980). A fundamental question is whether there are background $\delta^{34}S$ values which pertain to large areas of the earth. This question is addressed in Section 5.5.6.

If the area surrounding a dominant industrial emitter is examined randomly on many occasions, the data tend to fit a pattern such as that shown in Figure 5.7. The spread in $\delta^{34}S$ values at low concentrations reflects many minor sources. These sources are not evident at higher concentrations which are dominated by the industrial source. A given point is primarily a function of wind direction which determines the relative contributions from the various sources. Biological activity may impose a seasonal dependence upon some sources.

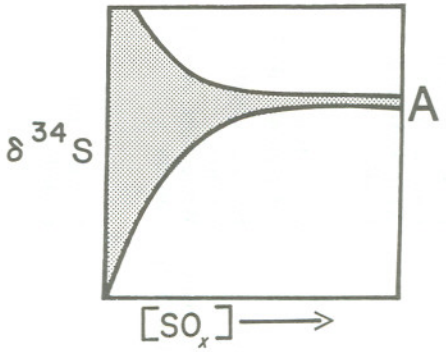

Figure 5.7 The $\delta^{34}S$ values versus concentration for a dominant source with δ_A and numerous minor sources with various $\delta^{34}S$ values and emission rates. The minor sources are only evident at lower concentrations

5.5.2 Use of $\delta^{34}S$ and concentration data to identify sources of SO_4^{2-} in precipitation

Extension of the hypothetical models of Section 5.5.1 to precipitation and water bodies must recognize that variable evaporation and dilution may alter the $[SO_4^{2-}]$ drastically. Whereas the $[SO_4^{2-}]$ alone may not be useful, the problem may be overcome by referring it to the concentrations of other ions. If there is a seawater SO_4^{2-} component, the $[Cl^-]$ may be used (Mizutani and Rafter, 1969; Cortecci and Longinelli, 1970; Wakshal and Nielsen, 1982). The approach of these authors is illustrated in Section 5.5.4. The data of Mizutani and Rafter were alternately interpreted in terms of three sources by Krouse (1980). In that case, the approach of Figure 5.6 was used with normalized units corresponding to the amount of SO_4^{2-} in a sample containing a fixed amount of Cl^-.

5.5.3 Use of $\delta^{18}O$ and concentration data to identify sources of SO_4^{2-} in precipitation

If sulphate from two or more sources were dissolved in precipitation, then the mixing models discussed in Section 5.5.2 should apply.

Whereas the sulphur isotope composition does not change markedly during oxidation of H_2S and SO_2 to SO_4^{2-}, the oxygen isotope composition varies drastically depending upon the mechanism and the relative amounts of oxygen incorporated from O_2 and H_2O molecules (Holt and Kumar, Chapter 2). If all the SO_4^{2-} in precipitation resulted from *in situ* oxidation, then the $\delta^{18}O$ value of SO_4^{2-} should correlate well with that of the water. Such appears to be the case in Figure 5.8 where the following linear relationship was found:

$$\delta^{18}O_{\text{sulphate}} = 16.0 \pm 0.9 + (0.4 \pm 0.1)\ \delta^{18}O_{\text{water}}$$

However, most data in the literature are not so well behaved. In the case of Gracefield, New Zealand, plotting of $\delta^{18}O$ of SO_4^{2-} versus that of H_2O does not reveal a simple relationship (Mizutani and Rafter, 1969). For example, in this data set, the sample which had SO_4^{2-} similar in both $\delta^{34}S$ and $\delta^{18}O$ to the marine values, had a $\delta^{18}O$ value of −15‰ for the H_2O. Clearly the oxygen isotope composition of the bulk of the SO_4^{2-} had been determined prior to its incorporation in the rain. In the same data set the average $\delta^{18}O$ value for water was −5‰ but the $\delta^{34}S$ and $\delta^{18}O$ values of SO_4^{2-} were lower.

If one compares average values for Gracefield (Mizutani and Rafter, 1969), Venice (Longinelli and Bartelloni, 1978), and Lublin (Figure 5.8), one finds the $\delta^{18}O$ differences between SO_4^{2-} and water are 15, 20, and

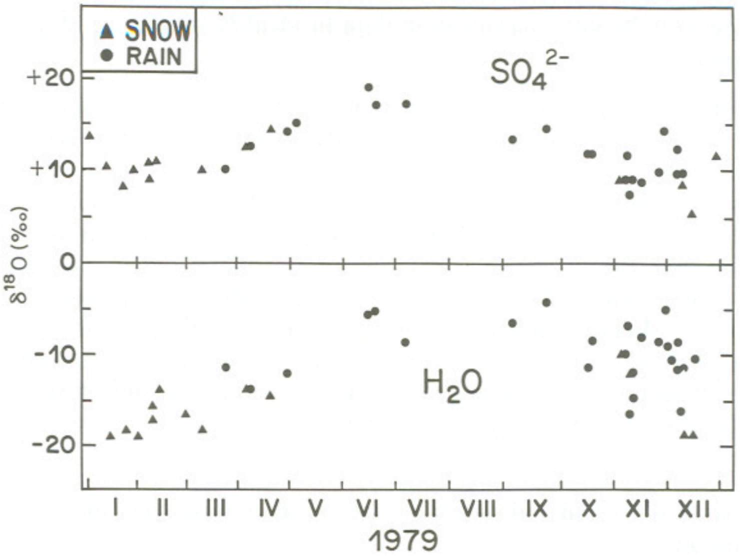

Figure 5.8 The $\delta^{18}O$ values for SO_4^{2-} and H_2O in precipitation in Lublin, Poland (data provided by A. Trembaczowski and S. Halas)

