SULPHUR ISOTOPES IN METEORITES

VARIATIONS IN THE RATIOS
OF THE
FOUR STABLE SULPHUR ISOTOPES IN METEORITES
AND
THEIR RELATION TO CHEMICAL AND NUCLEAR EFFECTS

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TITLE: Variations in the Ratios of the Four Stable Sulphur Isotopes in Meteorites and their Relation to Chemical and Nuclear Effects

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SCOPE AND CONTENTS: The isotopic ratios S^{33}/S^{32}, S^{34}/S^{32} and S^{36}/S^{32} of different forms of sulphur in a number of meteorites have been studied. The results obtained indicate that processes of chemical fractionation have occurred in some meteorites but that the isotopic composition of the total sulphur in a single meteorite is remarkably constant from meteorite to meteorite. The relationships between the S^{33}, S^{34} and S^{36} isotope abundances indicate that variations in these abundances due to inhomogeneities in the processes of nucleosynthesis are not detectable.

Isotopic analysis of sulphur from the iron phase of the Clark County, Pinon and Tlacotepic meteorites has shown the presence of cosmic ray induced spallation S^{36} and S^{33}. These spallation results are in reasonable agreement with predictions based on production rates of other nuclei.

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I am indebted to Dr. I.R. Kaplan who extracted sulphate, sulphide and elemental sulphur from a number of meteorites and provided samples in the form of Ag_2S. Dr. C.B. Moore, Director of the Nininger Meteorite Collection provided the iron meteorite samples used in the search for spallation sulphur.

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I INTRODUCTION

Man has long been interested in falls of bodies called meteorites from the sky, and scientific work in the field of meteorites has been recorded since J.B. Biot in 1803 convinced the scientific world of the genuineness of these falls from the sky. Since the advent of mass spectrometry and low background counting techniques our knowledge of the isotopic composition of meteorites has increased enormously, and so has our knowledge of their origin and properties. As meteorites come to us from outside the earth's atmosphere they offer the scientist the best source of material from our solar system. It is generally believed that the average composition of meteoritic matter probably provides the best information of the relative abundances of the non-volatile elements. This information is of fundamental importance not only to the geochemist but also to the nuclear physicists and the astrophysicists who are concerned with processes of element formation.

The first reported study of S^{34}/S^{32} ratios of meteorites was that of Trofimov (1949) who found a maximum spread of 6‰ for the four meteorites examined. This was quickly followed by the more accurate work of MacNamara and Thode (1950) who reported that in contrast to most other sources of sulphur, the isotope ratio S^{34}/S^{32} in meteorites was constant within $1.5^{o}/_{oo}$. This work was confirmed by Vinogradov in 1958, who although he assigned a different S^{34}/S^{32} ratio to his standard, found the S^{34}/S^{32} ratio in meteorites to be constant within his experimental error. Thode, Monster and Dunford (1961) further reduced this variation to $0.4^{o}/_{oo}$. Since that date however, Monster, Anders and Thode (1962) have found that different forms of sulphur namely S^{o}, $S^{=}$ and $SO_4^{=}$ present in the Orgueil meteorite show sulphur isotope variations of several per mil ($^{o}/_{oo}$), but that a weighted average of these results comes very close to that of other meteorites.

The differences found for the Orgueil meteorite between the S^{34} content of the various forms of sulphur in the meteorite should be of interest in the explanation of the chemical evolution of meteorites. Before briefly reviewing current theories of the chemical evolution of meteorites it is however as well to heed the following comments of Urey (1964) ... "the meteorites have such complicated physical structures and such puzzling chemical compositions that no theories for their origin account for all details. In fact attempts to explain certain details always seem to lead to such specialized hypotheses that no one except the author accepts the explanations as reasonable."

Most workers agree that the meteorite parent body (or bodies) is formed by accretion from a cold dust cloud of solar composition. After the accretion stage it is assumed that the parent body (or bodies) possessed a composition similar to that of carbonaceous chondrites but perhaps containing a higher concentration of volatiles. From here on the theories diverge somewhat. Urey (1964) considers that these bodies were moon sized and accumulated inside large gas spheres and that high temperatures were produced at the surface of these objects as the gas mass contracted. First the iron sulphide melted and sank in pools below the surface carrying the chalcophile elements with it. It is assumed that this iron sulphide was lost to space with excess silicates or is still buried below the surface of primary objects such as Ceres or the moon. At higher temperatures silicates melted, and oxidized iron was reduced by hydrogen and carbon or methane or other carbonaceous material and sank below the surface carrying with it the siderophile elements. After much of the hydrogen had been lost and the body had cooled considerably hydrogen sulphide could react with iron oxide in the silicates to produce iron sulphide that was relatively free of the chalcophile elements and could thus supply the troilites of the meteorites. It is then supposed that most of these primary objects were broken up by collisions.

Ringwood (1961) used a planetary model in which the planet was subjected to internal heating which caused melting to occur in the deep interior. Convection set in and the molten chondritic material containing water and carbon under confining pressure rose to the surface of the planet where the pressure was released and the volatiles rapidly escaped. Under these conditions the surface of the planet was subject to volcanism on a grand scale. These conditions lead to the formation of chondritic material in certain regions of the planet while in the deep interior oxidized iron and nickel were reduced to the metallic phase. Subsequently after cooling to below 500°C the planet disrupted into fragments which have since been colliding with themselves.

Fish, Goles and Anders (1960) consider the breakup of a large single planet unlikely and postulated that the parent bodies were asteroid size (planetesimals) which were heated to melting temperatures by some transient internal energy source such as extinct radioactivity. In this way a stratification into an inner core of metal, an outer layer of molten silicates, a sintered mantle and an unconsolidated surface layer could result. Further rise in temperature would result in quasi-volcanic eruptions with the evolution of gases and vapours (e.g. S, CO, SiS). In addition certain cycling processes occur in the interior.

Although current ideas are obviously in a state of flux, it will be seen that there are some similarities between the hypotheses described above which may be helpful in discussing the differences in S^{34} in the different forms of sulphur in meteorites such as Orgueil.

By measurement of the three isotopic ratios S^{33}/S^{32}, S^{34}/S^{32}, S^{36}/S^{32} the present work aimed to be able to distinguish three separate processes which would produce variations of these ratios in meteorites. These are:-

(a) Isotopic fractionation in meteorites or meteorite parent bodies due to chemical or physical processes.

(b) Variations associated with the nucleosynthesis of the elements.

(c) Cosmic ray induced spallation.

(a) ISOTOPIC FRACTIONATION - According to the theory of equilibrium and kinetic isotope effects (Bigeleisen and Wolfsberg, 1958) an approximately linear relationship should exist between the isotope fractionation and the mass difference of the isotopes being studied. The isotope fractionation is usually expressed in terms of the δ-value which by convention is defined by the equation

$$\delta S^{x} = \left[\frac{(S^{x}/S^{32})\ \text{sample}}{(S^{x}/S^{32})\ \text{standard}} - 1\right] \times 1000\ (^{0}/_{00})$$

All δ-value measurements listed in this work use the troilite phase of the Canyon Diablo meteorite as the primary standard. The equilibrium constant K for the isotope exchange reaction

$$H_2S^{x} + S^{32}O_2 \rightleftharpoons H_2S^{32} + S^{x}O_2$$

is given by

$$K = \frac{Q'(S^{x}O_2)/Q'(S^{32}O_2)}{Q'(H_2S^{x})/Q'(H_2S^{32})}$$

where $Q' = \sum_i \exp(-e_i/kT)$ is the partition function of the molecule involved. Since previous calculations of equilibrium isotope effects (Tudge and Thode, 1950) have dealt virtually exclusively with S^{34}/S^{32} fractionation the partition function ratios for S^{33}/S^{32}, S^{34}/S^{32}, and S^{36}/S^{32} of a number of sulphur compounds have been calculated in Appendix A. The results obtained would indicate that the relationships between the δ-values in any equilibrium process are not exactly linear but for small variations the following equations hold

$$\delta S^{36} = 1.90\ \delta S^{34}$$

$$\delta S^{34} = 1.94\ \delta S^{33}$$

(for larger fractionations it is necessary to use the logarithmic form of the δ-value - see Appendix A).

Similar results are to be expected for fractionation resulting from the kinetic isotope effect or from diffusion processes.

(b) NUCLEOSYNTHESIS - Theories of the nucleosynthesis of the elements and the formation of the sun and planets have been discussed by Burbridge, Burbridge, Fowler & Hoyle (1957) and by Cameron (1957, 1962, 1963). These workers have attempted to postulate feasible mechanisms by which the present abundance of the elements can be explained within at least a few orders of magnitude. It would seem most probable that S^{32}, S^{33} and S^{34} have been produced by neutron capture processes on a slow time scale, whereas S^{36} has been produced by neutron capture on a fast time scale in a Type II supernova explosion (Cameron, 1962). At the time the present work was being planned a number of isotopic anomalies in meteorites had been observed (e.g. Murthy, 1960; Reynolds, 1960; Clarke and Thode 1961,) and it was felt worthwhile to make a systematic search in meteorites for possible S^{36} variations due to incomplete mixing of the products of the various processes of nucleosynthesis.

While the study was in progress, Fowler, Greenstein and Hoyle (1962) published their paper postulating that certain light elements (Li, B, Be) were produced by spallation reactions during an intermediate stage in the early history of the solar system. In this intermediate stage they postulated that the planetary material consisted largely of solid planetesimals of the order of 10 metres in diameter but that only the outer one-tenth of these bodies was subject to irradiation. From the spallation and neutron flux data given in their paper it was estimated (see Section 3.3) that S^{36} and S^{33} would have been enriched in this outer one-tenth of the planetesimals by 80‰ and 300‰ respectively. This result would suggest the possibility of both S^{33} and S^{36} anomalies in sulphur from various parts of the solar system.

(c) SPALLATION - The possibility of spallation induced nuclei existing in meteorites was first suggested by Bauer (1947) as an explanation for some of the helium contained in meteorites and this was later confirmed by the presence of He^{3} in meteoritic helium (Paneth et al, 1952) since He^{3} cannot be produced from uranium and thorium disintegrations but only through spallation reactions. Since that time many more spallation products, stable and radioactive nuclides of the lighter elements (up to iron and nickel) have been detected in meteorites. Since the radioactive nuclides range in half life from a few days to millions of years their measurement provides evidence concerning the intensity and distribution of cosmic radiation in space, its possible variation with time, and events in the history of the meteorites - the pre-atmospheric size, the so called cosmic ray ages and the time of their fall. Anders (1962, 1963) has reviewed the method of these age measurements and provides a summary of meteorite ages known up to that date.

It was thought that since S^{36} is the least abundant stable sulphur isotope the chances of detecting spallation product sulphur would be greatest for this isotope. The stable element closest to sulphur in the periodic table for which spallation products had been measured in meteorite samples was the rare gas isotope Ar^{38} measured by Signer and Nier (1962). By using their results together with a spallation theory, see below, it was estimated that it should be possible to detect spallation S^{36} in iron meteorites of the oldest known cosmic ray ages provided that the non-spallation sulphur content in these samples was below one part in twenty thousand. Since Mason (1962) quotes a number of determinations of sulphur in the iron phase of meteorites of this order or less it was felt that provided a 50-100 gram sample could be obtained that the chance of detecting spallation S^{36} was high.

The precise calculation of spallation production in iron meteorites would require a knowledge of the spallation cross section vs energy for each target element present in the meteorite and integration over the total flux distribution at the location of the sample in the particular meteorite.

i.e. $$P(A,Z) = \sum_{A_t, Z_t} \sum_{q} \int S(q,E)\, \sigma\,(A,Z \mid A_t,\, Z_t,\, q,\, E)\; N\,(A_t,\, Z_t)\, dE$$

where $S(q,E)dE$ is the flux density of particle q in the energy interval E to E + dE and $\sigma\,(A,Z|A_t,Z_t,q,E)$ is the cross section for the production of particles of mass number A and atomic number Z from a target nucleus of A_t, Z_t. The only portion of this information of which experimental data is available is the chemical composition $(N(A_t,Z_t))$ and even some uncertainties exist in this due to inhomogeneties from inclusions such as troilite (FeS), lawrencite ($FeCl_2$) etc. The remainder of the data must be predicted from available information.

The spallation process has been reviewed by Miller and Hudis (1959). In general the model employed divides high energy reactions into two phases, an initial interaction phase (the knock-on phase) in which the incident high energy particle strikes the target nucleus and ejects a number of particles by direct interaction leaving a residual excited nucleus (A', Z', excitation energy U', and angular momentum J), followed by the de-excitation of the excited residual nucleus (A', Z') usually through the emission of particles and photons (often called evaporation). We may write this two step picture as follows:

$$\sigma(A,Z|A_t,Z_t,q,E) = \sum_{A'}\sum_{Z'}\sum_{J}\int \sigma'(A',Z',U',J\ |A_t,Z_t,q,E)$$
$$n(A,Z|A',Z',U',J)dU$$

where the σ' term refers to the knock-on phase and the n function refers to the de-excitation phase. The knock-on phase has been calculated by the use of Monte Carlo calculations in which the nucleus is considered as a collection of individual nucleons obeying Fermi Dirac statistics and the motion of the incident and struck nucleons is considered in terms of a succession of two-body collisions. Such calculations have been made by Metropolis et al (1958, 1958a) and others and have given reasonable agreement with experiment.

The evaporation phase can be treated by the compound nucleus model and the evaporation cascade may also be treated by the Monte Carlo method.

Rudstam (1956) has discussed the isobaric yield for the overall process in terms of a gaussian distribution and has fitted experimental data to the semi-emperical relationship.

$$\sigma (A,Z) = \exp (PA-Q-R(Z-SA)^2)$$

The first term of this equation indicates that for a given target the total isobaric yield varies smoothly with product A, while the last term indicates that for a given A, the $\ln\sigma$ v Z curve is of parabolic form. The constants P and Q are functions of energy, but R and S are not. Honda and Lal (1960) found this equation to give agreement within a factor of two and studied the variation of σ with energy. They derived the relationships $P = 10.2E^{-0.63}$ (E in Mev) and

$$\exp(-Q) = \frac{P\sigma_i(R/\pi)^{1/2}}{\exp(PA_t) - \exp(PA_t/2)} \qquad (1.1)$$

(where σ_i is the total inelastic cross section of the target nucleus) for medium weight products and energies above 100 Mev. Combining the above formulae and neglecting the exp $(PA_t/2)$ term we obtain

$$\sigma (A,Z) = P\sigma_i(R/\pi)^{1/2} \exp(P(A-A_t) - P(Z-SA)^2) \qquad (1.2)$$

Metropolis et al (1958) found from Monte Carlo calculations that σ_i is only slightly less than the geometrical cross-section.

This work thus aimed to measure sulphur in a number of different chemical phases of meteorites, extending the work of Monster, Anders and Thode (1962) on the Orgueil meteorite and secondly to search for spallation sulphur isotopes in a few of the meteorites of large cosmic ray age.

