CHAPTER 3

The Isotopic Analysis of Sulphur and Oxygen

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3.1 THE ISOTOPIC ANALYSIS OF SULPHUR*

3.1.1 Introduction

This chapter is concerned with the ways in which sulphur samples are treated chemically, converted to a suitable gaseous form, and analysed mass spectrometrically. In order for sulphur isotope analyses to be useful it is necessary that sample handling introduces no isotope fractionation. In general this means that extractions, chemical reactions, etc., should be quantitative.

The total range of $\delta^{34}S$ values encountered in nature is ~150‰. Modern mass spectrometers can analyse sulphur isotope ratios with a reproducibility of ~±0.05‰, whereas the overall reproducibility for sample preparation and analysis is usually closer to ±0.2‰. Precision can be checked within a laboratory by replicate analysis of particular samples. In order to check accuracy, though, it is desirable to perform analyses on standard materials. There are two isotope reference materials for sulphur available from the International Atomic Energy Authority, Vienna (Gonfiantini, 1978), while in addition a set of 10 silver sulphide samples prepared at McMaster University has been widely circulated (Rees, 1978).

3.1.2 The chemical pretreatment of sulphur samples

3.1.2.1 *Introduction*

Chemical pretreatment of sulphur samples is necessary in order to convert the sulphur in the sample to a form (usually silver sulphide, Ag_2S, or barium sulphate, $BaSO_4$) that is suitable for further processing to sulphur dioxide (or sulphur hexafluoride) for mass spectrometric analysis (see Sections 3.1.3 and 3.1.4). In simple cases there may be only one form of sulphur present

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in the sample or different forms of sulphur may be combined for the analysis of total sulphur. In other cases it may be desirable to separate different forms of sulphur so that their individual concentrations and isotopic compositions may be determined. Thus it is clearly not possible to set out a procedure that will be applicable under all circumstances. The chemical pretreatment strategy will vary according to what forms of sulphur are present, in what matrix (if any) they are contained, and the extent to which separation and individual analysis of particular components are required.

This section does not give complete details of particular schemes of chemical pretreatment. Instead a number of such schemes are outlined and the sources are indicated where complete details may be found.

3.1.2.2 *The conversion of barium sulphate to silver sulphide*

This conversion is necessary if sulphur dioxide or sulphur hexafluoride is to be produced from silver sulphide.

Rafter (1967) described the conversion of barium sulphate to barium sulphide (BaS) by reaction with graphite at 1050–1100 °C. The BaS so produced is converted to silver sulphide by reaction with silver nitrate ($AgNO_3$). A modification of this method can be used not only to produce BaS but also to convert the oxygen from the sulphate to carbon dioxide for oxygen isotopic analysis of sulphate.

Thode *et al.* (1961) described the use of 'reducing mixture' to convert barium sulphate and other sulphates to hydrogen sulphide. The reducing mixture, originally introduced by Auger and Gabillon (1911), consists of 500 ml HI, 816 ml concentrated HCl, and 245 ml H_3PO_2 (50%). Reduction is carried out in a 200−ml flask provided with a reflux condenser. The H_2S swept out with a stream of nitrogen is washed with distilled water and finally absorbed in a solution containing cadmium acetate and distilled water. The cadmium sulphide produced is converted to silver sulphide by adding silver nitrate.

3.1.2.3 *Sulphur in the atmosphere and in water*

Forrest and Newman (1973) have reported a method for sampling atmospheric oxides and for processing the samples for the determination of $\delta^{34}S$ values. Particulate sulphate is collected on glass filters while atmospheric sulphur dioxide is absorbed on alkali-impregnated filter paper. Filter packs are assembled from a commercial high-volume sampler modified to hold the particulate prefilter followed by one or more sulphur dioxide absorbers. The same technique has also been used to sample sulphur compounds in the plumes from the stacks of power plants and smelters (Newman *et al.*, 1975; Forrest and Newman, 1977a, 1977b). Forrest *et al.* (1973) devised a high-temperature probe to collect separately sulphur dioxide and sulphur trioxide in power plant flue gases.

Chemical pretreatment of such samples prior to the production of sulphur dioxide for mass spectrometric analysis includes the oxidation of sulphur dioxide to sulphate by treatment with hydrogen peroxide (H_2O_2), the precipitation of barium sulphate by the addition to sulphate in acid solution of barium chloride, and the conversion of barium sulphate to silver sulphide as described in Section 3.1.2.2 above. Sulphur is determined at the silver sulphide stage by using silver containing a ^{110}Ag tracer and gamma counting the resultant activity in the silver sulphide (Forrest and Newman, 1977c).

Sulphate in water samples such as rain, river water, lake water, ocean water, etc., is converted to $BaSO_4$ by the addition of barium chloride. Sulphate may be preconcentrated from dilute solutions using ion exchange columns (e.g. Mizutani and Rafter, 1969). The $BaSO_4$ is further processed as required (e.g. Holt *et al.*, 1972; Nriagu and Coker, 1978; Rees *et al.*, 1978).