25‰ corresponding to average $\delta^{18}O$ values of precipitation of −5, −7, and −14‰, respectively. This implies that the ratio of previously formed SO_4^{2-} to that generated by oxidation within droplets is quite different at the three locations. It is interesting to note that the average values in the Venice study fit the linear relationship found for Lublin whereas this is not the case for the New Zealand data. It is also noted that the average $\delta^{18}O$ values for SO_4^{2-} at the three locations differ by less than 3‰.

In summary, mixing of previously formed SO_4^{2-} with SO_4^{2-} formed entirely by oxidation within precipitation droplets can be modelled and interpreted. However, in natural situations, mixing and oxidation parameters may vary to complicate the interpretation. For example, consider the emission of SO_2 from one hot stack. Sulphate formed near the stack would probably incorporate more O_2 with quite positive $\delta^{18}O$ values (Section 2.2.4), whereas further downwind at cooler temperatures oxygen more depleted in ^{18}O might be incorporated from H_2O droplets.

5.5.4 Isotopic delineation of sources of sulphur emissions in local situations

Isotopic differentiation of sources of atmospheric sulphur compounds have been most successful over distances of a few tens of kilometres. In an early study in the vicinity of a large copper smelter near Salt Lake City, Utah, USA (Dequasi and Grey, 1970; Grey and Jensen, 1972), the industrial operation effectively ceased during an extended workers' strike. It was found that the $\delta^{34}S$ for both precipitation and atmospheric sulphur averaged +2‰ during smelting as compared to +6‰ during the strike. Values near +9‰ were found in a remote 'control' area. It was further concluded that during the shutdown period, about 90% of the atmospheric sulphur was biogenic whereas 10% came from other anthropogenic sources.

Mizutani and Rafter (1969) determined the isotopic composition of both S and O in rainwater SO_4^{2-} over a five-month period in Gracefield, New Zealand. They plotted $\delta^{34}S$ and $\delta^{18}O$ values against a parameter A which measures the percentage of marine SO_4^{2-} in a given sample on the basis of $[Cl^-]$ and $[SO_4^{2-}]$, where

$$A = \frac{[Cl^-]_{\text{measured}}}{7.1 \times [SO_4^{2-}]_{\text{measured}}} \times 100$$

On this basis (see Section 5.5.6), it was concluded that the intercept at $A = 0$ (no marine SO_4^{2-}) corresponded to a source with $\delta^{34}S = 0$. These authors felt that they could not differentiate between biogenic and industrial contributions to this component. It is interesting to note that a three-source model with $\delta^{34}S$ values of +20 (ocean SO_4^{2-}), +3, and −4‰ includes all the data points of Mizutani and Rafter (Krouse, 1980). By coincidence, Nakai *et al.* (see Section 8.5.5) selected values of +3.4 and −4‰ for natural H_2S and anthropogenic sulphur respectively, to calculate the atmospheric sulphur balance in Japan.

Studies around sour gas plant operations in Alberta have proved informative since the $\delta^{34}S$ values of the emissions (+15 to +30‰) are substantially higher than those of environmental receptors (−30 to 0‰) (Section 8.2). In a fashion similar to the copper refinery study cited above, the startup of a sour gas plant may be monitored by measuring the $\delta^{34}S$ values of ground-level SO_2 and particulates (Figure 5.9). The change in the isotopic composition of the SO_2 is better behaved than that of the particulates. Plotting of $\delta^{34}S$ versus $[SO_2]^{-1}$ yields straight lines for each sampling station which extrapolate to +29‰ on the y axis (Krouse, 1980). It is noted that this is consistent with data obtained by high-volume sampling of the plume with a helicopter (Figure 5.3).

Examples of trends using wind directionally controlled high-volume sampling in the vicinity of sour gas plants are given in Section 8.2. The areal distribution of $\delta^{34}S$ in vegetation and soil receptors in response to atmospheric sulphur near these plants is also discussed.

5.5.5 Construction of regional balances of atmospheric sulphur

As shown in the following examples and case studies in Chapter 8, stable isotopes can be used to evaluate regional balances of atmospheric sulphur.