II EXPERIMENTAL

SAMPLE PREPARATION

2.1 Chemical Separation and Preparation as Sulphur Dioxide

In the isotopic analysis of sulphur, samples are usually introduced into a mass spectrometer in the form of SO_2. (Thode, MacNamara and Collins, 1949; Hulston and Shilton, 1958; Ault and Kulp, 1959). In particular this gas has been found to be satisfactory for the analyses of S^{34}. Memory effects are minimal and reproducible results may be obtained provided isotope fractionation is avoided in sample preparation. In this regard care must be taken to use the same source of oxygen in all sample preparations and to avoid oxygen isotope fractionation in the handling of the samples. In the case of S^{34} analyses the O^{18} part of the mass 66 peak ($S^{32}\ O^{16}\ O^{18}$) is much smaller than the S^{34} part ($S^{34}\ O^{16}\ O^{16}$) and if the O^{18} content is kept reasonably constant satisfactory S^{34} analyses can be obtained with an accuracy of $\pm\ 0.2^{\circ}/_{oo}$. Although in the case of S^{36} analyses the O^{18} contribution ($S^{34}\ O^{16}\ O^{18}$) to mass 68 is of the same order as the S^{36} contribution ($S^{36}\ O^{16}\ O^{16}$), SO_2 was nevertheless used in the preliminary part of this investigation. The SO_2 is prepared (Thode, Monster and Dunford, 1961) by passing oxygen over a silver sulphide sample in a furnace heated to approximately 1300°C. The sulphur dioxide gas is then purified using a dry ice trap (to remove water) and an ethyl chloride trap (to remove carbon dioxide) before being sealed in a breakseal tube (Cragg 1961).

The most easily obtained samples of meteoritic sulphur came from the troilite (FeS) phase of iron meteorites. These samples are boiled with 2:1 HCl for forty-five minutes in a 200 ml flask provided with a reflux condenser. The H_2S produced is swept out in a stream of nitrogen, washed with distilled water and finally absorbed in a solution containing cadmium acetate, acetic acid and distilled water (Harrison, 1956). Following the practice of Thode, Monster and Dunford (1961) the cadmium sulphide is then converted to Ag_2S by adding 0.1 N $AgNO_3$. After coagulation on heating, the Ag_2S is filtered through glass wool and washed twice with concentrated NH_4OH. The Ag_2S is then dried in an oven at 120°C.

A number of meteorite samples were collected by Dr. Ian Kaplan for the further investigation of their S^{34} content and in particular to determine the S^{34} distribution between the different forms of sulphur. The various forms of sulphur were extracted and prepared in the form of SO_2

gas at the California Institute of Technology, and were sent to us for analysis in a joint venture. The Ag_2S from some of these samples later became available for the present S^{36} and S^{33} study.

2.2 Preparation of Spallation Samples

The extraction of spallation sulphur from the nickel-iron phase of meteorites is more difficult in view of the larger quantity of material which must be dissolved and the low sulphur content of these samples. The procedure used for these meteorite specimens is as follows:- The oxidised outer edges of the meteorites were removed by cutting or grinding procedures and the samples were cut with a hack-saw to suitable sizes for insertion in the 200 ml reaction flasks. After weighing and cleaning in diluted hydrochloric acid the samples are reacted with 100 ml of 1:2 HCl in the same apparatus as described above for troilite samples. To prevent the reaction from becoming too vigorous the 200 ml flask is warmed only. Since the hydrogen produced provided some flushing action for the H_2S, the nitrogen flow is reduced to approximately half that normally used with this apparatus. When the acid appears to be expended the flask is removed, and the majority of the solution decanted off, more 1:2 HCl is added and the reaction continued. When the metal has reacted completely the quantity of cadmium sulphide produced is estimated visually and if the yield appears to be less than one part in ten thousand, a further sample of metal from the same meteorite is reacted. Once a sample of cadmium sulphide considered large enough for analysis is obtained the CdS is converted to Ag_2S by the method described above. This sample is listed as "H_2S fraction" in the table of results (Table 4-1).

Although it was expected that the spallation S^{36} in the lattice structure of the metal would be released as H_2S by the above procedure, it was considered most desirable to analyse the solution remaining for either elemental sulphur or sulphate-sulphur. These samples have been labelled "Res S," (residual sulphur). In two cases 1 mgm of sulphur as calcium sulphate was added as a carrier to assist in the recovery of any $S^{36}O_4^=$ ions in the solution. In certain other samples this "Res S" fraction was separated into "Solids" and "Soln". The residual sulphur samples were treated as follows:-
The solution is decantered off the solid residue which has not reacted with the hydrochloric acid. This material is treated by aqua regia and then evaporated to dryness a number of times with concentrated HCl (approximately 50 mgm of NaCl is added initially to prevent the possible evaporation of S in the form of H_2SO_4). The sulphur present in the decanted solution is oxidized to sulphate-

sulphur by adding 5 ml of bromine to the solution and allowing it to stand overnight. The solution is then transferred to the steam bath and after the bromine has been driven off slowly the solution is evaporated almost to dryness. Distilled water is then added to bring the solution back to the original volume. By this technique it is possible to obtain a suitable pH for the precipitation of $BaSO_4$ without the precipitation of the large quantity of ferric chloride present. Except where specifically stated the oxidized products from the aqua regia treated portion and the bromine treated portion of the residual sulphur is then mixed together. Barium sulphate is precipitated by bringing the solution to a boil, adding 25 ml of boiling 10% $BaCl_2$ solution, boiling for a further thirty minutes and then transferring the beaker to the steam bath overnight. This solution is allowed to cool to room temperature before filtering through No. 42 Watman paper. The filter paper is then ashed and the $BaSO_4$ reduced to H_2S and hence Ag_2S by a boiling mixture of HI, H_3PO_2 and HCl using the standard reduction method described by Thode, Monster and Dunford (1961).

The sulphur content of all samples was estimated by titrating the excess silver nitrate used in the conversion to Ag_2S with 0.1N NH_4CNS using Volhard's indicator. Because the relative accuracy of this method drops considerably for samples containing less than 1 mgm S the sulphur content of these samples was also estimated by weighing the Ag_2S recovered. Because the precipitate is difficult to remove from the bubbling tube and because of the difficulty of removing all traces of glass wool before weighing the accuracy of this method in the less than 1 mgm S range is estimated to be of the order of 20% + 0.1 mgm.

2.3 Contamination Difficulties with the SO_2 Method

The measurement of the S^{36} content of SO_2 gas samples was found to present some difficulties due to contamination at mass 68. Attempts were made to reduce this contamination by distillation procedures and by gas chromatography. The latter procedure appeared to remove the contamination but unfortunately altered the O^{18} content of the sample. The distillation procedures improved the situation but the results were never completely satisfactory. The main source of the contamination appeared to be stopcock grease used on the sample preparation line. However in spite of these difficulties a number of determinations were made with SO_2 samples. It was finally decided to analyse samples as SF_6 in order to eliminate the contamination problems and also to avoid the oxygen isotope problem.

2.4 The Sulphur Hexafluoride Method

Hoering (1962) has reported some success in the use of sulphur hexafluoride (SF_6) prepared by reacting sulphide samples with bromine trifluoride and purifying the gases produced on a gas chromatograph using a column filled with molecular sieve type 5A.

In this work sulphur hexafluoride was prepared by the reaction of silver sulphide samples with fluorine gas. The fluorine line used in the preparation of the samples was essentially that described by Krouse (1960) (see Fig. 2-1). After initially flushing the fluorine sample line with nitrogen the following procedure was followed in the preparation of samples:-

(a) With Hoke valves V5 and V6 closed and trap 1 cooled by liquid oxygen, the silver sulphide sample in a monel boat is introduced at the Hoke Coupling C2. Both couplings C1 and C2 are then tightened and this section of the apparatus evacuated slowly through V6.

(b) After checking the vacuum with a tesla the line between V5 and V8 is warmed to approximately 100°C to remove moisture. Evacuation is continued for a further period of ten minutes while the line cools.

(c) The stopcock on the sample bottle and the valve V7 are then closed and the line filled with nitrogen

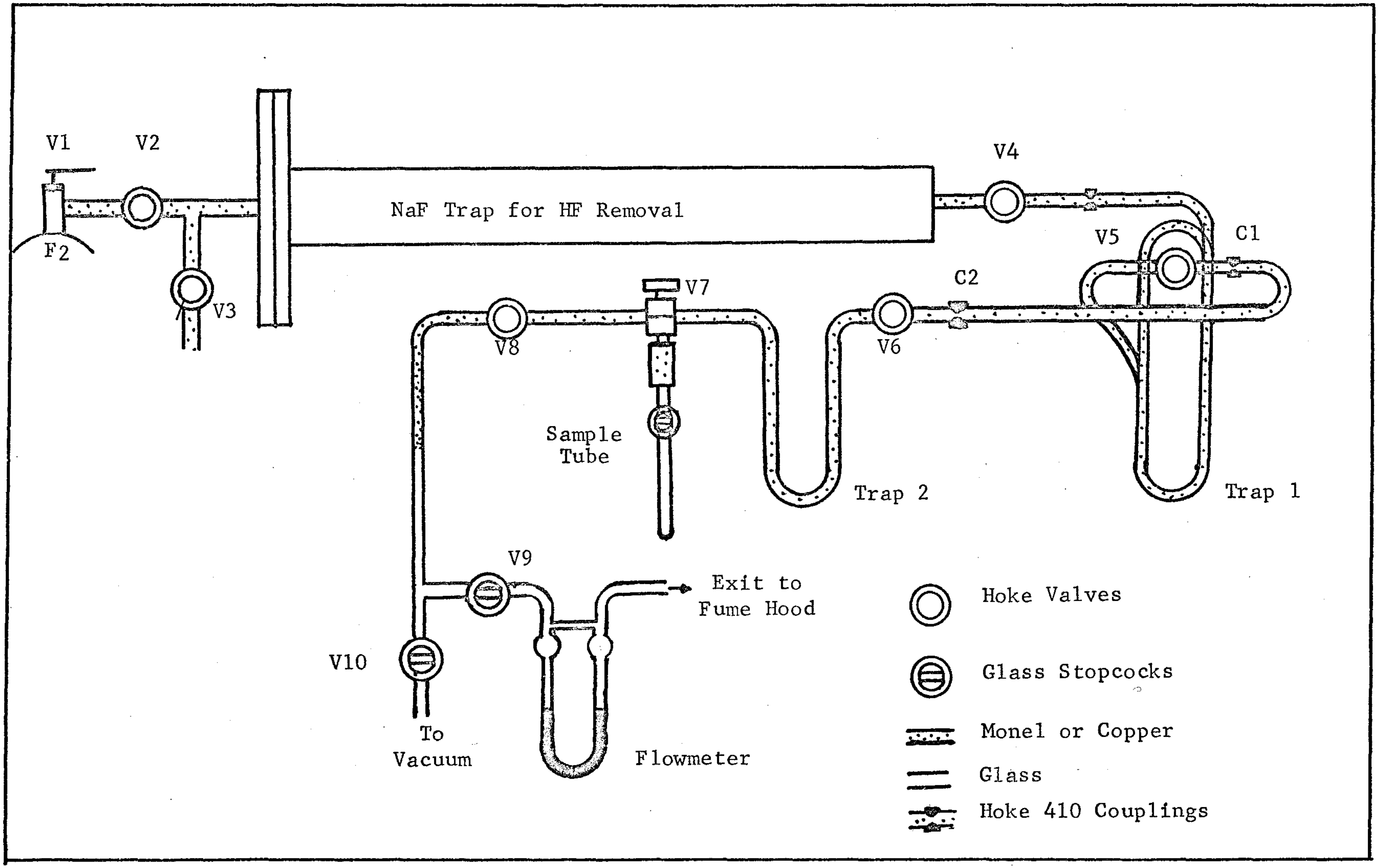


Fig. 2-1 Fluorine Line

via V5. The nitrogen flow is then adjusted to 25 ml/minute and a liquid oxygen trap is placed on trap 2.

(d) Wearing the neoprene gloves and the face mask as a safety precaution, the main fluorine cylinder valve V1 is opened. The needle valve V2 is adjusted until the total gas flow is approximately 100 ml/minute. After flowing at this rate for six or seven minutes it should be possible to detect fluorine at the outlet by means of a paper moistened with KI solution.

(e) After the fluorine has been flowing for ten minutes V1 is closed off and V2 slowly opened to release the fluorine trapped between these two valves. The nitrogen flow is left at 25 ml/minute for thirty minutes to push the fluorine slowly through the system. After this the nitrogen flow is increased to 100 ml/minute to speed up the flushing process.

(f) When fluorine can no longer be detected in the outflow (this usually takes a further thirty minutes) the nitrogen flow is cut off, V5 closed and the rest of the system evacuated. The sample tube is then re-evacuated, V6 and V8 closed and the sample transferred into the sample tube.

As with the BrF_3 preparation method used by Hoering it was not possible to obtain greater than 70% yields of sulphur hexafluoride by the above method. However comparisons with S^{34} results of samples prepared by the SO_2 method indicated that the reproducibility was similar to that of the SO_2 method i.e. ~ 0.2‰ (Thode, Monster and Dunford, 1961).

The gas chromatographic purification system used for these samples is shown in Fig. 2-2. The samples are introduced into the lower arm of the U-tube trap U_1 on an independent vacuum system. Trap U_1 is then reconnected to the gas chromatograph with the helium flow through the upper arm of U_1. The helium flow in U_2 should be through the lower arm of that trap. Once the helium flow has reached 75 ml/minute liquid air is placed around trap U_2. Then at a time t_o stopcocks T_1 and T_2 are reversed introducing the sample into the helium flow. Forty-five seconds later stopcocks T_3 and T_4 are reversed in preparation for the arrival of the purified sample in the upper arm of U_2. After the arrival of the sample at the detector (as indicated by the recorder) a period of 20 seconds is allowed before reversing T_3 and T_4 once again. The purified sample is transferred into a sample bottle on the separate vacuum system. It was found that some of the contaminents, particularly those which produce $C_3F_5^+$ peaks in the mass spectrometer (which would interfere with the $S^{36}F_5^+$ peak at mass 131) were collected in the lower arm