3.1.2.4 *Sulphur in vegetation, soils, and sediments*

Sulphur in samples of vegetation can be extracted by Parr bomb conversion to sulphate (Case and Krouse, 1980) or by oxidizing fusion to sulphate (Mekhtiyeva *et al.*, 1976), precipitation of barium sulphate following in each case. For samples with very low sulphur contents, preliminary ashing to reduce the bulk of the sample may be desirable (Johnson and Nishita, 1952).

For soil samples it may be desirable to separate different forms of sulphur for individual analysis. Thus Lowe *et al.* (1971) separated out soluble sulphate fractions by leaching with distilled water. The polysaccharide sulphate fraction was extracted by leaching the residue of the first step with 1% NaCl and humic acid fractions were obtained by extraction with 0.1 N NaOH. Sulphur from all three fractions was converted to barium sulphate prior to conversion to silver sulphide.

Freshly formed sediments contain appreciable amounts of pore water which may contain hydrogen sulphide (if the sedimentation conditions are anoxic) and will also contain dissolved sulphate. In addition, the sediment may contain acid-soluble sulphides, elemental sulphur, pyrite, and organic sulphur. Care must be taken when handling such sediments that hydrogen sulphide and iron monosulphides are not oxidized accidentally by exposure to the atmosphere.

Various procedures have been used to extract different forms of sulphur from both fresh and ancient sediments, although none of them seems to be entirely satisfactory. Detailed procedures are given in, for example, Thode *et al.* (1960), Vinogradov *et al.* (1962), Kaplan *et al.* (1963), Smith *et al.* (1964), Nriagu (1975), and Nriagu and Coker (1976).

A typical procedure would be:

(a) Strip the sample of H_2S by flushing with nitrogen. The H_2S is absorbed in a cadmium acetate solution for further processing.
(b) Add HCl to the residue of the previous step to liberate H_2S from acid-soluble sulphide. The H_2S is absorbed in a cadmium acetate solution.
(c) Filter the residue of the previous step and add $BaCl_2$ to the filtrate to precipitate sulphate as $BaSO_4$.
(d) Extract elemental sulphur from the solid residue of the previous step by Soxhlet extraction with benzene. The extracted sulphur is oxidized to sulphate with a HNO_3–Br_2 mixture and precipitated as $BaSO_4$.
(e) Treat the residue of the previous step with 6N HNO_3 to oxidize pyrite sulphur to sulphate. The material is filtered and the sulphate in the filtrate is precipitated as $BaSO_4$.
(f) Convert the organic sulphur in the solid residue of the previous step to sulphate by fusion oxidation or treatment with HNO_3–Br_2.

The difficulties which may arise include the accidental oxidation of hydrogen sulphide and acid-soluble sulphide before analysis, the overestimation of elemental sulphur by producing it during the extraction of the acid-soluble sulphide step (Berner, 1974), the partial extraction of organic sulphur together with pyrite, and the failure to extract all pyrite, some of which may then be included in the organic sulphur fraction. With regard to the separation of pyrite sulphur and organic sulphur, Monster (1978a) has critically compared the Li–Al–H_4 method (Smith *et al.*, 1964) and the nitric acid method, outlined above.

Some separation procedures employ solvent extraction for organic sulphur. Monster (1978b) has pointed out the well-known fact that only a fractional amount of the total amount of organic material in recent sediments is extractable with organic solvents (see also Smith, 1952, 1954).

Sasaki *et al.* (1979) have cautioned against the use of the reducing mixture reaction for the extraction of whole rock sulphur, pointing out that this reagent reacts with pyrite slowly so that quantitative extraction of sulphur is a barely accomplished event after several tens of hours processing. Further, because silicates are not decomposed by the reducing mixtures, fine-grained inclusions of sulphur-bearing material therein may have no chance to react with the solution.

Tin (II)–strong phosphoric acid (Kiba reagent) was first described by Kiba *et al.* (1955) as a powerful reducing agent capable of taking sulphate to hydrogen sulphide. Sasaki *et al.* (1979) described the use of this reagent in sulphur isotope studies. They found that Kiba reagent converts both sulphate and pyrite to hydrogen sulphide but some other minerals including copper sulphides, arsenopyrite, and molybdenite do not react completely. Therefore caution must be used when determining whole rock sulphur.

More recently Ueda and Sakai (1983) discussed the use of Kiba reagent in the extraction from rock samples of sulphate sulphur as sulphur dioxide and of sulphide sulphur as hydrogen sulphide. These gases may be separated by vacuum distillation for volumetric determinations of sulphate and sulphide concentrations and subsequent isotopic analysis.

3.1.2.5 *Sulphur in petroleum, coal, and sulphur ores*

Sulphur in petroleum is extracted by Parr bomb oxidation to sulphate followed by precipitation of barium sulphate.