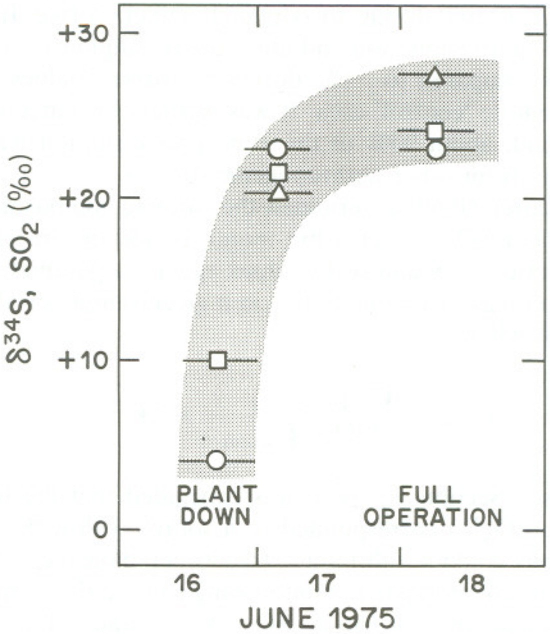

Figure 5.9 Isotopic monitoring of a sour gas plant startup with ground-level high-volume sampling of atmospheric SO_2, Crossfield, Alberta (from Krouse, 1980). The three sampling stations are indicated by different symbols

It is interesting to compare data from two different areas in the Mediterranean region: Pisa and Venice, Italy (Cortecci and Longinelli, 1970; Longinelli and Bartelloni, 1978), and northern Israel (Wakshal and Nielsen, 1982).

From $[Cl^-]$ and $[SO_4^{2-}]$ and isotopic measurements on SO_4^{2-}, Cortecci and Longinelli (1970) calculated that the seawater spray contribution in 64 rainwater samples at Pisa was 35% for 1 sample, 10–30% for 9 samples, and less than 10% for 54 samples. The main source of sulphate according to these authors was atmospheric oxidation of SO_2 from industrial emissions. The possible contribution of biogenic H_2S was not evaluated. The range in $\delta^{34}S$ values (−2.5 to +7.1‰) was very similar to that reported for rainfall in Venice (−0.2 to +8.3‰) by Longinelli and Bartelloni (1978). The average value for the latter (+3.0‰) was slightly higher than that of the former (+1.1‰).

In the Venice study, the $\delta^{18}O$ values of SO_4^{2-} were low between December 1974 and January 1975, became more positive during the summer, and decreased again during the autumn and winter of 1975. Since this trend was consistent with that of the isotopic composition of the rain water, much of the SO_4^{2-} was attributed to oxidation of local emissions. Sulphate crusts on monuments were also examined isotopically and the data used to argue that they formed as a consequence of industrial emissions. This is consistent with the fact that the crusts had not been observed prior to industrial activities.

In northern Israel, $\delta^{34}S$ values for SO_4^{2-} in rain water, ranging from +4.5 to +14.3‰, were more positive than those of Pisa and Venice. In most samples, the marine SO_4^{2-} contribution was calculated to be less than 40%. The SO_4^{2-} was found to be more enriched in ^{34}S on the Coastal Plain (+7.5 to +14.3‰; average, +9.5‰). The mean decreased to +5.3‰ upon approaching the summit of central Upper Galilea. Using the *A* parameter of Mizutani and Rafter (1969), the extrapolated $\delta^{34}S$ value for zero marine SO_4^{2-} contribution was found to be between +1 and +2‰ dependent upon the sampling location. This value is not radically different from the means and the minimum $\delta^{34}S$ values found at Pisa and Venice.

Nriagu and Coker (1978a) investigated sulphur isotope and $[SO_4^{2-}]$ variations over distances of the order of 1000 km in the Great Lakes of North America over two years from 1973 to 1975. Average values for urban, rural, and remote stations were found to show a strong seasonal dependence with the urban $\delta^{34}S$ values about 2‰ heavier (Figure 5.10). The maximum $\delta^{34}S$ values in January–February were about 4‰ heavier than the minima

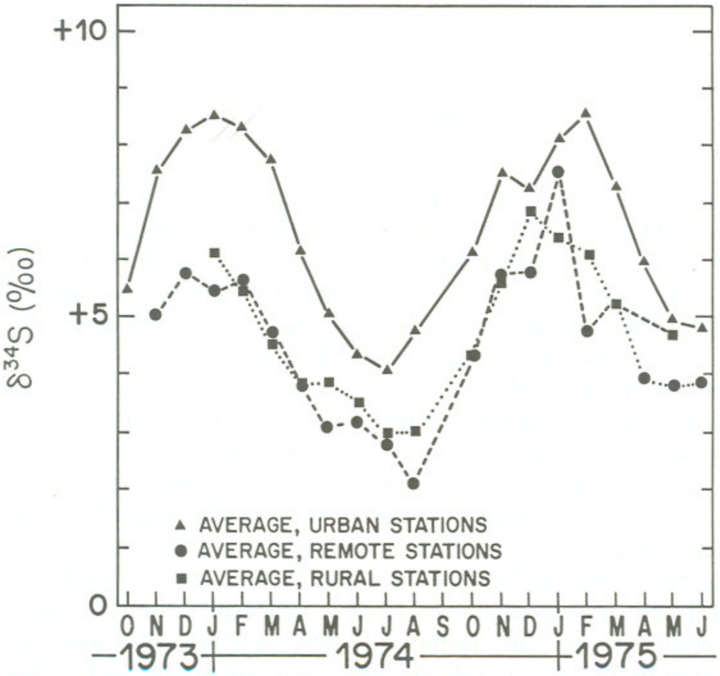

Figure 5.10 Seasonal variations for average $\delta^{34}S$ values for precipitation in the Great Lakes Basin (after Nriagu and Coker, 1978a)