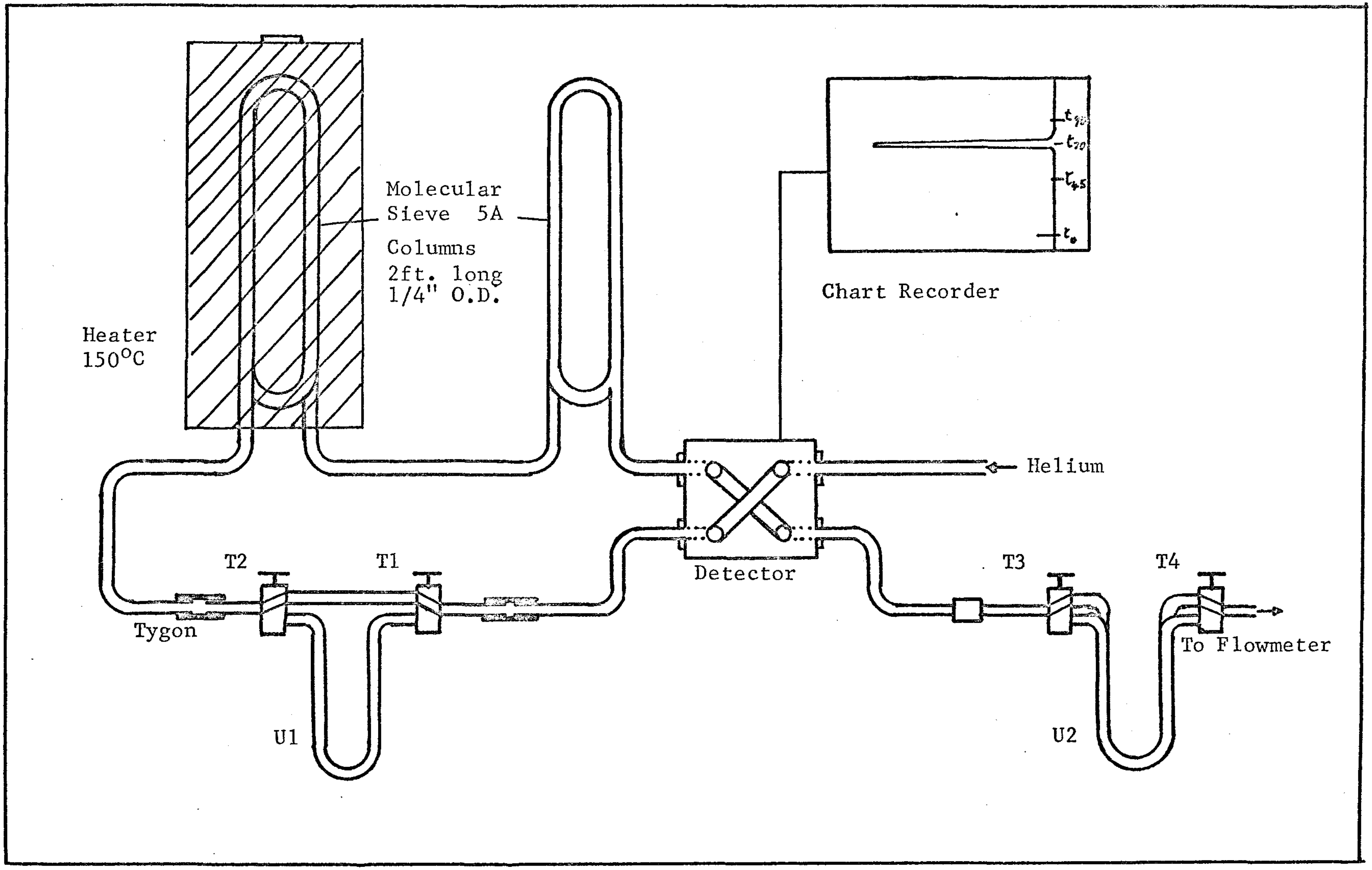


Fig. 2-2 Gas Chromatographic Purification System

of U_2 while other contaminants were held in the chromatographic column. In order to reduce the effects of the gradual release of this latter contaminant the detector cell and both sections of the chromatographic column were baked overnight at 220°C with helium flow in the reverse direction. After purification, each sample is analysed on the mass spectrometer, then later repurified and reanalysed to ensure that all the mass 131 contaminants have been removed.

In the mass spectrometer determination of δS^{33}, δS^{34} and δS^{36} a cylinder of commercial sulphur hexafluoride (Matheson Company) was used as a secondary standard. This standard was also purified using the gas chromatograph described above.

MASS SPECTROMETRY

2.5 General

The mass spectrometer used for this work was basically that described by Wanless and Thode (1953). The main improvements in the instrument since 1953 have been the substitution of a second vibrating reed electrometer in place of the d.c. amplifier and the use of a demountable type, all metal, mass spectrometer tube. The instrument as currently used is capable of measuring

S^{34} values to within ± 0.1‰.

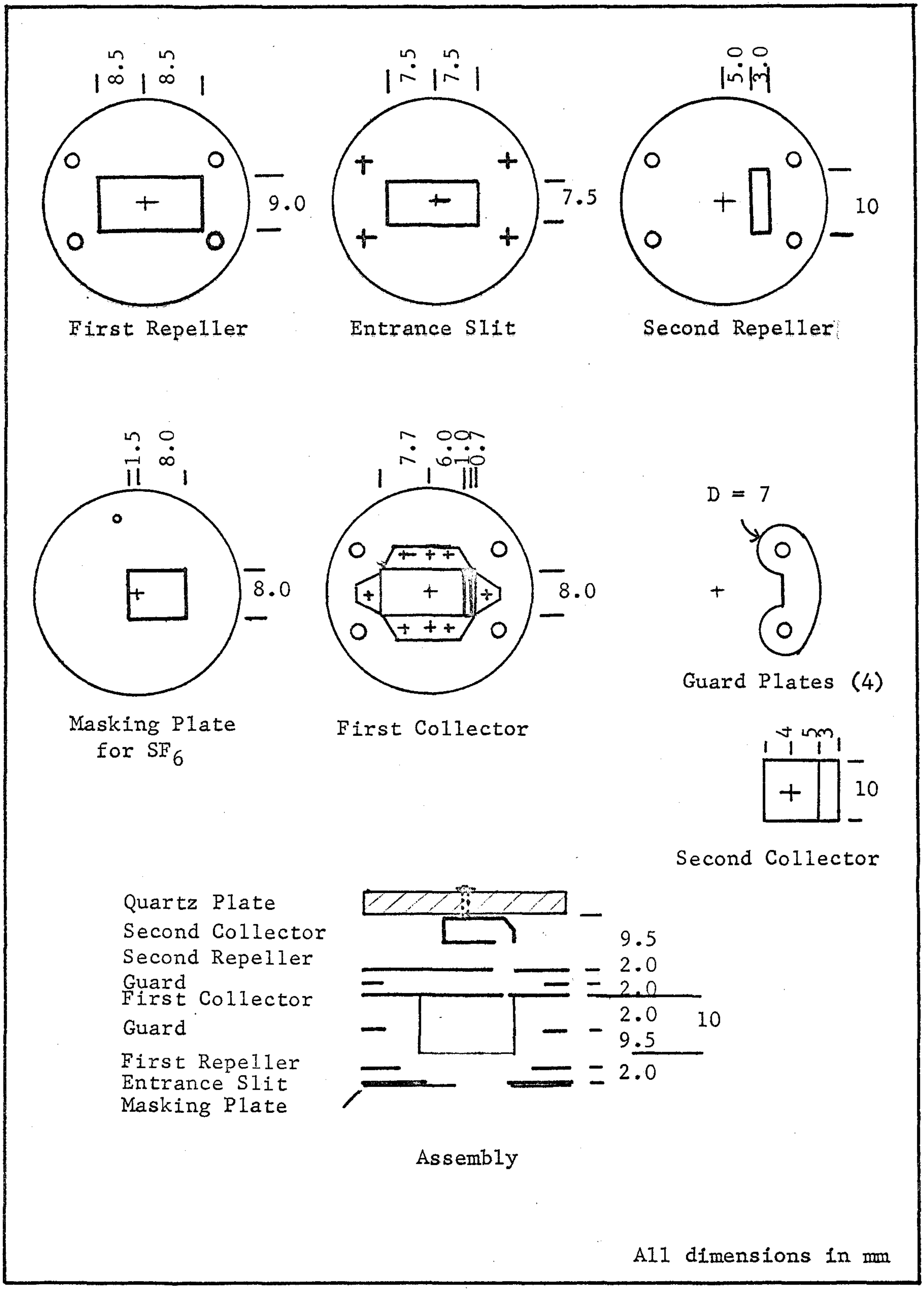
Since the normal abundance of S^{36} is only about 1 part in 7000 the first problem was to obtain adequate sensitivity for its measurement. The S^{36}/S^{32} ratio to be measured is approximately 0.00015 as compared to 0.008 and 0.045 for S^{33}/S^{32} and S^{34}/S^{32} respectively. Firstly an estimation of the statistical fluctuations due to the arrival of individual S^{36} ions was made as follows: Working on the basis of a S^{32} ion current of 2×10^{-9} amps it was estimated that approximately 2×10^{6} ions per second would fall on the S^{36} collector plate hence the statistical noise averaged over a 1 second period would represent approximately 1 in 1500. If conditions could be held stable for the order of 100 seconds the standard deviation of an average taken over this period would thus be approximately 1 in 15,000. Thus the theoretical limit to a measurement of δS^{36} under these conditions is of the order of 0.1‰. In practice it was found possible to obtain measurement standard deviations of the order of 0.3 to 0.5‰.

2.6 Ion Collection System

As it was desired to make δS^{33}, δS^{34} and δS^{36} measurements on a single sample in succession, it was necessary to modify the fixed collector system used by

Wanless and Thode (1953) to the wide and narrow slit combination developed by Nier (1947). The actual design used is shown in Fig. 2-3. The box shown on the wide collector plate was added to ensure the full collection of the S^{32} ions. Without this box it was found that some ions were deflected from the collector plate due to charges built up on insulated layers (Barnard, 1952) which form on the plate in the region where the S^{32} ions hit.

It was found that more care than usual in selection of the secondary electron repeller voltages was necessary in order to reduce the stray ion and electron pick up of the narrow collector to below 2% of the S^{36} peak i.e. to below 1 part in 300,000 of the S^{32} peak. The use of -300 volts on the narrow collector repeller plate was found effective in the suppression of any negative ions travelling along with the beam and of electrons arising from secondary electron emission in the wide collector system. The voltage applied to the wide collector repeller plate was however found to accelerate positive ions (presumably diffracted from the edges of the wide slit) towards the narrow collector if more than -6 volts was applied. The effect of these positive ions was to "dilute" the S^{36} peak and thus the δS^{36} value of samples could be in error by up to one-fifth. Inspection of the mass spectrum above mass 40 when argon was being analysed and the spectrum above



All dimensions in mm

Fig. 2-3 Ion Collection System

mass 129 when sulphur hexafluoride was being analysed indicated that the combination of -300 volts on the narrow collector repeller plate and 0 to -5 volts on the wide collector repeller plate would keep the stray ions down to approximately 1% of the S^{36} peak. The repeller voltages were therefore set at -300 volts and -3 volts respectively.

In order to obtain maximum sensitivity when measuring S^{36} and S^{33} isotopes, a commercial input resistor turret switch was purchased and modified for use in the simultaneous collection circuit shown in Fig. 2-4. It was found necessary to add the "critical damping" modification shown in this figure in order to reduce the time constant of the vibrating reed electrometer amplifier A2 from the 5 second period normally obtained with a $3x10^{11}$ ohm input resistor down to approximately 1 second. This decrease in time constant is beneficial in two ways. Firstly it speeds-up the response of the circuit to adjustments and thus prevents these adjustments from becoming slow and tedious. Secondly it allows alpha particle pulses from the materials used in the construction of the reed to be recognised as such and hence enables them to be ignored in the analysis of the recorder trace. These pulses, which arrive at the rate of approximately 30 per hour and carry an average charge of $5x10^{-15}$ coulombs each are made

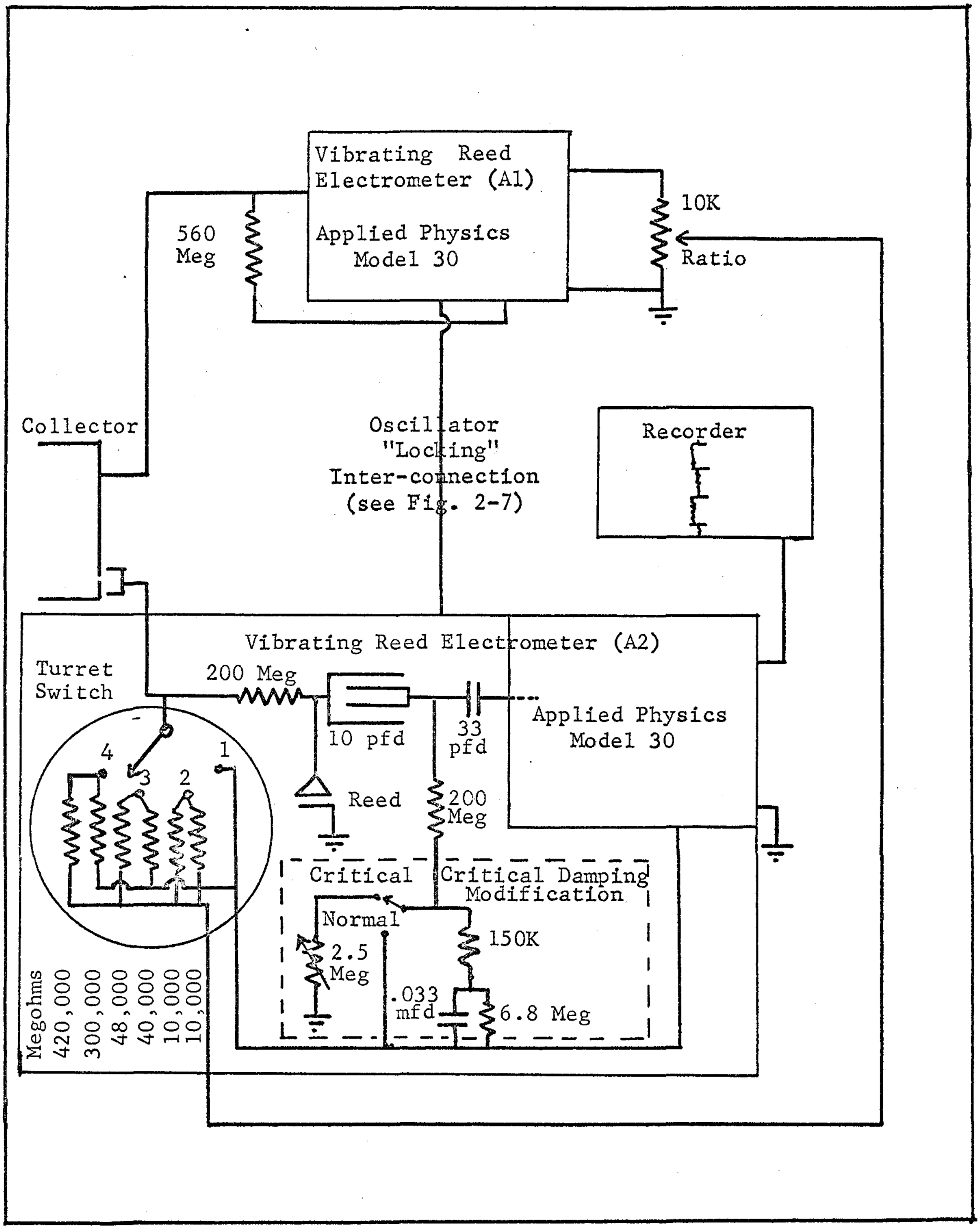


Fig. 2-4 Simultaneous Collection Circuit

shorter and larger by this decrease in time constant. The resistor R in Fig. 3-2 is adjusted to make the circuit critically damped when using the 3×10^{11} ohm input resistor (S^{36}/S^{32} measurements). When the lower valued input resistors are used (S^{33}/S^{32} and S^{34}/S^{32} measurements) the modification is switched out of circuit otherwise the inverse feedback circuit of the vibrating reed amplifier A_2 is not fully stabilised and overshoot may occur.