Coal contains sulphur in various chemical forms and oxidation states—including pyrite, other metallic sulphides, sulphates, and organic sulphur. In some cases it may be sufficient to measure the total sulphur concentration and its isotopic composition whereas in other cases it may be desirable to determine the isotopic compositions of different extracts.

For total sulphur determinations either the Eschka (ASTM, 1971) or Parr bomb method may be used. Hicks *et al*. (1974) have recommended the Parr bomb method as being faster than the Eschka method, but personal experience in this laboratory suggests that the Parr bomb method is subject to variable yields.

Various schemes exist for the sequential extraction of different forms of sulphur for isotopic analysis. A recent article by Westgate and Anderson (1982) refers to previous work and gives details of an extraction scheme which includes:

(a) Massive pyrite removal
(b) Extraction of acid-soluble sulphides
(c) Extraction of sulphate sulphur
(d) Extraction of different disseminated pyrite
(e) Extraction of organic sulphur

Thus the extraction of sulphur from coal is similar to the extraction of sulphur from other sediment samples in terms of the need to make effective separations of different forms of sulphur which may differ drastically in their isotopic compositions.

Two recent developments deserve mention. Krouse *et al*. (1987) described experiments involving the release of H_2S from fossil fuels during linearly temperature programmed pyrolysis. This technique may have application as an analytical technique for sulphur compounds and as a means of understanding the organic geochemistry of sulphur in fossil fuels.

Kelly *et al.* (1982) described the extraction of total sulphur from coal for sulphur concentration determination by isotope dilution mass spectometry. This technique is likely to become the method against which other techniques will be tested.

Sulphur ores can be treated with hydrochloric acid if they are acid-soluble forms or oxidized to sulphate using HNO_3–Br_2, as in the case of pyrite.

3.1.3 The preparation of sulphur samples for mass spectrometry

3.1.3.1 *Introduction*

The isotopic analysis of sulphur requires the production of a suitable gaseous compound of the element which can be introduced into the source region of a gas source mass spectrometer. The normal gas used for sulphur isotope analysis is sulphur dioxide and there are three distinct methods used for its production:

(a) The high-temperature combustion of sulphide sulphur in a stream of oxygen or oxygen plus nitrogen
(b) The high-temperature oxidation of sulphide sulphur using a solid oxygen donor such as vanadium pentoxide (V_2O_5) or copper oxide (CuO or Cu_2O)
(c) The direct, high-temperature, conversion of sulphate sulphur to sulphur dioxide

The first of those methods is now largely of historical interest and is not widely used. However, a brief description of the method is given below because it serves as a convenient introduction to the advantages of the latter two methods.

A small number of laboratories use or have used the gas sulphur hexafluoride (SF_6) for sulphur isotope analysis. The preparation of sulphur hexafluoride is less convenient than the preparation of sulphur dioxide but the sulphur hexafluoride method has some advantages over the sulphur dioxide method when very high accuracy and precision are required. Since fluorine has only one stable isotope, the sulphur hexafluoride is also to be recommended when measurements of the rare isotopes ^{33}S and ^{36}S are to be made.

3.1.3.2 *Combustion of sulphides in oxygen*

Descriptions of this method have been given by Thode *et al.* (1949), Rafter (1957), and Thode *et al.* (1961). The last cited authors, for example, used silver sulphide samples which were placed in quartz boats and burned in a stream of oxygen inside a fused quartz tube at a temperature of 1350 °C, the temperature of the tube being maintained by an electric furnace. The oxygen used was purified by passage through ascarite (NaOH), anhydrone ($MgClO_4$), and concentrated sulphuric acid. Hydrocarbons were elimimated by passing the oxygen through a zircon tube at 1350 °C. After the removal of excess oxygen, together with water and carbon dioxide, the sulphur dioxide samples were collected in pyrex breakseal tubes which were sealed off and stored for mass spectrometric analysis.

It is necessary to use high temperatures of combustion with this method in order to minimize the production of sulphur trioxide (SO_3). This compound is produced according to the reaction

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3$$

At low temperatures the production of SO_3 is favoured. With increasing temperature the ratio of SO_2 to SO_3 increases (see, for example, Robinson and Kusakabe, 1975). Isotope exchange between SO_2 and SO_3 leads to the enrichment of ^{32}S in SO_2; i.e. for the isotope exchange reaction

$$^{34}SO_2 + {}^{32}SO_3 \rightleftharpoons {}^{32}SO_2 + {}^{34}SO_3$$

the isotope equilibrium constant is greater than unity (Tudge and Thode, 1950). Sakai and Yamamoto (1966) have calculated values for this equilibrium constant of 1.0046 and 1.0035 at temperatures of 1000 and 1200 °C respectively, so that both the yield of SO_3 and the isotope fractionation between SO_2 and SO_3 decrease with increasing temperature.