occurring in July–August. In contrast, the [SO_4^{2-}] fluctuated considerably and it is difficult to discern any seasonal dependence. They concluded that the seasonal trends reflected the dominance of anthropogenic inputs with greater biogenic emissions in the summer months. The biogenic component was judged to account for 10–30% of the total SO_4^{2-}.

The study of Nriagu and Coker (1978a) for sites generally north of the Great Lakes is complemented by those of Newman and Forrest over a larger area south and east of the Great Lakes (Section 8.4). It is noted that the range in $\delta^{34}S$ values for particulate sulphur of the latter (+1 to +13‰) is slightly larger than that of SO_4^{2-} in the former (+1 to +9‰). However, very few data of Newman and Forrest are above +9‰ (Figure 8.15). The similarity is not surprising, considering the large number of anthropogenic sources and the storm patterns over this large region. For these reasons, precipitation in the remote areas studied by Nriagu and Coker (1978a) contain significant anthropogenic sulphur.

Nakai *et al*. (Section 8.5) have estimated average $\delta^{34}S$ values for three main sources of SO_4^{2-} in rain water in Japan. They calculated the contribution of these three sources at polluted sites by the following equations:

$$\delta^{34}S_{SO_4{}^{2-}} = a\delta^{34}S_a + b\delta^{34}S_b + c\delta^{34}S_c \quad (1)$$

$$a + b + c = 1.0 \quad (2)$$

$$\frac{b}{a} = 0.58 \quad (3)$$

where *a* is the fraction of sea spray SO_4^{2-} with $\delta^{34}S_a = +20.3‰$, *b* is the fraction of SO_4^{2-} from oxidation of natural H_2S emissions with $\delta^{34}S_b = +3.4‰$, and *c* is the fraction of SO_4^{2-} from oxidation of anthropogenic SO_2 with $\delta^{34}S_c = -4.0‰$. They concluded that the contribution of anthropogenic SO_2, which was 40–50% of the total atmospheric sulphur in industrial and urban sites of Japan in 1960, increased to 75% in 1973 and then decreased to about 60%.

In summary, for a number of regions of the world, rain water contains minor marine SO_4^{2-} and one or more components with $\delta^{34}S$ values not far removed from 0‰. In many cases, these have been attributed to industrial emissions. However, this small range in $\delta^{34}S$ values suggests a common source such as marine sulphide emissions, particularly in coastal regions. At high latitudes, the seasonal dependence of $\delta^{34}S$ may delineate anthropogenic and natural emissions as in the study of Nriagu and Coker (1978a). Nakai *et al*. (Section 8.5) not only isotopically differentiated anthropogenic from natural emissions in Japan but divided the latter into marine and continental.

5.5.6 Estimate of the isotopic composition of biogenic sulphur in the atmosphere

An average $\delta^{34}S$ value for biogenic sulphur released to the atmosphere from oceans and continents is required for modelling the atmospheric sulphur budget. At the present time, relevant data are sparse. Nonetheless, some general ideas may be formulated from previous investigations.

In earlier studies, biogenic sulphur was identified with H_2S, and it was assumed that the isotopic composition of other reduced compounds (DMS, CS_2, COS, etc.) did not differ from that of H_2S. The present analysis recognizes that reduced biogenic sulphur compounds originate from essentially two different sources.

Firstly, H_2S and possibly other reduced sulphur compounds are released during bacterial SO_4^{2-} reduction. The isotope composition of this H_2S depends upon the rate of SO_4^{2-} reduction and redox conditions (Nakai and Jensen, 1964; Kemp and Thode, 1968; Rees, 1978) in the environment. Its $\delta^{34}S$ values vary from −28 to −15‰ in shallow marine regions, whereas in estuaries and coastal tidal zones the range is −22 to +12‰ (Grinenko and Grinenko, 1974). The average $\delta^{34}S$ for H_2S and its derivatives formed under such conditions is probably close to −10‰. In freshwater lakes with low $[SO_4^{2-}]$, the evolved H_2S has nearly the same $\delta^{34}S$ value as the SO_4^{2-} (−20 to +20‰; average +8‰; SCOPE 19, 1983, Chapter 5).