2.7 Improvements to Electronics

During the early part of this work the emission regulated filament power supply was replaced by the transistor type supply shown in Fig. 2-5. The circuit of this unit is a modification of that described by Russell and Kollar (1960), the chief changes being the use of 82 volt Zener diodes in place of the glow discharge tubes, the replacement of the single 27 volt Zener diode by four 6 volt Zeners in order to take advantage of the latter's lower temperature coefficient and internal impedence, and the increase of the maximum available case current to 4 mA. After making this latter modification it was found necessary to add the voltage doubler circuit shown, to supply the voltage amplifier stage, otherwise good regulation against mains voltage variations could not be obtained. The stabilization ratio of the final circuit was 200:1 and the stability after initial warm-up was better than 1 part in 2,000 which is considerably better than the tube type

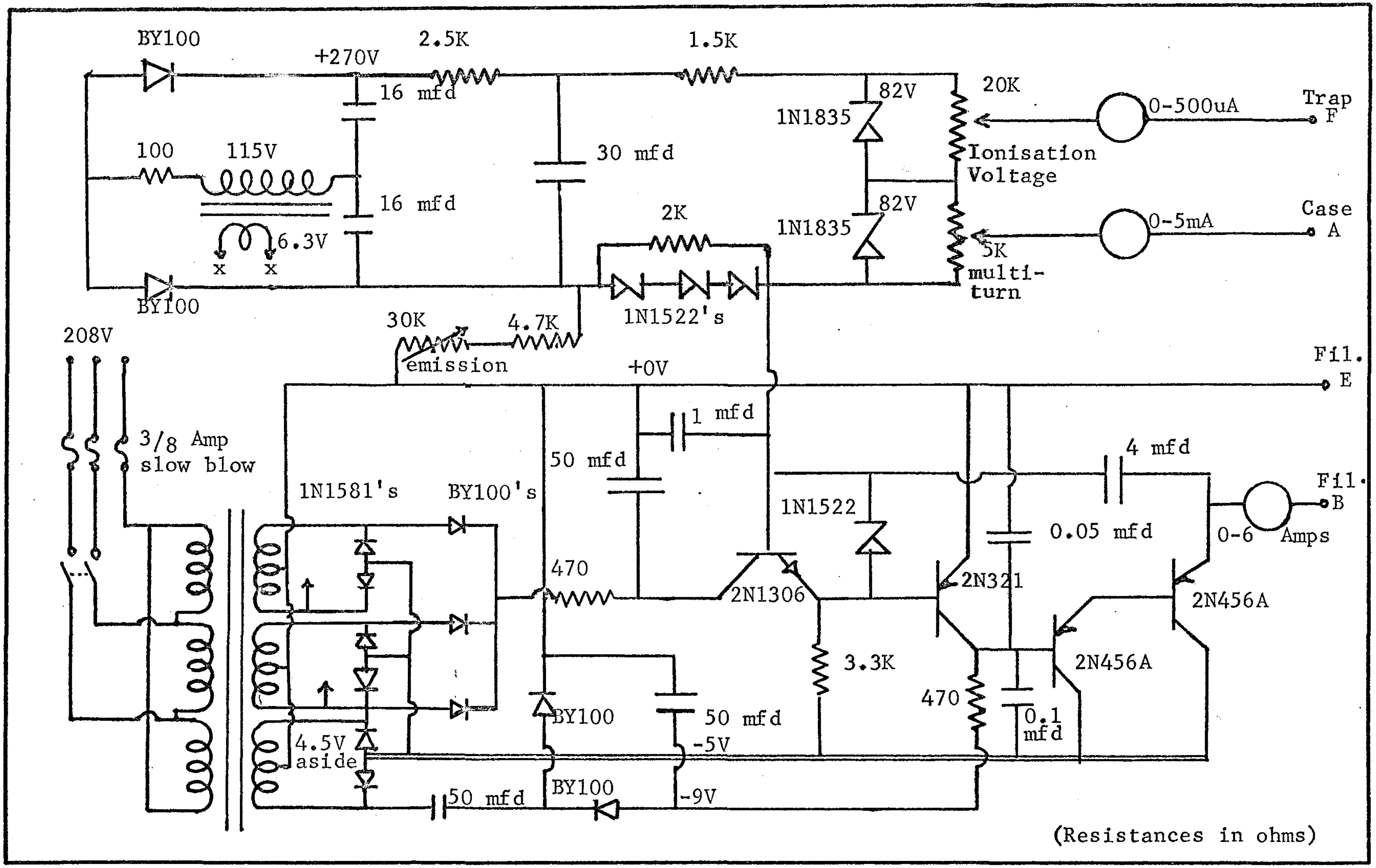


Fig. 2-5 Transistor Type Filament Power Supply

supply. In addition the tube type supply had a 15 volt 120 cycle ripple on the filament to case voltage whereas this ripple is below 1 volt in the transistor unit. This effect was important at one stage of the work when it was thought that some of the contamination obtained might be eliminated by using a lower than normal ionization voltage.

Two modifications were made to the sample switching valve circuit as shown in Fig. 2-6. The high value electrolytic capacitors were added across each coil in order to delay their closing by a fraction of a second at switchover. In this manner the sudden dip in the vibrating reed output voltages was considerably reduced. The diodes prevent the capacitors from loading the coils at switch on. The 20 ohm resistor was added in series with one coil to balance the effects of the stray magnetic field from these sample switching valve coils on the analyser magnetic field. Without this resistor the difference between the stray fields from the two coils was sufficient to shift the beam slightly when switching from standard to sample.

It was found that a low frequency oscillation of 1 to 10 mV amplitude occasionally appeared on the output of the vibrating reed electrometers. This was finally traced to a leakage of the reed drive voltage from one vibrating reed electrometer into the input of the other.

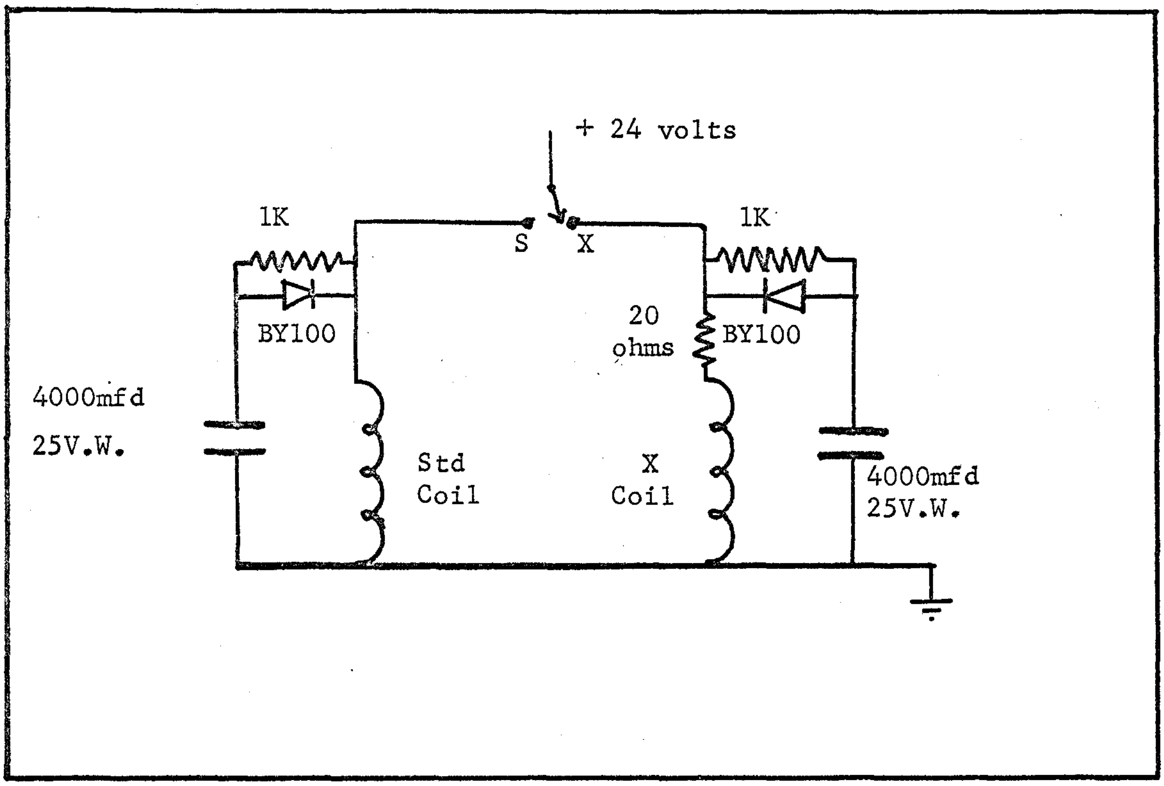


Fig. 2-6 Sample Switching System

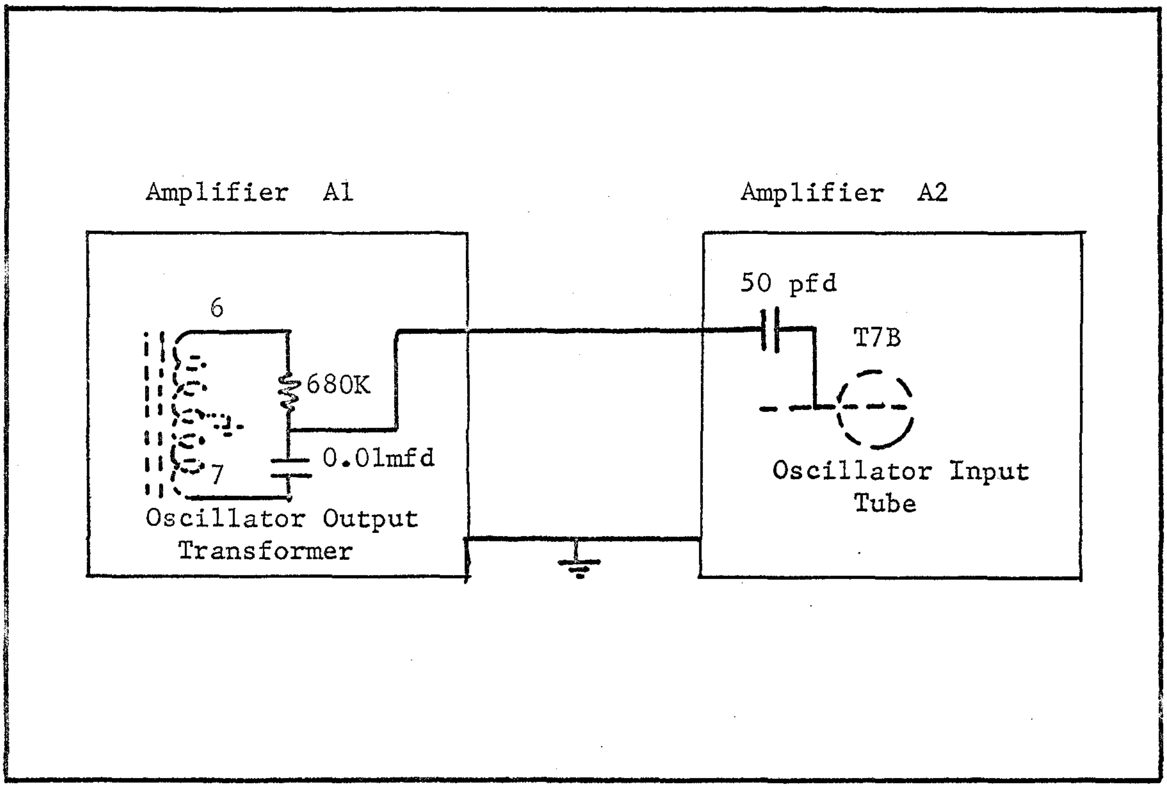


Fig. 2-7 Vibrating Reed "Locking" Circuit

vibrating reed electrometer. When the reed drive frequencies (at approximately 450 cps) drifted within five cps of each other the resultant beat frequency passed through the output filter circuits and could be observed on both the output meters and on the recorder. As it was found virtually impossible to significantly reduce this leakage the problem was overcome (as in commercial master-slave pairs) by "locking" the frequencies of the oscillators of the two units using the circuit shown in Fig. 2-7.

2.8 Measurement of Samples

Sulphur dioxide samples were analysed using the SO_2^+ ions at masses 64-68. The calculation of δS^{34} values from 66/64 by a convenient formula has been described by Hulston and Shilton (1958), Ault and Kulp (1959) and others, and has been reviewed by Hulston (1962). For completeness the full calculation of this formula has been reproduced in general terms in Appendix B together with similar calculations for δS^{33} and δS^{36}. The results of these calculations are as follows:

$$\delta S^{33} = 1.098\ \delta(65) - 0.05\ \delta O^{18}$$

$$\delta S^{34} = 1.095\ \delta(66) - 0.091\ \delta O^{18}$$

$$\delta S^{36} = 2.23\ \delta(68) - 0.78\ \delta O^{18}$$

Where δS^{33}, δS^{34} and δS^{36} have previously been defined (see Introduction) and where

$$\delta(65) = \left[\frac{\left(\frac{\text{mass } 65}{\text{mass } 64}\right) \text{sample}}{\left(\frac{\text{mass } 65}{\text{mass } 64}\right) \text{standard}} - 1 \right] \times 1000$$

$$\delta(66) = \left[\frac{\left(\frac{\text{mass } 66}{\text{mass } 64 + \text{mass } 65}\right) \text{sample}}{\left(\frac{\text{mass } 66}{\text{mass } 64 + \text{mass } 65}\right) \text{standard}} - 1 \right] \times 1000$$

$$\delta(68) = \left[\frac{\left(\frac{\text{mass } 68}{\text{mass } 64 + \text{mass } 65 + \text{mass } 66}\right) \text{sample}}{\left(\frac{\text{mass } 68}{\text{mass } 64 + \text{mass } 65 + \text{mass } 66}\right) \text{standard}} - 1 \right] \times 1000$$

and δO^{18} represents the difference, in parts per thousand, between the O^{18} content of the oxygen in the sample and that of the standard SO_2 gas. Assuming that the relation $\delta S^{36} = 1.9\ \delta S^{34}$ (see Appendix A) holds, the latter reduces to

$$\delta S^{36} = \delta(68) - 0.78\delta O^{18}$$

it will immediately be seen that the O^{18} isotope contributes heavily to the mass 68 peak through the molecular species $S^{34}O^{18}O^{16}$ thus making the δS^{36} measurement very susceptible to any change in the oxygen isotopic ratio.

Some concern was felt as to the possibility of oxygen exchange with traces of water in the system causing the apparent δS^{36} value to change. To check this possibility,

δS^{36} and δS^{34} were also determined by measuring the SO^+ ion currents in the 48 to 52 mass range. In this case there is only one oxygen atom in the ion and the O^{18} contribution to the mass 52 peak is only half the O^{18} contribution to the mass 68 peak. The resultant SO+ δ-values together with those obtained for the SO_2^+ ions can in principle be used to determine δO^{18} and δS^{36} unambiguously, but it was found experimentally that contamination in the sample at mass 52 was more serious than at mass 68 and thus this method was not pursued further.

Sulphur hexafluoride differs from many fluorine compounds in its inertness to attack by water. Thus it is not hydrolised in the presence of traces of water as is selenium hexafluoride (Krouse, 1960). As indicated by its sublimation point (-80°C) it is similar to carbon dioxide in the manner in which it handles in the mass spectrometer. In this respect it has the advantage over sulphur dioxide in that it has much less tendency to stick to the walls of the vacuum line running from the leaks to the ionization source region and thus sample switch-over is much sharper than when using sulphur dioxide. On the other hand it has the disadvantage of having an appreciable vapour pressure at temperatures in the -130 to -150°C region and thus gives a small background pressure in the mass spectrometer as the liquid nitrogen level in the mercury diffusion pump cold traps recedes. This effect can be reduced to a minimum by keeping the traps full while measurements are being made and by allowing the liquid nitrogen level to drop overnight.