The influence of SO_3 production on measured $\delta^{34}S$ values is easy to calculate. If combustion at 1200 °C produces 95% SO_2 and 5% SO_3 which equilibrate isotopically then by the isotopic mass balance

$$0.95\,\delta^{34}S(SO_2) + 0.05\,\delta^{34}S(SO_3) = \delta^{34}S\text{ (original sulphur)}$$

and

$$\delta^{34}S(SO_3) - \delta^{34}S(SO_2) = 3.5‰$$

so that

$$\delta^{34}S(SO_2) = \delta^{34}S\text{ (original sulphur)} - 0.175‰$$

This shift in the isotopic composition of SO_2 relative to the starting material will not introduce serious difficulties so long as all samples and standards are combusted identically, with constant yields of SO_3. Thode *et al.* (1961) minimized this isotopic shift by combusting at the highest practical temperature (1350 °C). Sakai and Yamamoto (1966), on the other hand, showed that combustion at lower temperatures, with a reduced partial pressure of oxygen, could achieve the same end.

In their experiments, Sakai and Yamamoto (1966) combusted silver sulphide samples in streams of oxygen that contained different proportions of nitrogen. They showed that the production of SO_3 was reduced when the partial pressure of oxygen was reduced. The optimum operating conditions determined involved a 15:1 nitrogen to oxygen ratio at a combustion temperature of 1200 °C. Under these conditions 98% yields of SO_2 were obtained and it was found that the lifetime of the combustion tube was considerably extended compared to the lifetime for combustions with pure oxygen.

3.1.3.3 *Oxidation of sulphides using a solid oxygen donor*

Vinogradov *et al.* (1956) produced sulphur dioxide for mass spectrometric analysis by reacting pyrite with lead oxide (PbO) at 850–900 °C under vacuum. Subsequently Gavelin *et al.* (1960) reported the use of vanadium pentoxide (V_2O_5) as an oxidant. The V_2O_5 method was refined by Ricke (1964) and is still in use in a number of laboratories.

Grinenko (1962) first reported the use of cupric oxide (CuO) for oxidation of sulphides, as did Kaplan *et al.* (1970). Monster (1973) performed oxidations with both CuO and Cu_2O and recommended the use of CuO because he was able to obtain better yields at lower temperatures than with Cu_2O and because CuO is stable with respect to storage in atmospheric oxygen whereas Cu_2O is not. Fritz *et al.* (1974) also performed experiments with both oxidants and also concluded that CuO was to be preferred to Cu_2O. They noted that commercially available Cu_2O can contain up to 0.3% oil, which is used as a preservative against oxidation by atmospheric oxygen. Unless removed, this oil of course gives rise to the coproduction of carbon dioxide and water along with the sulphur dioxide.

Robinson and Kusakabe (1975) showed that pure Cu_2O could be made from reagent grade CuO by heating it at 800 °C in the furnace tube of a vacuum line maintained at 10^{-4} bar. They advised against the preparation of large quantities of Cu_2O at one time because of the possibility of it oxidizing or absorbing gases with time. They also presented cogent reasons for the use of Cu_2O as oxidant rather than CuO, pointing out that when excess CuO is used for burning at high temperatures the P_{O_2} conditions may favour the production of SO_3 or metal sulphates. According to them, burnings with Cu_2O favour low P_{O_2} conditions and SO_3 production can be ignored.

The method employed by Robinson and Kusakabe (1975) is as follows. Sulphide samples are intimately mixed with an excess (twice the stoichiometric amount) of Cu_2O and ground to a grain size of about 150 μm in a small agate mortar. The sample plus Cu_2O in a small ceramic boat that has been preheated to remove sulphur contamination, is placed inside a quartz tube, which is sealed at one end, together with a magnetic pusher, and the quartz tube is connected to a vacuum line and evacuated. Following evacuation and the attainment of a temperature of 800 °C in a small furnace surrounding the quartz tube the sample boat is pushed into the heated region. The chosen temperature of 800 °C is low enough to enhance the life of the furnace windings and high enough to obtain 99–100% of the theoretical yield of SO_2 from silver sulphide (Ag_2S) within 10 minutes. Gas yields are measured using a Wallace and Tiernan absolute pressure gauge with an accuracy of ± 0.4%.

Robinson and Kusakabe (1975) noted, as did Fritz *et al.* (1974), that difficulties are experienced burning minerals such as ZnS, PbS, etc., so that they are converted to Ag_2S. This procedure also removes silicates and other impurities from the minerals. Pyrite may be combusted directly but requires 15 minutes at 1000 °C.

3.1.3.4 *Direct conversion of barium sulphate to sulphur dioxide*

Holt and Engelkemeir (1970) reported a method for the direct conversion of barium sulphate ($BaSO_4$) to SO_2 according to the net reaction

$$BaSO_4 \rightarrow BaO + SO_2 + \tfrac{1}{2}O_2$$

According to their method the $BaSO_4$, covered with pulverized quartz powder in a fused quartz tube, was heated to the softening point of quartz (about 1400 °C), the SO_2 produced being collected in a cold trap and the oxygen pumped away.