Secondly, H_2S and other reduced sulphur compounds are evolved during decay of sea and land biota. Complete decomposition must correspond to no isotope fractionation. Since organic S of marine organisms has $\delta^{34}S$ values close to that of seawater SO_4^{2-} (Kaplan and Rittenberg, 1964; Mekhtiyeva and Pankina, 1968), the $\delta^{34}S$ value of reduced sulphur compounds from this decay should be near +18‰. The same was found for terrestrial flora and fauna on Heron Island, Great Barrier Reef, Australia (Krouse and Herbert, 1988). Since the assimilated S for freshwater lake biota is familiar in isotope composition to the SO_4^{2-}, reduced S compounds from their decay should average +8‰.

Although the most frequent $\delta^{34}S$ values for SO_4^{2-} in rivers is about +6‰, the mean weighted flux to the ocean is estimated to have a $\delta^{34}S$ value of +8‰ (SCOPE 19, 1983, Chapter 5). Since the $[SO_4^{2-}]$ is low, reduction is controlled by SO_4^{2-} uptake and hence will not display a large isotope selectivity. Further, under the typical aerobic conditions of flowing rivers, the amount of H_2S escaping to the atmosphere should be small. When water levels drop, there may be some decay of aqueous biota which would release a variety of sulphide gases to the atmosphere. Their mean $\delta^{34}S$ value should also be +8‰. However, one must bear in mind that bacterial SO_4^{2-} reduction also occurs in continental saline water bodies. The total surface area of such water bodies is three times that of the oceanic shelf. Therefore, it may be assumed that their sediments accumulate triple the amount of reduced sulphur (9 Tg S y^{-1}). Since the $\delta^{34}S$ value for SO_4^{2-} in these reservoirs is, on average, close to +15‰ and the rate of bacterial reduction is somewhat higher compared to that on the shelf, the mean $\delta^{34}S$ value for biogenic sulphide may be taken as −10‰ (SCOPE 19, 1983, Chapter 6). The amount of reduced sulphur buried in freshwater sediments is 16 Tg S y^{-1}. If it is assumed that bacterial H_2S emitted to the continental atmosphere from fresh and saline basins is proportional to sulphide buried in their sediments, then this H_2S has a mean value near +1‰ (Figure 5.11), as calculated from the mass isotopic balance equation.

9 Tg S (−10‰) + 16 Tg S (+8‰) = 25 Tg $\delta^{34}S_{mean}$. If the value +6‰ is used for freshwater sulphate, the mean $\delta^{34}S$ value is closer to zero. A similar mass balance equation also gives a mean $\delta^{34}S$ value near 0‰ for total sulphide emissions from the oceans.

Terrestrial plants contain sulphur with an isotopic composition similar to that of soil sulphur if ambient SO_2 levels are low (Chapter 7). According to Chukhrov *et al.* (1977, 1978), the $\delta^{34}S$ values for soils and plants over the Soviet Union average +3‰. This appears to be a reasonable average value for all soil and plant data in the literature (Sections 7.1.3 and 7.2.1).

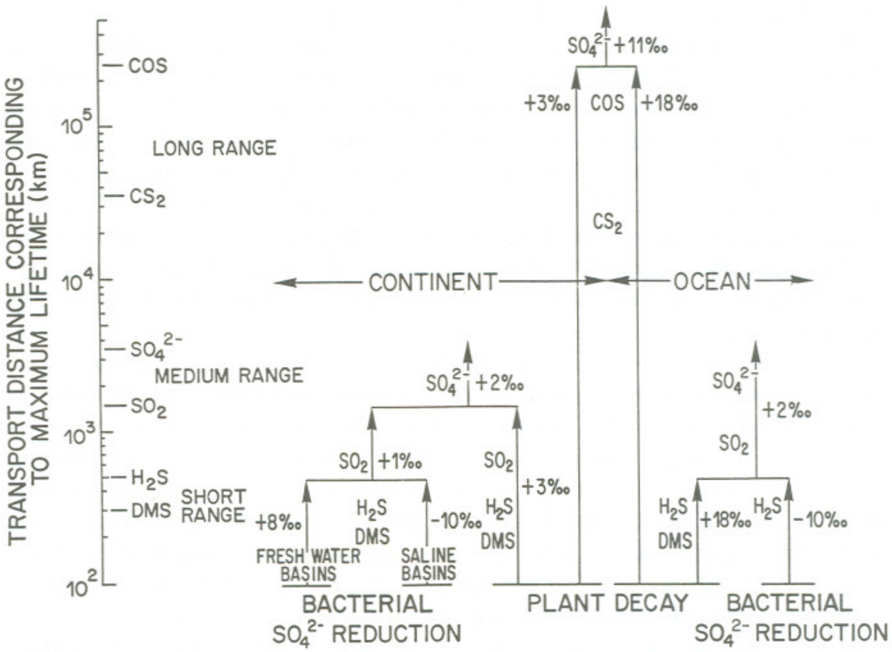

Figure 5.11 Estimated $\delta^{34}S$ values for atmospheric biogenic sulphides as a function of the maximum transport distance

Therefore it may be assumed that DMS, H_2S, CS_2, COS, etc., from biological decay have $\delta^{34}S$ values that average +3‰.