The predominant peaks in the mass spectrum of sulphur hexafluoride are those of the SF_5^+ ion at masses 127-131. The collector system described in Sec. 2.6 has adequate mass resolution in this mass range. It was found necessary to keep the mass spectrometer pressure as read on the source ionisation gauge, below 1.5×10^{-6} Torr in order to keep the tailing contribution at mass 131 less than 5%.

In the measurement of δS^{36}, the S^{34}, S^{33} and S^{32} beams all fall on the one plate. To obtain δS^{36} from the $\delta(131)$ measurement it was therefore necessary to take this into account and make corrections to $\delta(131)$ as shown in Appendix B.

III RESULTS AND DISCUSSION

PART 1 - S^{33}, S^{34} AND S^{36} ABUNDANCES IN METEORITES

3.1 Results of S^{33}, S^{34} and S^{36} Determinations of Sulphur in Meteorites

The mass spectrometer results obtained from the various forms of sulphur in stone meteorites and from troilite nodules in iron meteorites are listed in Tables 3-1 to 3-6 and the results for a few representative terrestrial samples are listed in Table 3-7. In these tables the values of δS^{33}, δS^{34} and δS^{36} express the difference in parts per thousand between the S^{33}/S^{32}, S^{34}/S^{32} and S^{36}/S^{32} ratios (respectively) of the sample being measured as compared to the corresponding ratios of the generally accepted sulphur isotope standard, namely the troilite phase of the Canyon Diablo meteorite. The samples listed in Tables 3-1, 3-2 and 3-3 were analysed as SO_2 gas in the mass spectrometer while those listed in Tables 3-4 through 3-7 were analysed as SF_6 gas.

The δS^{33} values of the samples listed in Tables 3-1 to 3-7 have been plotted against their respective δS^{34} values in Fig. 3-1. Different symbols are used to indicate the method of sample preparation and to distinguish

TABLE 3-1

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(CHONDRITES) *

No.	Sample Description	δS^{33} (^{o}/oo)	δS^{34} (^{o}/oo)	"δS^{36}" (^{o}/oo)
	Enstatite Chondrites			
47	Abee MnS 1st 18 hrs.	-0.2	-0.2	+1.8
48	Abee MnS last 2 hrs.	+0.1	+0.4	+0.7
49	Abee CaS (H_2O Sol)	+0.9	+1.6	+10
50	Abee S^o	-0.7	-1.7	-1.4
35a	Hvittis CaS (as sulphide)	+1.4	+2.5	+5.8
35b	Hvittis CaS (Ox to SO_4)	--	-0.8	+40
36	Hvittis FeS	-0.3	+0.1	-1.4
37	Hvittis Residual S	+0.0	+0.2	+2.4
	Olivine - Bronzite Chondrites			
8	Richardton FeS (a)	+0.1	+0.5	+0.0
27	Richardton FeS (b)	+0.2	+0.2	+6
29	Richardton Chondrules FeS	-0.1	+0.1	+10
58	Richardton S^o	+0.5	+0.3	+3.6
9	Richardton Total S	+0.1	+0.5	+0.7
	Olivine - Hyperstene Chondrites			
31	Bjurbole FeS	+0.4	+0.3	+4.7
32	Bjurbole Residual S	-0.5	-1.7	15
30	Bjurbole Chondrules FeS	+0.1	+0.1	+1.6
66	Ehole S^o (Shima)	+0.3	+0.2	+2.2
59	Holmstead II SO_4 (Shima)	+1.8	+2.1	+6.6

δ-values relative to sulphur in Canyon Diablo troilite.

* Determinations made using SO_2.

TABLE 3-2

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(CARBONACEOUS CHONDRITES) *

No.	Sample Description	δS^{33} (‰)	δS^{34} (‰)	"δS^{36}" (‰)
	Type I			
19	Orgueil SO_4 (H_2O sol)	-0.9	-1.6	-0.8
22	Orgueil SO_4 (HCl sol)	-0.1	0.0	+0.2
67	Orgueil SO_4	-1.0	-1.7	+0.5
	Type II			
43	Cold Bokkeveld SO_4 (H_2O sol)	+0.2	+0.7	+1.7
56	Cold Bokkeveld S^o (3rd)	+0.3	+0.2	+0.9
44	Mighei SO_4 (H_2O sol)	+0.2	+0.0	+1.1
46	Mighei FeS	+0.9	+1.7	+6.0
51	Mighei Residual S	-0.4	-1.5	+2.8
57	Mighei S^o (3rd)	+0.5	+0.4	+7
13	Murray FeS	+1.1	+2.5	+3.8
12	Murray SO_4 (H_2O sol)	-1.0	-1.7	-2.7
14	Murray SO_4 (HCl sol)	-0.2	-0.2	+0.2
17	Murray Residual S	+0.3	+0.3	+0.5
	Type III +			
11	Felix FeS	+0.1	+0.3	+0.9
39	Lance FeS	+0.3	+0.5	+2.5
16	Mokoia FeS	-0.7	-1.4	-0.8
15	Mokoia SO_4 (H_2O sol)	+1.2	+1.3	+3.9
40	Warrenton FeS	+0.1	+0.4	+0.8

+ Olivine - Pigeonite Chondrites

δ-values relative to sulphur in Canyon Diablo troilite

* Determinations made using SO_2

TABLE 3-3

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(IRONS AND ACHONDRITES) *

No.	Sample Description	δS^{33} (°/oo)	δS^{34} (°/oo)	"δS^{36}" (°/oo)
	IRONS			
	Hexahedrites			
24	Coahuila FeS	+0.1	+0.4	+6
5	Indian Valley FeS	+0.0	+0.0	-0.8
	Octahedrites - coarse			
1	Canyon Diablo FeS	0.0	0.	0.0
1c	Canyon Diablo Repeat	+0.1	+0.05	+4.4
	- medium			
4	Merceditas FeS	+0.2	+0.3	+2.3
3	Toluca FeS	+0.0	+0.1	+0.9
	- fine			
6	Ballinoo FeS	+0.1	+0.6	+1.0
	ACHONDRITES			
	Enstatite			
34	Norton County FeS	-0.1	-0.2	+2.2
33	Norton County SO_4 (CaS)	-2.9	-5.5	-4.5
38	Norton County Residual S	+1.2	+1.4	+15

δ-values relative to sulphur in Canyon Diablo troilite

*Determinations made using SO_2.

TABLE 3-4

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(CHONDRITES) *

No	Sample Description	δS^{33} (‰)	δS^{34} (‰)	δS^{36} (‰)
	Enstatite Chondrites			
50	Abee FeS	-0.2	-0.2	+0.4
	Olivine - Bronzite Chondrites			
183	Hugaton FeS	-0.1	+0.1	+0.8
	Olivine - Hyperstene Chondrites			
182	Brudeheim FeS	+0.2	+0.2	+0.7
31	Bjurbole (Matrix) FeS	+0.2	+0.5	+1.1
30	Bjurbole (Chondrites) FeS	-0.0	-0.1	-0.1
65	Ehole FeS (Shima)			
78	Ehole Total S	-0.1	-0.5	-
79	Ehole (HAc vol $S^=$) (1)	-0.0	-0.1	+0.8
80	Ehole (HAc vol $S^=$) (2)	+0.0	+0.1	+1.4
81	Ehole FeS (HCl vol $S^=$)	-0.8	-1.6	-
181	La Lande FeS	-0.1	-0.2	+0.3
185	Potter FeS	+0.5	+1.1	+2.9

δ-values relative to sulphur in Canyon Diablo troilite.

* Determinations made using SF_6.

TABLE 3-5

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(CARBONACEOUS CHONDRITES) *

No.	Sample Description	δS^{33} (‰)	δS^{34} (‰)	δS^{36} (‰)
	Type I			
20	Orgueil FeS	+2±1	+3±1	Too small
53	Orgueil S^{o} (1st)	+0.7	+1.8	+3.2
69	Orgueil Total S	-0.0	-0.0	+0.2
93	Orgueil S^{o} (re-extraction)	+0.7	+1.0	+2.8
203	Orgueil S^{o} (Calvin)	+1.8	+3.3	+6.6
	Type II			
45	Cold Bokkeveld FeS	+1.2	+2.2	+4.4
55	Cold Bokkeveld S^{o} (2nd)	-0.4	-0.6	-
179	Murray FeS	+0.3	+0.8	+1.7
	Type III +			
18	Mokoia Residual S	+0.0	+0.4	+1.2
18I	Mokoia Res S (re-extraction)	+0.0	+0.1	+0.6
71	Mokoia Total S	+0.2	+0.3	+0.5
23	Karoonda $SO_4^{=}$ (HCl sol)	+0.3	+0.4	Too small
70	Karoonda Total S	+0.0	+0.2	0.9
90	Karoonda Residual S	-0.4	-0.8	-0.4
91	Karoonda S^{o}	-0.1	-0.2	+0.8

+ Olivine-Pigeonite Chondrites

δ-values relative to sulphur in Canyon Diablo troilite

* Determinations made using SF_6

TABLE 3-6

SULPHUR ISOTOPE DISTRIBUTION IN METEORITES

(IRONS AND ACHONDRITES)*

No	Sample Description	δS^{33} (‰)	δS^{34} (‰)	δS^{36} (‰)
	IRONS			
	Hexahedrites			
24	Coahuila FeS	+0.3	+0.4	+1.1
	Octahedrites - coarse			
188	Canyon Diablo FeS (McMaster)	(0.0)	(0.0)	(0.0)
1A	Canyon Diablo FeS (Cal Tech)	+0.0	+0.0	+0.3
	- medium			
186	Xiquipilco (Toluca)	+0.0	+0.1	+0.8
	- fine			
178	Betta Rocca	+0.0	+0.1	-0.1
180	Bear Creek	+0.0	+0.1	+0.0
	Nickel Rich Ataxites			
184	Monahans	+0.0	+0.2	+0.4
	ACHONDRITES			
	Enstatite			
34	Norton County FeS	+0.1	+0.0	+0.0
331	Norton County SO_4 (H_2O Sol)	-3.0	-5.7	-10.9
92	Norton County Total S	-0.1	+0.0	-

δ-values relative to sulphur in Canyon Diablo troilite.

* Determinations made using SF_6.

TABLE 3-7

SULPHUR ISOTOPE ABUNDANCES IN SELECTED TERRESTRIAL SAMPLES *

No	Sample Description	δS^{33} (°/oo)	δS^{34} (°/oo)	δS^{36} (°/oo)
200	NBS Galena	+ 0.3	+ 0.6	+ 1.4
120	NBS Sulphur	+ 0.8	+ 1.4	+ 2.2
102	Cylinder H_2S	+ 1.3	+ 2.2	+ 5.1
100	Cylinder SF_6	+ 1.4	+ 2.55	+ 4.8
103	Merck Sulphur	+ 3.4	+ 6.7	+14.0
201	$BaSO_4$ Reagent	+ 5.0	+10.1	+18.4
202	Sea water SO_4	+10.1	+20.1	+38.0

δ-values relative to sulphur in Canyon Diablo troilite.

* Determinations made using SF_6.

between meteoritic and terrestrial samples. It will be seen that within the limits of measurement of these very small variations in meteorite samples the results fall on a straight line of slope about 0.5 as do those for terrestrial samples. As mentioned earlier the SO_2 method for determination of δS^{36} is unsatisfactory because of contamination effects. The scatter of points in Fig. 3-2 is a clear indication of this. However, the lower envelope of the points appears to fall on a line of slope approximately 2. In the case of SF_6 samples contamination problems were reduced to a minimum and it is seen that in the δS^{36} vs δS^{34} plot (Fig. 3-3) the points fall on a straight line of slope 1.9 within the limits of the precision of the measurements. It is also seen that the δS^{36} values for terrestrial samples also fall on this line of slope 1.9.

According to theory the fractionation of the isotopes S^{33}, S^{34}, S^{36} with respect to S^{32} in chemical and physical processes will be approximately proportional to the percentage mass difference. This means that a plot of δS^{33} vs δS^{34} will give a line of slope approximately one-half, and a plot of δS^{36} vs δS^{34} a line of slope approximately two. The exact slopes predicted by the theory, see Appendix A, are 0.51 and 1.9 respectively. As seen from Fig. 3-1 to 3-3 this relation between δS^{33}, δS^{34} and δS^{36}

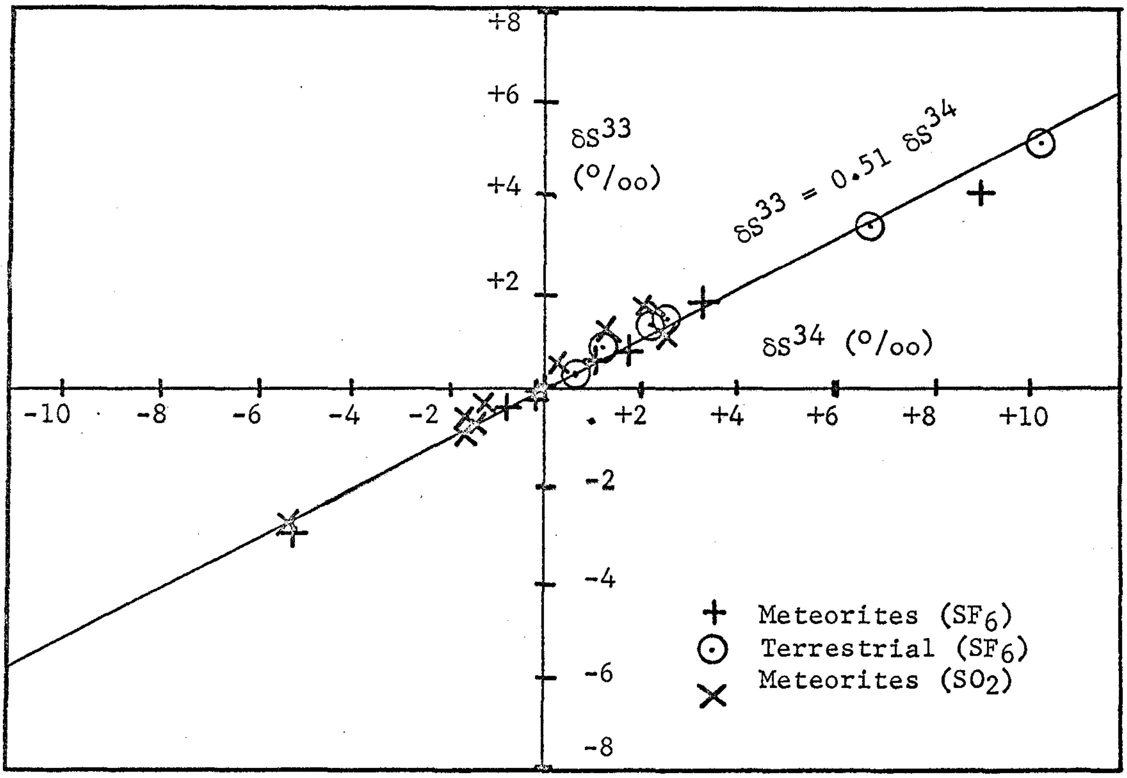


Fig. 3-1 Relationship between δS^{33} and δS^{34} for Meteorite and Terrestrial Samples