This method offers the advantage that oxidized forms of sulphur need not be processed chemically to silver sulphide before preparation of sulphur dioxide for mass spectrometry.

Bailey and Smith (1972) suggested a modified technique in which the vacuum system included an auxiliary furnace containing copper turnings heated to 800 °C. They argued that the method of Holt and Engelkemeir gave rise to the production of SO_3, because of the liberation of oxygen, with consequent displacement of the $\delta^{34}S$ of the sulphur dioxide from that of the original sample. The purpose of the copper heated to 800 °C was to reduce the partial pressure of oxygen in the system and to facilitate the conversion of any SO_3 to SO_2.

The temperature at which $BaSO_4$ is converted to SO_2 was reduced significantly in the method reported by Haur *et al.* (1973) by the addition to the reaction mixture of vanadium pentoxide (V_2O_5). These workers used a mixture of $BaSO_4$, V_2O_5 and SiO_2 in the proportions by weight 1:3:2 and a reaction temperature of 1000–1050 °C. Copper was used to bind free oxygen formed in the reaction by including copper wire in the reaction tube.

Coleman and Moore (1978) used cuprous oxide (Cu_2O) rather than V_2O_5 and employed reaction mixtures of 15 mg $BaSO_4$ ground with 200 mg Cu_2O and 600 mg SiO_2 with a reaction temperature of 1120 °C. A separate furnace containing copper at 800 °C was used for oxygen suppression and the elimination of SO_3.

Halas and Wolacewicz (1981) and Halas *et al.* (1982) have described the use of sodium metaphosphate ($NaPO_3$) at 1000 °C to produce SO_3 by the reaction

$$BaSO_4 + NaPO_3 \rightarrow NaBaPO_4 + SO_3$$

The SO_3 is converted to SO_2 on copper in a cooler part of the reaction chamber.

The V_2O_5 method introduced by Haur *et al.* (1973) has been refined by Yanagisawa and Sakai (1983). These authors recommend the use of mixtures of $BaSo_4$, V_2O_5 and SiO_2 in the proportions 1:10:10 with a reaction temperature of 900 °C. As in other methods the partial pressure of oxygen is minimized by the use of copper wire placed a few centimetres above the mixture to assure negligible formation of SO_3. The high ratio of V_2O_5 + SiO_2 to $BaSO_4$ ensures that the oxygen isotopic composition of the SO_2 is completely controlled by these components and is independent of the original oxygen isotopic composition of the $BaSO_4$. Ueda and Krouse (1987) have extended this technique to other sulphates and sulphide minerals.

3.1.3.5 *The purification and storage of sulphur dioxide*

The preparation methods mentioned in Sections 3.1.3.2 and 3.1.3.4 above usually give rise to sulphur dioxide which is contaminated to a greater or lesser extent with water and carbon dioxide. The vacuum lines used for sample preparation must therefore include provision for the elimination of these contaminants before storage of sulphur dioxide prior to mass spectrometry.

The normal purification procedure is to trap the $H_2O + SO_2 + CO_2$ mixture in a U-trap, using liquid nitrogen, and then to raise the temperature of the U-trap to −80 °C by replacing the liquid nitrogen with a dry ice–acetone slush so that H_2O is retained while SO_2 and CO_2 are vacuum transferred to a further trap at liquid nitrogen temperature. The temperature of this trap is then raised to −131 °C, the temperature of freezing n-pentane (Oano and Ishikawa, 1966), so that CO_2 is pumped away to waste while SO_2 is retained. The arrangement of traps employed by Coleman and Moore (1978) appears to be particularly convenient. Finally, the temperature of the trap containing the SO_2 is raised further so that the SO_2 can be transferred to a storage vessel.

Rather than using liquids with characteristic temperatures (dry ice–acetone, freezing n-pentane) to control temperatures it may be more convenient to use a true variable temperature cold trap. Hayes *et al.* (1978) have described a trap of this type for the purification of carbon dioxide samples for mass spectrometric analysis, where the trap is cooled by liquid nitrogen but can also be heated electrically via windings around the body of the U. With this arrangement, any desired temperature or series of temperatures can be obtained by adjustment of the current to the heater windings.

It is uncommon for sulphur dioxide samples to be taken directly from the preparation line to the inlet system of the mass spectrometer—normally the samples are stored for hours, days, or weeks prior to analysis. The simplest storage device is a pyrex tube which is fused at one end and has a stopcock at the other, together with a suitable fitting for attachment to the preparation line or mass spectrometer. The stopcocks can either be of the type that use vacuum grease or of the newer type with teflon barrels and elastomer O-ring seals. If long-term storage is required, there is the risk of leakage and the possible need for repurification of samples. In such cases it is more desirable to store samples in sealed vessels.

Conventional breakseal tubes offer secure long-term storage but are difficult to make or expensive to purchase. The tube cracker device described by Desmarais and Hayes (1976) permits samples to be stored in simple lengths of 6 mm o.d. pyrex or quartz tubing fused at both ends, until required for mass spectrometry, when the tube is cracked under vacuum and the sample transferred to the spectrometer.