At the time of writing, there were no data on the amount of H_2S released to the continental atmosphere from bacterial reduction and plant decay. However, even if these fluxes differ from each other by a factor of 3, the mean $\delta^{34}S$ value may still be taken as +1‰.

When considering the atmospheric sulphur cycle, one should bear in mind that various reduced sulphur compounds are oxidized to SO_2 at different rates (SCOPE 19, 1983, Chapter 4). The average residence time is the least for DMS (< 1 day). It is about 1 day for H_2S and SO_2, and 70 and 500 days for CS_2 and COS respectively (SCOPE 19, 1983, Chapter 5). Consequently, these compounds are transported over different mean distances from their place of origin (Figure 5.11). The fluxes of DMS and H_2S from seas and continents should mix only within a few hundred kilometres of the coast line. The compounds that are more resistant to oxidation, such as CS_2 and COS, can mix over a longer range. If it is assumed that the fluxes of these sulphur compounds are proportional to the organic matter produced by photosynthesis (roughly the same for oceans and continents), then the mean $\delta^{34}S$ value for such sulphur is +11‰. Note that the contributions from plants in freshwater and saline reservoirs were omitted in this mass balance calculation. However, their extent is relatively minor and, further, their mean $\delta^{34}S$ value is also close to +11‰ (for simplicity, this flux is omitted in Figure 5.11).

The mean isotopic composition of total biogenic sulphide from the oceans and continents is difficult to determine since the ratio of emissions from SO_4^{2-} reduction and plant decay is unknown. This problem may be solved by analysis of atmospheric sulphur isotope data published for coastal environments, as summarized in Table 5.3. If it is assumed that sampling was performed during the period of sea-to-shore winds, biogenic sulphur was then the main source of SO_2 and H_2S. The only possible mode of SO_2 production should be oxidation of reduced sulphur compounds in the atmosphere. For this reason, gaseous compounds are ideal for characterizing the mean isotopic composition of biogenic sulphur from oceans. The subsequent process of SO_2 oxidation to sulphate should not be accompanied by significant sulphur isotope fractionation (Section 5.2.3). The data of Table 5.3 suggest that the $\delta^{34}S$ value for gaseous forms of sulphur varies from −4 to +6‰ with a mean value of 0‰. These data are too few and it is noted that the spread of $\delta^{34}S$ values is much larger in sulphate aerosols.

Another approach may be used to estimate the mean isotopic composition of the biogenic sulphur flux. Sulphur isotope data have been published for rainwater SO_4^{2-} in coastal zones of New Zealand and Israel (Mizutani and Rafter, 1969; Wakshal and Nielsen, 1982). It is possible to estimate the contribution of marine sulphate using $[SO_4^{2-}]/[Cl^-]$ ratios. It is noted that most points for both data sets are located near the line passing through a $\delta^{34}S$ value equal to +20‰ (100% marine SO_4^{2-}) and approximately 0‰ (0% marine SO_4^{2-}) (Figure 5.12).

In Figure 5.12, a line is drawn from the $\delta^{34}S$ value of +20‰ (100% marine SO_4^{2-}) to −10‰ (0% marine SO_4^{2-}). The latter value is that estimated for biogenic sulphide produced by SO_4^{2-} reduction. A near-horizontal line at $\delta^{34}S$ just under +20‰ would correspond to an admixture of marine SO_4^{2-} and biogenic sulphide derived entirely from the decay of marine plants. However, the data fall well below this hypothetical line, implying that sulphide production by this mode is smaller than by SO_4^{2-} reduction. It is seen that, with one exception, all data fall below the line from +20‰ (100% marine SO_4^{2-}) to +5‰ (0% marine SO_4^{2-}). If it is assumed that the anthropogenic influence is negligible, isotope balance calculations show that the line going through 0‰ corresponds to the biogenic sulphide generated from SO_4^{2-} reduction, being twice that arising from decay of marine plants. Table 5.4 presents $\delta^{34}S$ values for SO_4^{2-} in atmospheric precipitation over remote regions of the globe. Sulphur isotope data may be used to attempt estimates of the percentage of biogenic sulphur in the atmosphere over the open ocean. It may be assumed that the