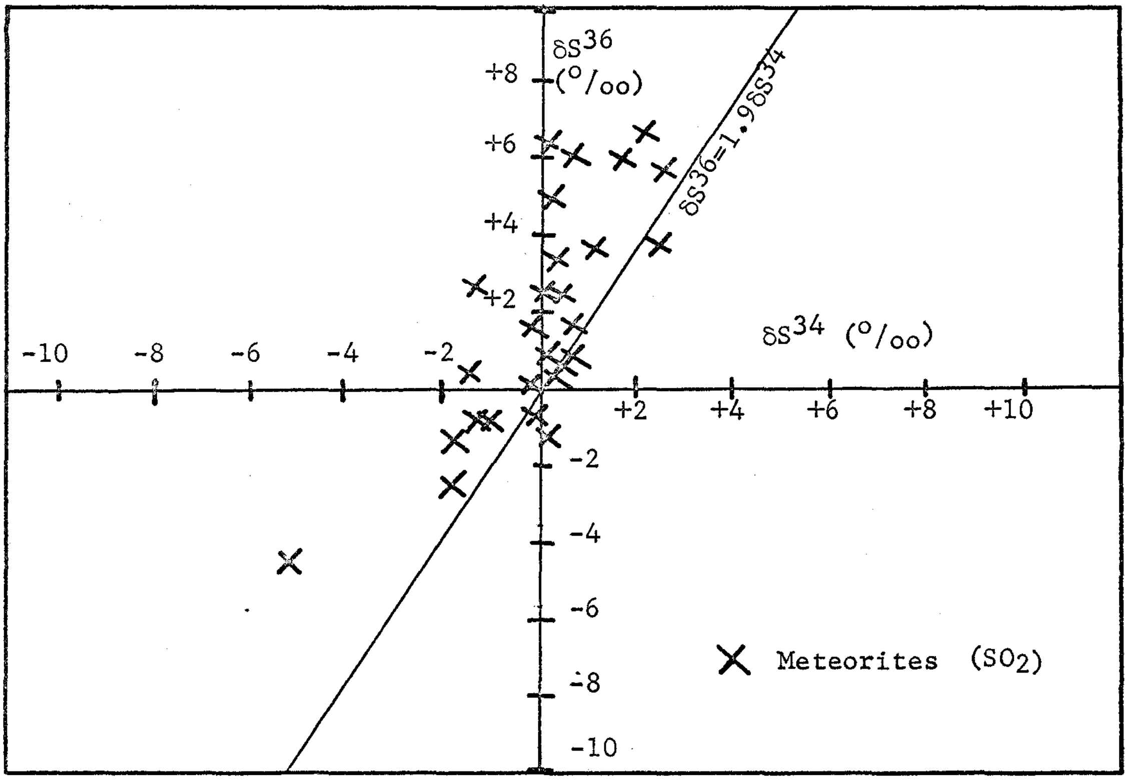


Fig. 3-2 Relationship between δS^{36} and δS^{34} for Meteorite samples (SO_2)

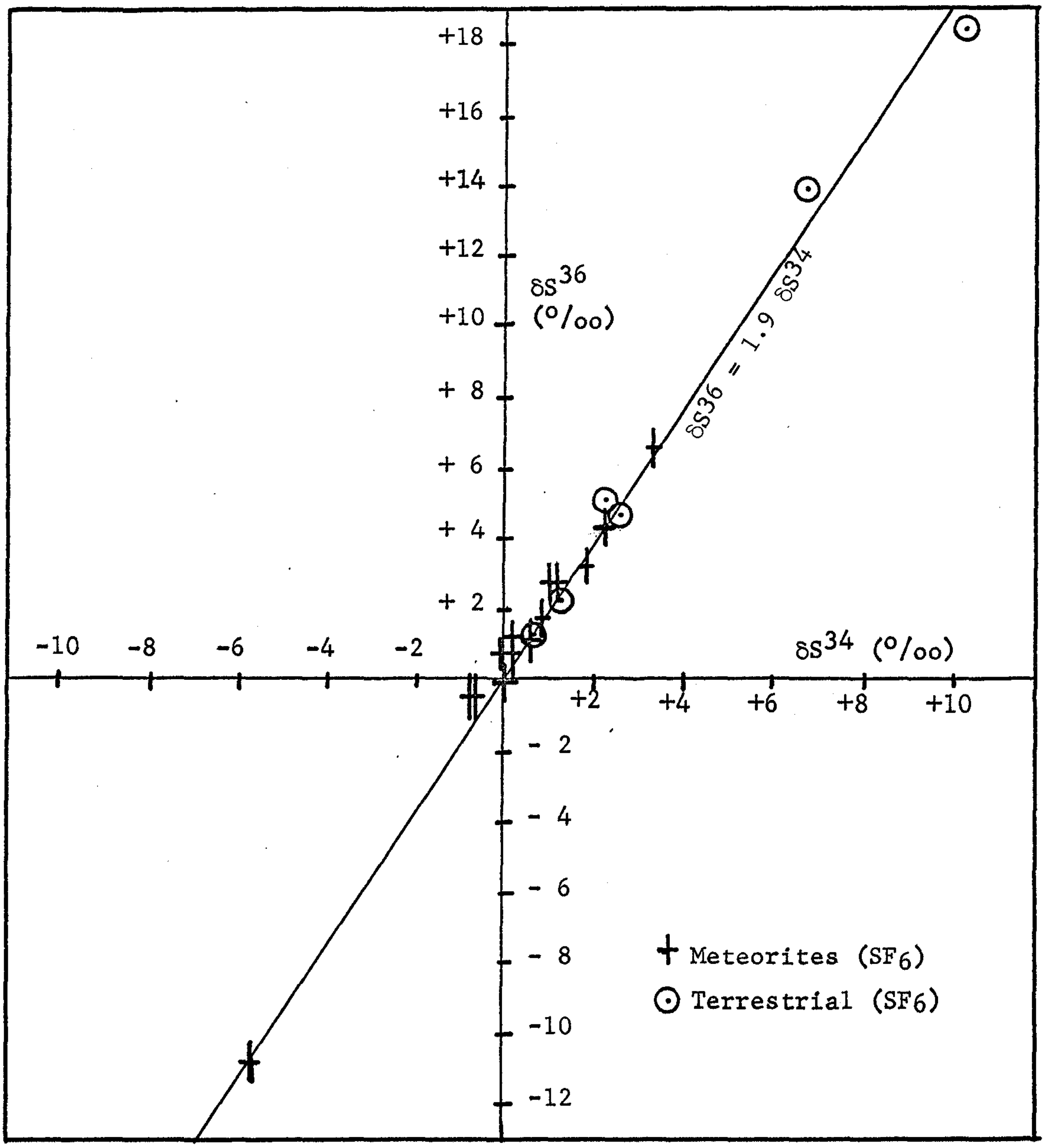


Figure 3-3 Relationship between δS^{36} and δS^{34} for Meteorite and Terrestrial samples (SF_6)

does exist for the meteoritic sulphur samples in that in the δS^{33} vs δS^{34} and δS^{36} vs δS^{34} plots the points do fall on straight lines of slopes 0.51 and 1.9 respectively within the precision of the measurements. These results indicate that the variations in the S^{33}, S^{34} and S^{36} content of sulphur in meteorites are due to fractionation in chemical and physical processes.

3.2 S^{34} Variations

In considering the distribution of the sulphur isotopes between the various forms of sulphur in a given meteorite the discussion may be confined to S^{34} in view of the higher accuracy of this measurement. These S^{34} results have been summarised in Table 3-8. Columns 2 to 9 give the δS^{34} value and also the percentage of sulphur in the FeS, $SO_4^=$, S^o and Residual S (aqua regia) fractions extracted from the meteorite specimens. Column 10 gives the total sulphur content of the meteorite while the weighted average δS^{34} value for the meteorite is given in column 11. It should be pointed out first that although there is a variation in the S^{34} content from one form of sulphur to another in a given meteorite the weighted average of δS^{34} for each meteorite is the same and close to $\delta S^{34} = 0.0$ within 0.5‰. Thus these results again show the remarkable constancy of the S^{34} content of meteorites and indicate a common source for meteoritic sulphur.

TABLE 3-8 S^{34} ABUNDANCE OF DIFFERENT FORMS OF SULPHUR IN CHONDRITES AND ACHONDRITES

	Troilite (FeS)		Sulphate		Sulphur (S^o)		Residual S		Total S	Weighted *
Type and Meteorite	δS^{34}	%S	δS^{34}	%S	δS^{34}	%S	δS^{34}	%S	(%)	Av. δS^{34}
CHONDRITES										
Enstatite										
Abee	-0.2	4.6	+1.6	0.13	-1.7	Trace			6.7	0.1
Hvittis	+0.1	3.1	-0.8	0.11			+0.0	0.24	3.5	0.1
Olivine - Bronzite										
Hugoton	+0.1	-								
Richardton (matrix)	+0.2	2			+0.3	0.12			2	+0.2 (+0.5)
Richardton (chondrules)	+0.1	0.8							0.8	+0.1
Olivine - Hypersthene										
Bjurbole (matrix)	+0.4	2.2					-1.7	0.05	2.2	+0.2
Bjurbole (chondrules)	+0.1	1.4							1.4	+0.1
Ehole	-1.6				+0.2					(-0.5)
Carbonaceous - Type I										
Orgueil	$+3\pm1$	0.04	-1.5	2.6	+1.8	1.35			4.0	-0.4 (-0.0)
- Type II										
Murray	+2.5	0.06	-1.4	0.5			+0.3	1.7	2.3	+0.0
Cold Bokkeveld	+2.2	0.01	+0.7	1.0	+0.2	0.5			1.6	+0.5
Mighei	+1.7	0.18	+0.0	0.5	0.4	1.6	-1.5	0.15	2.4	+0.3
- Type III										
Felix	+0.3	1.8							1.8	+0.3
Mokoia	-1.4	0.15	+1.3	0.15			+0.1	1.8	2.1	+0.0
Karoonda			+0.4		-0.2		-0.8		-	(+0.2)
Warrenton	+0.4	1.6								
ACHONDRITES										
Enstatite										
Norton County	-0.1	0.34	-5.6	0.13	-		+1.4	0.18	0.65	-0.8 (-0.1)

* Direct determinations of δS^{34} of the total sulphur are given in parenthesis

It is clear from the previous section that the variations in S^{34} content in the different forms of sulphur in a meteorite are due to fractionation in chemical processes. The question arises as to the nature of these processes. It should be pointed out first that although there is definite evidence of sulphur isotope fractionation between sulphate, sulphide and elemental sulphur in carbonaceous meteorites, as in the case of terrestrial samples, the fractionations to be explained of up to $4^{o}/_{oo}$ in the S^{34} content are very much less than obtained for terrestrial samples which can show variations greater than $100^{o}/_{oo}$. Further it is interesting to note that in the comparison of sulphate with troilite and elemental sulphur that in three cases, Orgueil, Murray and Mighei the sulphate is depleted in S^{34} as compared to other forms whereas in terrestrial situations where sulphate, elemental sulphur, and sulphide are associated together the reverse is usually true. In this connection it is known that equilibrium processes and also unidirectional processes involving the reduction of sulphate (e.g. bacterial reduction) lead to S^{34} enrichment in the sulphate fraction as in terrestrial situations. The depletion of S^{34} in the sulphate fraction in Orgueil, Murray and Mighei meteorites could however be the result of some oxidization process in which the S^{32} species reacts faster than that of S^{34}.

In discussing the results shown in Table 3-8 in the light of the theories of evolution of meteorites reviewed in the Introduction we observe first the large variation in the total sulphur content of the chondrites and achondrites. In addition iron meteorites usually contain an average of 1% sulphur in the form of troilite nodules (Mason, 1962). Since it has been observed above that the average δS^{34} value of these meteorites is very constant, it is obvious that any postulated process for the loss of sulphur from the parent body must be one in which virtually no isotopic fractionation occurs. The loss of sulphur as H_2S might be such a process. According to Mueller (1964) H_2S could be associated with an equilibrium with molten FeS in the interior of the meteorite parent body. Although isotopic partition function ratios for FeS are not available we may estimate that they would be similar to those for SiS and PbS vapours. From the tables shown in Appendix A it will be seen that under these conditions relatively little fractionation would occur at 1000°C.

It is clear from the distribution of sulphur isotopes between the different forms of sulphur within a single meteorite that some sulphur isotope fractionation has occurred due to chemical and physical processes. However it is difficult to assign the exact process responsible for the isotope fractionation. Whatever processes are postulated we must obviously take into account the experimental results which indicate that the total sulphur in a meteorite remains unchanged in isotopic composition. It thus seems unlikely that sulphur has been lost from the carbonaceous chondrites since the fractionation of the sulphur isotopes occurred between $S^=$, $SO_4^=$ and S^o. It would be very difficult for example to imagine a process whereby $S^=$, $SO_4^=$ and S^o would be lost with equal ease and any preferential loss of say S^o would lead to a depletion of S^{34} in the meteorite.

In discussing these meteorites we can only speculate as to the chemical combination of the sulphur in the primary material from which these meteorites were formed. It may be that these originally had the composition similar to that of the Type I (e.g. Orgueil) meteorites in which case the δS^{34} values obtained for the Type I meteorites may represent the particular composition of the material which formed in the dust cloud from the solar nebula. In this case the hypothesis must allow for the evolution of sulphur in the other types of meteorites from this primary material. On the other hand however it may be that one phase only (e.g. troilite) condensed in the dust cloud and that the other forms of sulphur were produced from this phase in unidirectional processes. At the present time it would not seem possible to distinguish between these two processes.

While the data contained in Table 3-8 does not permit the unique postulation of the chemical evolution of sulphur in meteorites it does provide information and limitations which will be useful to those postulating mechanisms of chemical evolution on the basis of other evidence.

3.3 Effects due to Nucleosynthesis

From the relationships between δS^{33}, δS^{34} and δS^{36} discussed in Sec. 3.1 we concluded that these δ-values could be explained solely in terms of chemical and physical fractionation effects. In addition it was seen that the weighted average S^{34} content of each individual meteorite is remarkably constant from meteorite to meteorite. There would thus appear to be no evidence of variations in any of the sulphur isotope ratios arising from processes of nucleosynthesis. As mentioned in the Introduction two possible mechanisms of nucleosynthesis might have given variations in these isotopes. These mechanisms are discussed below separately.

Both Cameron (1957, 1962, 1963) and Burbridge, Burbridge, Fowler and Hoyle (1957) postulate that the isotopes S^{32}, S^{33} and S^{34} were largely produced by slow neutron capture processes where the radioactive species S^{35} would have been built up to a level sufficient to allow neutron capture to form S^{36}. Cameron (1962) considers that this formation of S^{36} would probably occur in a Type II supernova explosion. In order to explain the anomalously large abundance of the isotope Xe^{129} found in certain meteorites and commonly attributed to the decay of the extinct radioactivity I^{129} which has a half life of 17.2 million years, Cameron (1962) suggested that the interstellar medium was enriched with fresh radioactivities a relatively short time before the formation of the solar system. Presumably some S^{36} would also have been introduced at the same time. Since no evidence for S^{36} enrichment due to nucleosynthesis has been found in the course of this work it would seem that either the gas and dust forming the solar system has been very thoroughly mixed since the last injection of S^{36} or else S^{36} is not produced in quite the manner described by the above authors. Since the solar system has considerable angular momentum the thorough mixing of gas and dust is not very hard to envisage. Hence the thorough mixing explanation would seem the most likely.