3.1.3.6 *The preparation of sulphur hexafluoride*

The use of sulphur hexafluoride (SF_6) as a gas for sulphur isotope analyses was pioneered at the Carnegie Institution of Washington. Puchelt *et al.* (1971) have described the use of bromine trifluoride (BrF_3) as a fluorinating agent. Hulston and Thode (1965), on the other hand, used elemental fluorine for this purpose, while Thode and Rees (1971) used bromine pentafluoride (BrF_5) and Leskovsek *et al.* (1974) again used elemental fluorine.

The SF_6 method has now been used routinely at McMaster since 1970 with samples requiring measurement of ^{33}S and ^{36}S or very high precision with ^{34}S and for samples that are too small for analysis as SO_2 (see, for example, Rees *et al.*, 1978; Thode and Rees, 1979; McEwing *et al.*, 1980, and references therein). Silver sulphide samples are reacted with a 20× molar excess of BrF_5 for 16 h at 300 °C in nickel reaction tubes. The SF_6 produced is separated from unreacted BrF_5 and other reaction products by a series of vacuum distillations from traps cooled with dry ice–acetone baths to traps cooled with liquid nitrogen. Final SF_6 clean-up is effected gas chromatographically using a coiled 6−ft column of $\frac{1}{4}$ in o.d. copper tubing packed with a 5−Å molecular sieve. Care must be taken at this stage because experience in this laboratory as well as the results of Moiseyev and Platzner (1976) indicate that isotope fractionation can occur in the gas chromatography unless complete recovery of the SF_6 is effected.

3.1.4 The mass spectrometric analysis of sulphur

The isotopic analysis of sulphur is almost invariably performed by gas source mass spectrometry, usually with sulphur dioxide and less commonly with sulphur hexafluoride as the analysis gas. The advent of quadrupole mass spectrometers with sample introduction from solution and ionization in an inductively coupled plasma may be important in the future. Similarly, some work is in progress, at the National Bureau of Standards of the United States, on the solid source mass spectrometry of very small samples of sulphur (Paulsen and Kelley, 1984). These latter two types of analysis are not considered in this article.

The sulphur-containing gas is analysed in a conventional sector-type mass spectrometer equipped with two or more Faraday cups for ion detection. The sample of interest and a standard reference gas are admitted alternately so that isotopic differences can be determined under constant conditions and with consequent elimination of many instrumental biases (Nier, 1947; Nier *et al.*, 1947; McKinney *et al.*., 1950; Wanless and Thode, 1953). It is increasingly common for isotopic analyses to be performed with commercially available mass spectrometers. Because of this, the technical details of mass spectrometer design and construction will not be considered here. Even with commercially supplied instruments it is necessary to consider the corrections to raw data that are required because of background peaks in the mass spectrum, peak tailing, and inlet leak offsets (Craig, 1957; Deines, 1970; Mook and Grootes, 1973; Beckinsale *et al.*, 1973).

In the case of the mass spectrometric analysis of sulphur dioxide it is further necessary to take into account the interference in the SO^+ or $SO_2{}^+$ mass spectrum by ions containing ^{17}O and ^{18}O. Thode *et al.* (1949), Hulston and Shilton (1958), Ault and Kulp (1959), Hulston (1962), Holt and Engelkemeir (1970), Rees (1978), and Nord and Billstrom (1982) have developed corrections to be applied to raw mass spectrometric data which take into account this oxygen isotopic interference.

Rees (1978) has also pointed out that sulphur dioxide, unlike other gases such as nitrogen or carbon dioxide, gives rise to a mass spectrometer memory effect caused by the slow flushing of unknown samples and the standard reference gas from the inlet line of the mass spectrometer. This memory effect causes isotopic differences between samples to be underestimated.

There are not isotopic interferences to be considered in the case of the mass spectrometric analysis of SF_6 because fluorine has only one stable isotope. Rees (1978) has presented details of the conversion of raw mass spectrometric data to $\delta^{34}S$ values for this type of analysis.

3.2 OXYGEN ISOTOPES*

3.2.1 Introduction

Oxygen isotopic analyses of environmental materials of the atmosphere, hydrosphere, lithosphere, and biosphere are carried out by the following steps: (a) collection of samples, (b) conversion of the oxygen in each sample to either CO_2 or O_2, and (c) mass spectrometric analysis of the CO_2 or O_2.

3.2.2 Sample collection

The technique of collecting samples of sulphates and SO_2 in the atmosphere (Forrest and Newman, 1973) and sulphates in the hydrosphere, lithosphere, and biosphere for oxygen−18 analysis are generally identical to those for sulphur−34 analysis. These techniques are described or referenced in Section 3.1.2.