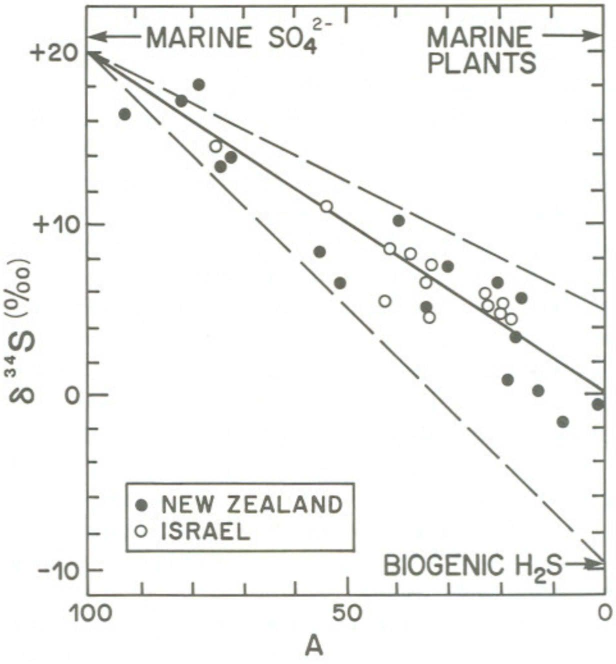

Figure 5.12 Relationship between $\delta^{34}S$ and *A* value of rain near coastal areas (data from Rafter and Mizutani, 1967, and Wakshal and Nielsen, 1982

contributions of anthropogenic and volcanic sulphur in precipitation over the open ocean and oceanic islands are rather small. The rainwater SO_4^{2-} must be composed almost entirely of sea spray SO_4^{2-} and oxidized biogenic sulphur. The $\delta^{34}S$ values in precipitation over oceans vary within the range of +9 to +16‰, with the average value of +13‰ (Table 5.4). If we accept the $\delta^{34}S$ value of 0‰ for the total biogenic sulphur released from oceans, the mass isotopic balance shows that biogenic sulphur accounts for one-third and sea spray for two-thirds of the total sulphur.

Of particular interest are the results of snow and ice sampling in Arctic and alpine regions. Most samples have rather high $\delta^{34}S$ values (Table 5.4). Comparative analyses of sulphur, sodium, and chloride concentrations in such samples indicate that only 10% of the sulphate is of marine origin (SCOPE 19, 1983, Chapter 4). Consequently, high $\delta^{34}S$ values in these samples are due to sources other than marine SO_4^{2-}. It is precisely in these samples that one should find biogenic sulphur from CS_2 and COS, since these compounds may be transported large distances. Such sulphur should be particularly detectable in central regions of the Antarctic, Greenland, and the Arctic. At present, the only data available are from snow and ice on Severnaya Zemlya Island (Table 5.4). The average $\delta^{34}S$ value was +10.7‰ and the variation between 1911 and the present time was only 1‰. This suggests that these samples were not influenced by industrial sulphur. If 10% of the sulphur is attributed to seawater SO_4^{2-}, a $\delta^{34}S$ value of +8.8‰ is obtained for the remaining sulphur (90%). Considering the uncertainties, this value compares reasonably well with the long-range estimate of +11‰ based on CS_2 and COS in Figure 5.11. Alternatively, if the value of +11‰ is assumed for biogenic sulphide, one must conclude that this component in the Severnaya Zemlya ice exceeds 70%. If the difference between the values +8.8 and +11‰ is real, this implies that roughly 20% of the sulphur should be attributed to other sources, such as volcanic sulphur and bacterial SO_4^{2-} reduction.

Using the above arguments with other data in Table 5.4, one concludes that CS_2 and COS are proportionally lower in high-mountain regions and do not exceed 50% of the total sulphur in snow and ice. It is noteworthy that in cold alpine regions of the Caucasus located between the Black and Caspian Seas, $\delta^{34}S$ values for SO_4^{2-} in precipitation are close to −1‰ (Table 5.4). These are probably indicative of a major contribution from marine biogenic gases, but volcanic activity is another possible contributor.

5.6 POTENTIAL OF USING ENRICHED SULPHUR ISOTOPES FOR STUDYING TRANSPORT, TRANSFORMATIONS, AND REMOVAL OF ATMOSPHERIC SULPHUR

5.6.1 Introduction

The most desirable tracer for a substance is the substance itself. Consequently, it is attractive to use stable isotopes of sulphur to follow transport and transformation of SO_2 in the atmosphere. The technical feasibility of stable tracers must address not only the long-range transport question but also whether they could be employed in directed embedded experiments such as examining transformations in a given cloud.

5.6.2 Background fluctuations

The technical feasibility can be addressed by considering questions raised in the following example. Assume that we want to follow the mixing and transformation of emitted SO_2 with an isotope ratio different from the background. What are the limitations for detecting this SO_2 as it co-mingles with the background SO_2? The ultimate permitted dilution corresponds to the δ^{34}S value of the mixture SO_2 falling within the random variability of the δ^{34}S value of the background or alternately within the precision of the measurements. The question can be expressed by the equation

$$E(f_E) + B(1 - f_E) = B \pm \Delta B$$

where

E = isotopic ratio of the emitted sulphur
f_E = fractional amount contributed to the background such that the change in the measured isotopic ratio of a sample either falls within the natural fluctuations of the analytical precision
B = isotopic ratio of the background
ΔB = random fluctuations in the background isotopic ratio and the analytical error

The equation can be rewritten in terms of δ^{34}S values and rearranged to yield

$$f_E = \frac{\delta^{34}S_B}{\delta^{34}S_E - \delta^{34}S_B}$$

A numerical example follows: if the emitted SO_2 has a δ^{34}S value that is 100‰ higher than the background (e.g. going from a $^{34}S/^{32}S$ of 0.045 to 0.0495) and the random fluctuation of the background is 1‰, $f_E = 0.01$. Consequently, the emitted SO_2 would contribute a change in the isotopic ratio that is no greater than the random fluctuation of the background when its fraction of the measured background concentration becomes 0.01. This value, or more appropriately about three times it, would be the ultimate dilution that would still permit recognition of the isotopic label. Other examples are shown in Table 5.6.