Fowler, Greenstein and Hoyle (1962) (usually referred to as FGH) have postulated that the light elements D, Li, B, Be were synthesised by spallation and neutron reactions simultaneously induced in the outer layers of the planetesimals by bombardment with high energy charged particles during an intermediate stage in the early history of the solar system. Using the methods of these writers and as much of their data as possible, it is shown below that this mechanism would also lead to the production of significant quantities of S^{33} and also a trace of S^{36}. We consider first the production due to the spallation process.

The average energy suggested for the particles causing spallation is 500 Mev. In Table 7 of this FGH paper the authors estimated using a cross section of 5 mb for Cl^{36} production, a cumulative Ar^{36} spallation yield of 4 atoms per 10^6 atoms of silicon. As this figure represents the Ar^{36} production average over the whole planetesimal, whereas it is postulated that only the outer one-tenth of the planetesimal was affected by the irradiation, this indicates that this outer one-tenth of the planetesimal would have been enriched in Ar^{36} to the extent of 40 atoms/10^6 Si.

Use of equation 1.2 (σ_i = 800 mb) in the Introduction gives for 0.5 Gev cumulative cross sections of 4.5 mb for Ar^{36}, 0.6 mb for S^{36} and 3 mb for S^{33}. By comparison with the above result for Ar^{36} we see that S^{36} and S^{33} spallation yields of 5 and 25 atoms/10^6 Si respectively are postulated. Using the sulphur abundance of 0.375 atoms per atom of silicon used by FGH, enrichments of $\delta S^{36} = 80‰$ and $\delta S^{33} = 10‰$

in the irradiated portion of the planetesimal are obtained.

These authors estimate that this spallation irradiation produced a time integrated neutron flux of $4 \times 10^{21} n/cm^2$. Using the S^{32} neutron capture cross section of 0.52 barns given in Table 9 of their paper an S^{33} enrichment of 0.21 atoms per 100 atoms of S^{32} is estimated for the irradiated portion of the planetesimal. Since the present S^{33} content of sulphur is 0.76 this represents an enrichment in S^{33} of 300‰ in the irradiated portion of the planetesimal.

The above calculations indicate that variations in the S^{33} isotope due to the mechanism postulated by Fowler, Greenstein and Hoyle (1962) will be much greater than in the S^{36} isotope. However since no evidence of S^{33} enrichment other than that due to chemical fractionation processes has been found in the meteorites analysed in this work it would seem again that either the S^{33} produced by the FGH hypothesis has been thoroughly mixed with the S^{33} already in the planetesimal or else the FGH theory requires considerable modification. The lack of evidence of S^{33} produced by the FGH mechanism confirms the results of Murthy and Schmitt (1963) who searched for depletion anomalies in certain rare earth isotopes of high thermal neutron capture cross sections, namely Sm^{149} (4.2 x 10^4 barns), Eu^{151} (8.7 x 10^3 barns) and Gd^{157} (2.4 x 10^5 barns). They studied two chondrites, one achondrite and one carbonaceous chondrite and found no significant differences in the contents of these isotopic species as compared to terrestrial Sm, Eu and Gd. Despite the smaller enrichment predicted for S^{33} in the outer layers of the planetesimals the S^{33} work described here would appear to be as sensitive for detecting isotope concentration changes due to the above neutron capture process as the work of Murthy and Schmitt because of the higher accuracy possible in measuring S^{33} differences.

In regard to these processes the results obtained for the carbonaceous chondrites should give the best test of the FGH hypothesis as these meteorites have been subject to much less alteration and hence mixing than other types of meteorites. It would seem rather difficult for sufficient mixing of material to occur between the planetesimal stage and the formation of the carbonaceous chondrites to explain the complete lack of evidence of S^{33} in the carbonaceous chondrites. Cameron (1962) has advocated the view that the interstellar medium always contains the presently observed abundances of D, Li, Be and B, and that the solar system was not subjected to neutron irradiation in the manner hypothesised by Fowler, Greenstein and Hoyle (1962). The above results are in agreement with Cameron's view but final confirmation really requires a result of a positive nature such as the identification of D, Li, Be in the interstellar medium with the abundances of the order of those in the solar system.

It seems likely that the variations of D/H ratio in meteorites found by Boato (1954) and the variations in the C^{13}/C^{12} ratio in meteorites found by Boato (1954) and by Clayton (1963) are also due to chemical and physical fractionation effects as in the case of the sulphur isotope variations. For example the value $\delta C^{13} = +60‰$ with respect to the terrestrial carbonate standard (PDB) (Peedee belemnite) found by Clayton (1963) for carbonate minerals in the Orgueil meteorite could be due to some low temperature equilibrium process similar to the equilibrium between CO_2 and CH_4 found in some hot springs of volcanic origin (Hulston and McCabe, 1962).

IV RESULTS AND DISCUSSION

PART 2 - COSMIC RAY PRODUCED SPALLATION SULPHUR

4.1 Results

The sulphur isotope results obtained for the iron phase of meteorites of high cosmic ray age and low sulphur content are shown in Table 4-1. This table gives the weight of sulphur in each fraction extracted from each specimen, along with the δS^{33}, δS^{34} and δS^{36} values. Although the δS^{34} values are in the range found previously for meteorites, much higher δS^{36} values are seen, for example Pinon, Tlacotepic and Clark County meteorites show δS^{36} values of 15.2, 6.3 and + 21‰ compared to δS^{34} equals +0.4, +0.0 and +0.9‰ respectively. If these variations were due to fractionation then the relationships

$$\delta S^{36} = 1.9\ \delta S^{34}$$
$$\delta S^{33} = 0.51\ \delta S^{34}$$

would be expected. We therefore conclude that the high δS^{36} values quoted above are definitely due to spallation. A closer look at these results shows that there is some evidence for spallation S^{33}. Although there may be spallation S^{34} present it presumably has been swamped out by the larger natural abundance of S^{34} as compared to the S^{33} and

TABLE 4-1 SULPHUR ISOTOPE RATIOS OF THE IRON PHASE OF METEORITES

Meteorite	Code No.	Wt. Specimen (gms)	Fraction	Wt. S (mgm)	δS^{33} (°/oo)	δS^{34} (°/oo)	δS^{36} (°/oo)
OCTAHEDRITES - coarse							
Canyon Diablo	CD1	60	H_2S	1.0	-0.1	-0.2	+1.2
- medium							
Carbo	Ca3	38	H_2S	4.1	+0.2	-0.2	+1.4
			Res S	Nil			
Clark County	CC1	10	H_2S	0.7	+0.4	+0.2	+3.5
	CC2	80	H_2S	1.5	+2.9	+0.9	+21.0
			Res S	3.8*	+1.4	+2.3	+5.0
	CC6	46	H_2S	36	-0.1	-0.5	-0.2
			Soln	0.8	+1.8	+3.1	-
			Solids	6.0		Lost	
Xiquipilco (Toluca)	X6	30	H_2S	15	-0.2	-0.3	-0.2
			Res S	1.3*	+0.7	+1.4	+2.9
NICKEL RICH ATAXITES							
Pinon	P2	89	H_2S	0.3	+1.0	+0.4	+15.2
			Res S				
Tlacotepic	T1	90	H_2S	0.5	+0.4	+0.0	+6.3
			Res S	Nil			

* Includes 1.0 mgm S as $CaSO_4 \cdot 2H_2O$ (δS^{34} = +0.5 °/oo) added as a carrier

S^{36} isotopes. On this basis a correction for possible isotopic fractionation effects has been made using the relationships above. Specifically we have calculated δS^{36}_{sp} and δS^{33}_{sp} defined by the following equations

$$\delta S^{36}_{sp} = \delta S^{36} - 1.9\ \delta S^{34}$$

$$\delta S^{33}_{sp} = \delta S^{33} - 0.51\ \delta S^{34}$$

These values of δS^{36}_{sp} and δS^{33}_{sp} have been listed in Table 4-2 along with the values of S^{33}_{sp}/S^{36}_{sp} calculated by multiplying the ratio $\delta S^{33}_{sp}/\delta S^{36}_{sp}$ by the ratio of the natural abundances S^{33}/S^{36} in the Canyon Diablo troilite standard. This relationship holds exactly provided that spallation produced S^{32} may be neglected. It will be seen from Table 4-2 that the values of S^{33}_{sp}/S^{36}_{sp} range between 3.0 and 6.7. This difference is much greater than the errors in the measurements. Table 4-3 gives the absolute quantities of S^{36}_{sp} and S^{33}_{sp} obtained. The values of S^{36}_{sp} µgm/gm and S^{33}_{sp} µgm/gm in the third and fourth columns are given by the equations

$$S^{36}_{sp} = \delta S^{36}_{sp}\ \frac{(1.6\text{x}10^{-4})\ \text{x}\ (\text{Wt S})}{\text{Wt. of specimen}}$$

$$S^{33}_{sp} = \delta S^{33}_{sp}\ \frac{(7.8\text{x}10^{-3})\ \text{x}\ (\text{Wt S})}{\text{Wt. of specimen}}$$

where $1.6\text{x}10^{-4}$ and $7.8\text{x}10^{-3}$ are the natural S^{36} and S^{33} contents of sulphur by weight. It can be seen that with the exception of the Carbo sample most of the error in the

TABLE 4-2

RELATIVE QUANTITIES AND RATIOS OF S^{36} AND S^{33} SPALLATION SULPHUR - EXPERIMENTAL

Sample		δS^{36}_{sp} (‰)	δS^{33}_{sp} (‰)	S^{33}_{sp}/S^{36}_{sp}*
Clark County	-CC1	+ 3.0 ± 1.0	+0.3 ± 0.2	-
	-CC2	+19.2 ± 1.0	+2.4 ± 0.2	6.7 ± 0.8
	-CC6	+ 0.8 ± 1.0	+0.1$_5$ ± 0.2	-
Pinon	-P2	14.4 ± 1.0	+0.8 ± 0.2	3.0 ± 0.8
Tlacotepic	-T1	+ 6.3 ± 1.0	+0.4 ± 0.2	3.4 ± 1.5
Carbo	-Ca3	+ 1.8 ± 1.0	+0.3 ± 0.2	-

* $S^{33}_{sp}/S^{36}_{sp} = (\delta S^{33}_{sp}/\delta S^{36}_{sp})\ (S^{33}/S^{36})_{Std}$ assuming natural S^{32} content not significantly increased by spallation.

TABLE 4-3

ABSOLUTE QUANTITIES OF S^{36} AND S^{33}

SPALLATION SULPHUR - EXPERIMENTAL

Sample	Quantity of S (mgm)	S^{36}_{sp} Yield (μgm/gm) x10^{-4}	S^{33}_{sp} Yield (μgm/gm) x10^{-4}
Clark County-CC1	0.7 ± 0.2	0.4 ± 0.3	$10\ ^{+12}_{-8}$
-CC2	1.5 ± 0.4	0.6 ± 0.2	3.6 ± 1.2
-CC6	36.0 ± 2	1 ± 1	8 ± 8
Pinon -P2	0.3 ± 0.1_5	0.08 ± 0.2	0.2 ± 0.1
Tlacotepic -T1	0.5 ± 0.1_5	0.06 ± 0.02	0.15 ± 0.1
Carbo -Ca3	4.1 ± 0.5	0.25 ± 0.15	2 ± 1.5

absolute yields of S^{36}_{sp} and S^{33}_{sp} is due to the large error in the determination of the small samples of sulphur obtained. Of the five meteorites shown in this Table the Clark County meteorite shows the highest spallation yields the values for S^{36}_{sp} and S^{33}_{sp} being almost ten times that of Pinon and Tlacotepic. This difference could be due either to Clark County being of higher cosmic ray exposure age or to the Pinon and Tlacotepic samples being located in the interior of meteorites of much larger size than the Clark County meteorite and thus being partially shielded from the cosmic radiation. In order to distinguish between these two effects it is necessary to consider the various mechanisms of spallation production in meteorites.

A number of methods of estimating cosmic ray spallation production rates have been used in the past. Two of these methods, which use experimental information on the cosmic radiation in different ways have been used in this work.

Arnold, Honda and Lal (1961) have used derived energy spectra of primary and secondary cosmic ray particles at 100gm/cm^2 and 10gm/cm^2 depths in a meteorite of radius 200gm/cm^2 combined with excitation functions, to yield estimated spallation production rates. They used an excitation function similar to that of Honda and Lal (1960), see Introduction equation (1-1), but normalised their curves to the measured spallation yields at 1 Gev, where available, rather than use the Rudstam formula (equation 1.2) in full. Table 4-4 lists a few of the results obtained by these workers.

Signer and Nier (1960, 1962) have used the cascade theory developed by Martin (1953) and later refined by Ebert and Wanke (1957). This theoretical model traces the development of the cascade, starting with primary particles of energies of a few Gev. It assumes that this primary cosmic ray radiation is attenuated exponentially without any essential change in the energy distribution. In the interaction of each primary particle with the target nucleus there are formed approximately three secondary particles of energy lower than the primary but still sufficiently high to interact with target nuclei. It is further assumed that the cross section for production of a given nuclei is only a slowly varying function of energy and may be approximated by two constants, one for primaries and one for secondaries. Signer and Nier (1960) in their calculation treated these two constants as free parameters and adjusted them to fit their experimental data for He^3, He^4, Ne^{21}, Ar^{38} in the Grant meteorite, on the basis that the exposure age of this meteorite is 600 million years.

TABLE 4-4

SPALLATION PRODUCTION RATES RELATIVE TO CHLORINE-36

(From Arnold, Honda and Lal, 1961)

Nuclide	Energy Spectrum "100gm/cm^2"	 "10gm/cm^2"	 "Primary"
He^3	27	23	17
He^4	135	108	63
Ne	0.73	0.81	1.3
Si^{32}	0.10	0.11	0.15
P^{32}	0.41	0.44	0.49
P^{33}	0.30	0.32	0.35
Cl^{36}	(1.0)	(1.0)	(1.0)
Ar^{36}	1.2	1.2	1.2
Ar^{38}	1.6	1.5	1.4
Ar^{40}	0.38	0.35	0.31
Ca^{41}	1.1	1.0	0.8
Mn^{54}	33.0	18.0	2.5
Fe^{55}	220	100	6.2

4.2 The Estimation of Spallation Sulphur Yields in Meteorites

As Arnold et al (1961) did not give spallation production rates for sulphur isotopes these have been evaluated using similar differential energy spectra as those used by Arnold et al (1961) together with values of the cross section for the particular species calculated from the Rudstam formula in the form which includes the excitation function (equation 1.2). The values $P=0.11E^{-0.64}$ (E in Gev) $R = 1.8$ and $S = 0.472$ were used in this calculation* and the integration was performed from 0.1 Gev to infinity using the analytical forms for the energy spectra given in Table 4-5. Non cumulative and cumulative yields calculated by this method are listed in Table 4-6, together with certain ratios of production yields.