Samples of sulphates in precipitation water (rain or snow), surface water (streams, lakes, and oceans), or ground water (springs and wells) must be protected from bacterial alteration, either by refrigeration or by the addition of a bacteriocide (e.g. CuCl), if the samples are to be stored for more than a day or two before isotopic analysis. Environmental water samples that are to be analysed for $\delta^{18}O$ of the H_2O must also be protected from alteration by evaporation of diffusion through container walls, prior to analysis.

Water vapour in the atmosphere is sampled by conducting a stream of air through a dry-ice cold trap for quantitative removal. The condensate is allowed to melt and the liquid water (5–10 ml) is sealed without delay in a small glass bottle or vial to avoid evaporation before analysis (Holt *et al.*, 1978).

3.2.3 Sample preparation

3.2.3.1 *Introduction*

Complete isotopic studies of mechanisms of sulphate formation may require the isotopic analysis not only of the sulphate but also of each of the reactants

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* B.D. Holt.

from which it was formed. For example, for the net reaction of catalysed aqueous air oxidation of SO_2,

$$SO_2 + \tfrac{1}{2}\, O_2 + H_2O \rightarrow H_2SO_4 \qquad (1)$$

the isotopic study may be based on the $\delta^{18}O$ values of the SO_2, O_2, H_2O, and SO_4^{2-}. To obtain the respective $\delta^{18}O$ values, each of these species is quantitatively converted to either CO_2 or O_2 for mass spectrometric analysis. The $^{12}C^{16}O^{18}O/^{12}C^{16}O^{16}O$ ratio, or the $^{16}O^{18}O/^{16}O^{16}O$ ratio, of the sample is then compared to the corresponding ratio of a standard to obtain the $\delta^{18}O$ values.

Conversion of oxygen-bearing compounds to O_2 is achieved by complete fluorination of each compound (Clayton and Meyeda, 1963). Conversion of many oxygen-bearing compounds to CO_2 can be achieved by reaction with hot carbon. Each of the compounds in equation (1) can be converted to CO_2 by reaction with hot graphite. Holt (1977) has described techniques by which a single graphite reduction furnace is used for this purpose.

3.2.3.2 *Sulphate*

Using standard analytical procedures, a sulphate sample is quantitatively converted to pure $BaSO_4$ by the addition of $BaCl_2$ to a hot aqueous solution of the sulphate acidified by HCl. After a few hours of aging to enhance crystallite growth, the $BaSO_4$ is separated from the supernatant liquid, washed with deionized distilled water until free of chlorides, intimately mixed with pure graphite powder, and heated to convert the oxygen in the sulphate to a mixture of CO and CO_2 by the reaction

$$(x + 2y)\, BaSO_4 + 4(x + y)\, C \rightarrow (x + 2y)\, BaS + 4x\, CO + 4y\, CO_2 \qquad (2)$$

where $x = o$ and $y = 0$ correspond to the two extremes of 100% CO_2 and 100% CO production respectively.

The carbon reduction of $BaSO_4$ can be carried out, with conventional furnaces (Rafter, 1967), electrical resistance heating of the sample holder (Mizutani, 1971; Sakai and Krouse, 1971), and radio-frequency induction heating (Clayton and Epstein, 1958; Longinelli and Craig, 1967; Lloyd, 1968; Holt, 1977). Figure 3.1 shows the resistance heating reactor used by Shakur (1982). Most of the reactor was constructed of stainless steel. The base of the reactor has eight vertical electrical leads, each of which is connected to a stainless steel rectangular block. Four platinum boats, containing the $BaSO_4$–graphite mixture, are clamped between pairs of block holders which are appropriately wired to heat the platinum by high-current, low-voltage power.

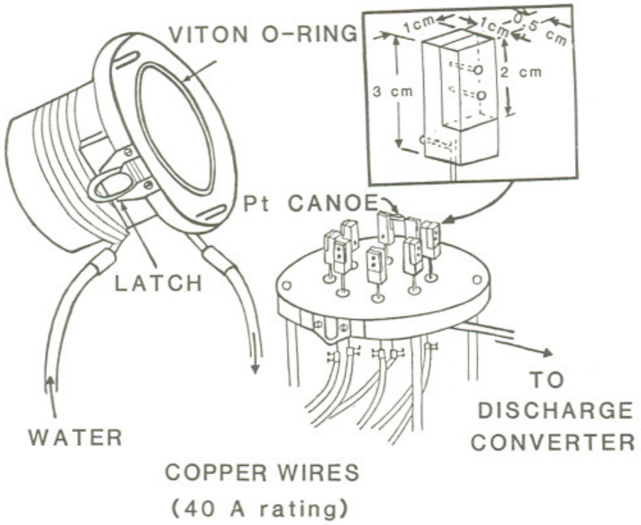

Figure 3.1 Electrical resistance reactor for the conversion of $BaSO_4$ to CO_2 for $\delta^{18}O$ measurements (Shakur, 1982)

Figure 3.2 shows the graphite crucible assembly used by Holt (1977). By this procedure, a slurry of the $BaSO_4$ and graphite powder is filtered directly from the precipitation beaker into a porous graphite capsule. After washing and drying, the capsule containing the mixture of $BaSO_4$ and graphite powder is placed in the graphite crucible. The crucible is mounted in a water-cooled transparent quartz chamber and heated by a surrounding induction-heating coil.