Tagging the SO_2 with an oxygen isotope is not viable because the oxygen atoms readily exchange with those in ambient H_2O. However, SO_4^{2-} might be labelled with both S and O isotopes for tracing its movement since the oxygens are not labile.

5.6.3 Dispersion and dilution

This aspect of the problem can be considered using arguments from a long-range transport experiment. Plumes from point sources do not follow straight lines as they sweep across large areas in response to wind. However, along any individual path, the plume expands in a fairly consistent way. Depending on meteorological conditions, the average lateral dispersion generally ranges between 5 and 15 degrees. Dilution at the source obviously depends on the wind speed u. If Q is the emission rate at a point source, then the dilution associated with an assumed 'top hat' plume concentration cross-section is given by

$$Q = xuhD \tan \theta$$

where x is the downwind concentration of the emitted substance, h the height of the mixed layer, D is the distance travelled, and consequently D

Table 5.6 Systematics of isotopic enrichment studies of atmospheric S

	Fraction contributed to the background by the source to make the measured isotopic ratio of a sample equal to the:		
The amount which the del value of the injected sulphur is different from background (‰)	Potential long-range and spatial fluctations of 10‰ in the background ratio	Spatially homogeneous near-field fluctuations of 1‰ in the background ratio	Limitation based on the analytical accuracy of 0.1‰ in ratio
20	0.5	0.05	0.005
100	0.1	0.01	0.001
1000	0.01	0.001	0.0001

tan θ is the width of the plume at the downwind distance. For typical conditions experienced during a long-range transport experiment (u = 10 m s^{-1} h = 1 km, D = 1000 km, and θ = 10°),

$$\frac{x}{Q} = 6 \times 10^{-10}\,\mathrm{Sm}^{-3}$$

Newman *et al.* (1975a, 1975b) have found that the isotopic ratio of $^{34}S/^{32}S$ in the atmosphere is generally about 0.045 corresponding to ^{34}S comprising 4.3% of the total. Random variations of this ratio have been observed to be as much as 10 del units (1%) over periods of hours (Newman, 1969; Krouse *et al.*, 1984). For a typical atmospheric concentration of 10 ppb for SO_2 (13 μg S m^{-3}), a potential variation of ^{34}S in the atmosphere of about 6 ng ^{34}S m^{-3} is anticipated. In order to perform a successful experiment it would seem reasonable that it is necessary to exceed this random variation by a factor of 10, so that the source should deliver about 60 ng ^{34}S m^{-3}. Therefore the point source for a 1000-km experiment would have to emit

$$Q = 100\ \mathrm{gm}\ {}^{34}\mathrm{S}\ \mathrm{s}^{-1}$$

It must be recognized that the above is an optimistic argument since transformations and dry and wet deposition have been neglected. At a distance of 500 km, measurements have shown that these processes can cause up to 90% removal (SCOPE 19, 1983, Chapter 4).

The necessary emission rate can be substantially reduced if one is able to select atmospheric conditions when the random fluctuations in del are less than 10‰, perhaps as low as 1‰. In addition, W.R. Kelly (personal communication, 1984) of The National Institute of Standards and Technology suggested that by measuring both $^{34}S/^{32}S$ and $^{34}S/^{32}S$ ratios, one could factor out the random atmospheric variations. Such measurements can be carried out mass spectrometrically using SF_6 (Chapter 3).

5.6.4 Economic evaluation

Releases that were found useful in a long range transport experiment were typically of 3 hours duration (R.N. Dietz, Brookhaven National Laboratory personal communication, 1983), which corresponds to 10^3 kg $^{34}SO_2$ using the above emission rate. Such quantities are not available and it would be prohibitively expensive to produce enough material using existing facilities. For short range experiments, natural sources with unique isotope compositions can be employed (Section 8.4; Newman, 1984).

A variety of isotope separation processes including liquid thermal diffusion, gas centrifugation, laser separation, and distillation techniques have been examined in the hope of reducing the cost by a factor of 10^3 in order to have an affordable experiment. This goal seems highly improbable for the immediate future (Newman, 1984).

Consideration should also be given to the use of ^{36}S since its natural abundance is only 0.017% (compared to 4.2% for ^{34}S). Experiments could be performed by releasing fewer grams of material. However, the production costs are much higher because of its low abundance, unless one could employ laser isotope separation.

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