By either system of heating, the $BaSO_4$–graphite mixture is first vacuum heated at ~600 °C for a few minutes to expel moisture and organic contaminants; then the temperature is raised to 1000–1150 °C. The CO_2 and CO are expelled into a vacuum line where the CO_2 is collected in a liquid-nitrogen cold trap and the CO is subjected to a high-voltage (~1 kV) electrical discharge between two platinum electrodes. The discharge causes the CO to disproportionate into carbon and CO_2. The newly formed CO_2 is continuously removed from the gas phase by condensation in the liquid-nitrogen cold trap. At the end of the heating period (~15–20 min), essentially all of the sample oxygen is collected in the cold trap as CO_2; BaS remains in the sample holder (platinum boat or graphite capsule, depending on the method used). The CO_2 is cryogenically transferred through a cold trap (temperature of melting pentane ~−132 °C) to a gas sample bulb (cooled to −196 °C) for subsequent transfer to a mass spectrometer.

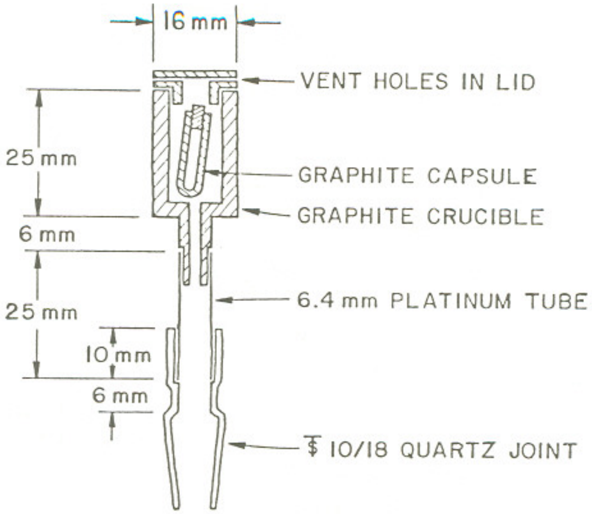

Figure 3.2 Radio-frequency heated graphite crucible for the conversion of $BaSO_4$ to CO_2 (Holt, 1977)

3.2.3.3 *Water*

By an older method for the determination of the $\delta^{18}O$ of water, a measured quantity of the water is equilibrated with a measured quantity of CO_2 known isotopic composition (Epstein and Mayeda, 1953). The equilibration is usually carried out by frequent agitation of the water and CO_2 for about three days at a constant temperature; with continuous agitation, the equilibration time can be reduced to less than one day. If the quantity of H_2O is much greater than that of the CO_2, then comparison of the isotopic compositions of the equilibrated CO_2 is equivalent to comparing the H_2O samples. If the H_2O sample is very small, the isotope separation factor for the equilibration temperature and a comparison of the $^{18}O/^{16}O$ ratios in the CO_2 before and after the equilibration are necessary to calculate the $\delta^{18}O$ of the water.

Majzoub (1966) developed a method for converting all of the oxygen in microquantities ($\sim 4\ \mu L$) of water to CO_2 for mass spectrometric analysis. The method was modified by Holt (1977) for adaptation to the same graphite-reduction apparatus that was used for $BaSO_4$ samples. The procedure consists of hot-graphite reduction of the water to CO and H_2, separation of the H_2 from the CO by diffusion through a palladium membrane, and conversion of the CO to CO_2 and carbon as described above. The advantages of the carbon-reduction method are that only very small samples are required and that the long equilibration period is avoided.

Similar advantages can be realized by reaction of H_2O with guanadine (Boyer *et al.*, 1961).

3.2.3.4 *SO_2 and O_2*

Holt (1977) used a Toepler pump to circulate samples (~2 mL, STP) of either O_2 or SO_2 through a closed loop for exposure to the inductively heated (~1200 °C) graphite crucible. The sample gas was quantitatively converted to CO and subsequently to CO_2 as described above. The procedure for SO_2 or O_2 is not applicable to oxygen in air because the N_2 in air combines with the O_2 to form nitrogen oxides in the high-voltage discharge. Instead, the graphite crucible (Figure 3.2) is covered with platinum gauze (catalyst) and heated to not more than ~600 °C (Horibe *et al.*, 1973). Under these conditions, the air oxygen is converted directly to CO_2, with negligible formation of CO.

3.2.4 The mass spectrometric analysis of oxygen

The CO_2 (or O_2, if the sample is fluorinated) which is obtained from the carbon reduction of $BaSO_4$, H_2O, SO_2, or O_2 is analysed with a high-precision, double-beam, isotope-ratio, gas mass spectrometer as described in Section 3.1.4.

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