It will be seen that the results which are in common with those given in Table 4-4 are in general agreement with those obtained by Arnold et al (1961). As in their case the results in columns two and three refer to depths of 100gm/cm^2 and 10gm/cm^2 in a meteorite of radius 200gm/cm^2 (26cm) while the fourth column refers to either a meteorite of very small mass or to the surface of an infinite body. It will be seen that in the mass range under consideration the ratio of light to heavy isotopes Ar^{36}/Ar^{38} and S^{33}/S^{36} decreases with increasing depth in the meteorite body. Comparison of the S^{33}/S^{36} predicted

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* It was assumed that the target was pure Fe^{56}

TABLE 4-5

ENERGY SPECTRA USED FOR THE ESTIMATION OF RELATIVE SPALLATION YIELDS

Description	0.1 - 3.0 Gev	Above 3.0 Gev
100gm/cm^2 depth	$0.57(0.2+E)^{-2.5}$	$(1+E)^{-2.5}$
10gm/cm^2 depth	$0.65(0.4+E)^{-2.5}$	$(1+E)^{-2.5}$
Primary	$1.4(1+1/E)^{-3.0*}$	$(1+E)^{-2.5}$

* $(1+E)^{-2.5}$ used between 1.0 and 3.0 Gev

production ratio with the experimental values of S^{33}_{sp}/S^{36}_{sp} given in Table 4-2 show that the Clark County result of 6.7 is in agreement with that predicted for the primary cosmic ray spectrum. The S^{33}_{sp}/S^{36}_{sp} values obtained for Pinon and Tlacotepic are lower than the predicted values given in Table 4-6. Since the ratio of light to heavy isotopes decreases with increasing depth in the meteorite these low results may indicate samples from very great depth in the meteorite.

TABLE 4-6

ESTIMATES OF SPALLATION PRODUCTION RATES OF SULPHUR ISOTOPES RELATIVE TO CHLORINE-36

Nuclide	Energy Spectrum "100gm/cm^2"	 "10gm/cm^2"	 "Primary"
Non-Cumulative			
P^{33}	0.37	0.38	0.42
S^{35}	0.54	0.55	0.56
S^{36}	0.17	0.17	0.17
Cl^{36}	(1.0)	(1.0)	(1.0)
Ar^{36}	0.16	0.16	0.16
S^{38}	0.002	0.002	0.001
Cl^{38}	0.27	0.27	0.25
Ar^{40}	0.44	0.42	0.36
Cumulative			
S^{32}	0.80	0.83	0.94
S^{33}	0.89	0.92	1.0
S^{34}	1.02	1.05	1.10
S^{36}	0.19	0.19	0.19
Ar^{36}	1.15	1.15	1.15
Ar^{38}	1.76	1.72	1.60
Ratios (Cumulative)			
S^{33}/S^{36}	4.7	4.9	5.4
Ar^{36}/Ar^{38}	0.65	0.67	0.72
S^{36}/Ar^{38}	0.10_5	0.11	0.11_5

It is possible to predict the absolute S^{36}_{sp} yield for the Clark County meteorite from the rare gas determinations of Signer and Nier (1962). According to them 69.0 $\times 10^{-8}$cc of Ar^{38} at STP have been produced per gram of meteorite. Since S^{36} is predicted to have a production rate one-tenth that of Ar^{38}, see Table 4-6, one obtains an S^{36} spallation yield of 6.9×10^{-8}cc/gm at STP i.e. 1.1×10^{-4} μgm/gm. This compares with the value (0.6 ± 0.2) $\times 10^{-4}$ μgm/gm determined experimentally and given in Table 4-3. Considering all the assumptions made in the calculations and the errors in the determinations this agreement is very good. Similarly the S^{36}_{sp} yield for the Carbo meteorite although limited in accuracy is of the order expected from the Ar^{38} value of 20×10^{-8}cc/gm at STP found by Signer and Nier (1962).

As Ar^{38} measurements have not so far been made on the Pinon and Tlacotepic meteorites it is necessary to compare the absolute S^{36}_{sp} yields obtained with He^3 and He^4 measurements made on these meteorites by Bauer (1963), see Table 4-7. Since these meteorite samples may originate from greater depths than 100gm/cm^2 this comparison has been made using cascade theory. From this theoretical model Signer and Nier (1960) have obtained curves of Ar^{38} production rates v He^3/He^4 ratios as a function of depth within and size of the preatmospheric body (the size of

TABLE 4-7

RARE GAS CONTENTS AND ESTIMATED EXPOSURE AGES * OF THE METEORITES STUDIED

Meteorite	Ar^{38}	He^3	He^4	He^3/He^4	%Ni	Exposure Age myr
	$\times 10^{-6}$	cm^3(STP)/gm				
Pinon		3.1	14.0	0.222	16.6	1140
Tlacotepic		5.4	21.9	0.249	16.2	870
Clark County	0.69	11.0	38.2	0.286	7.0	1030
Carbo (Centre)	0.17	2.8	12.2	0.232	~7	600
(Surface)	0.25	4.1	16.8	0.242		

* After Bauer (1963) and Signer and Nier (1962)

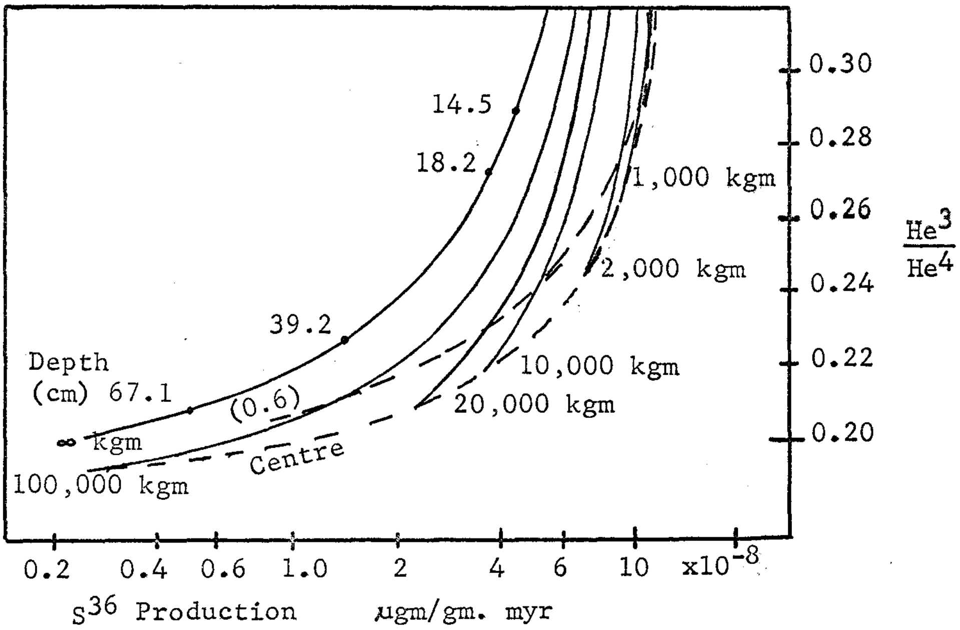

Fig. 4-1 Predicted Variation of He^3/He^4 with S^{36} production rate in Iron Meteorites of various sizes

the meteorite before entering the earth's atmosphere). Using the S^{36}/Ar^{38} ratios of 0.11_5 for the primary particles (from Table 4-6) and 0.09 for the secondary particles (from equation 1.2 at 0.3 Gev) similar curves have been obtained for S^{36} production rate v He^3/He^4 ratio, Fig. 4-1.

Using the curves in Fig. 4-1 with the data given in Table 4-7 it is seen that the He^3/He^4 ratios given for Pinon, Tlacotepic and Carbo meteorites indicate that these samples have come from depth within preatmospheric masses of greater than 6,000, 2,000 and 2,000 kgm respectively, while Clark County has either come from an intermediate depth in a 1,000 kgm body or else has been within approximately 15cm of the surface of a larger body. The Ar^{38} and Ne^{21} results of Signer and Nier (1962) would suggest that the former is the case. From the He^3/He^4 ratios and the estimated exposure age of the Pinon and Tlacotepic meteorite given in Table 4-7 it is predicted from Fig. 4-1 that there should be between (0.1 and 0.4) $\times 10^{-4}$ μgm/gm spallation S^{36} in the Pinon sample and between (0.15 and 0.5) $\times 10^{-4}$ μgm/gm spallation S^{36} in Tlacotepic. Comparison with the experimental results given in Table 4-3 show that although the Tlacotepic result is much lower than predicted the Pinon result is again in good agreement considering the assumptions and errors involved.

CONCLUSIONS - The results given above indicate that spallation S^{36} has definitely been found in three meteorites, Clark County, Pinon and Tlacotepic, and that spallation S^{33} is also in evidence. The S^{33}_{sp}/S^{36}_{sp} ratios found experimentally are in general agreement with theoretical predictions. With the exception of Tlacotepic these meteorites have given absolute S^{36} spallation yields which are in general agreement with predictions, based on the experimental results of spallation produced rare gases obtained by other workers. Further comparison will be possible when Ar^{38} results are available from the samples removed from the specimens used in this work.

APPENDIX A

THE RELATIONSHIP BETWEEN THE SULPHUR ISOTOPES RESULTING FROM CHEMICAL OR PHYSICAL FRACTIONATION

Although it will be shown that the resultant relationships are virtually independent of the mechanism of fractionation, it is necessary to treat separately the three main processes, chemical isotopic equilibria, kinetic isotope effects and the physical process of diffusion.

Equilibria constants for isotope exchange reactions may be calculated quite unambiguously once the characteristic vibration frequencies for the various species are known. A typical isotope exchange reaction may be written

$$aA_1 + bB_2 = aA_2 + bB_1$$

where the subscripts 1 and 2 indicate that the molecules A and B with one element as a common constituent contain only the light or the heavy isotope, respectively. For gaseous substances the equilibrium constant can be shown by statistical thermodynamics to be related to the partition function ratios by the relationship

$$K = \left[\frac{Q'_{A2}}{Q'_{A1}}\right]^a \Bigg/ \left[\frac{Q'_{B2}}{Q'_{B1}}\right]^b$$

the partition function being defined by the relationship

$$Q' = \sum_i g_i \exp \; (-e_i/kT)$$

Here the summation is over all the allowed energy levels of the molecules, and g_i is the statistical weight of the ith level.

The calculation of equilibrium constants therefore involves the direct calculation of partition function ratios for two isotopic species and is the product of two such ratios. Since the translational partition function is the same as the classical one at room temperature and the rotational partition function is classical at room temperature in all cases except hydrogen, these reduce in the partition function ratio to the ratios of masses and moments of inertia. By use of the Teller-Redlich product rule the moments of inertia and masses of the molecules are eliminated yielding a function depending only on the vibrational frequencies and the atomic masses.

$$\frac{Q_2'}{Q_1'} = \left[\frac{m_2}{m_1}\right]^{\frac{3}{2}} \cdot \frac{Q_2}{Q_1}$$

where * $Q = \frac{1}{s} \prod_i \frac{u_i \exp(-u_i/2)}{1 - \exp(-u_i)}$

*In the notation used here Q is a mathmatical convenience. Only Q_2/Q_1 has physical meaning.

s is the symmetry number of the isotopic species,

$$u_i = hv_i/kT$$

and the product is taken over the different vibration frequencies v_i of the molecules counting a g fold degenerate frequency g times. Since the masses m of the isotopically substituted atoms cancel in the calculation of the equilibrium constant it is usual to tabulate Q_2/Q_1 rather than Q_2'/Q_1'. Bigeleisen and Mayer (1947) and Bigeleisen (1958) have approximated the above relationship to

$$Q_2/Q_1 = (s_1/s_2)\ (1 + \Sigma G(u_i)\ \Delta u_i)$$

and $$\ln\ (Q_2/Q_1) = \ln(s_1/s_2) + \Sigma_i G(u_i) \Delta u_i)$$

Bigeleisen and Mayer have tabulated the function

$$G(u) = \frac{1}{2} - \frac{1}{u} + \frac{1}{\exp(u) - 1}$$

for values of u from 0 to 25.

Rees (1964) has noted that the first of the two equations above can under certain conditions give results differing considerably from the exact formula. We have confirmed this and prefer in the present work to use the second formula which omits one step in the approximations. It will be noted that this second formula is quoted in a footnote by Urey (1947) and presumably was the form which he preferred.

For a diatomic (X-Y) molecule the fundamental vibration frequency of vibration is given by

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}$$

where k is the force constant and m* is the reduced mass of the X-Y system i.e.

$$\frac{1}{m^*} = \frac{1}{m_x} + \frac{1}{m_y}$$

Defining $\mu_x = \frac{1}{m_x}$ and $\mu_y = \frac{1}{m_y}$ as the reciprocal masses we find

$$v = \frac{1}{2\pi} \sqrt{k(\mu_x + \mu_y)}$$

If X is isotopically substituted with a heavier atom of reciprocal mass $(\mu_x - \Delta\mu_x)$ then to a first approximation

$$\Delta v \propto \tfrac{1}{2}\Delta\mu_x$$

If the exact masses (Everling et al, 1960) are used to calculate the reciprocal masses of the stable sulphur isotopes S^{32}, S^{33}, S^{34}, S^{36} then it is found that

$$\Delta\mu_{(32-34)} = 1.94\ \Delta\mu_{(32-33)}$$

and

$$\Delta\mu_{(32-36)} = 1.89\ \Delta\mu_{(32-34)}$$

Since several approximations have been made above it was considered desirable to calculate predicted frequencies and hence S^{33}, S^{34} and S^{36}, for a number of molecules using the exact equation for the partition function ratios. Tables A-2 and A-3 show results calculated for the diatomic vapour molecules PbS and SiS respectively (Herzberg, 1950). In these tables the notation is as follows:

Q34/Q32 represents the partition function ratios of the S^{34} and S^{32} molecules

$$\delta 34 = (Q34/Q32 - 1)\times 10^3$$

and $D34 = \ln (Q34/Q32)\times 10^3$ corresponding to the two forms of the Bigeleisen equation above.

It will be seen that D36/D34 is essentially constant in the range 1.89 to 1.90 whereas the ratio δ36/δ34 takes on higher values than this for values of δ36 greater than approximately 15‰.

When a polyatomic molecule is considered the relations between Δv and Δu in general occur only through sum and product relations but essentially the same type of relationship as above may be expected. As an example of this we may consider the bent XY_2 molecule. The secular equation of this molecule may be solved to give the relationships

$$\lambda_1 + \lambda_2 = (C_d + C_{dd})\,(\mu_y + \mu_x\,(1 + \cos a)) + 2C_a\,(\mu_y + \mu_x\,(1 + \cos a)) - C_{da}\,\mu_x \sin a$$

$$\lambda_1 \cdot \lambda_2 = (2C_a(C_d + C_{dd}) - 4C_{da}^2)\,((\mu_x + \mu_y)^2 - \mu_x^2)$$

$$\lambda_3 = (C_d - C_{dd})\,(\mu_y + \mu_x\,(1 - \cos a))$$

where $\lambda = 4\pi^2 v^2$ and a is angle between the bonds.

The force constants for the bent XY_2 molecules SO_2 and H_2S have been calculated by Kivelson (1954) (SO_2), Smith and Linnet (1956) (H_2S) and by Gamo (1955) (H_2S) and are shown in Table A-1 together with values calculated from the D_2S zero order frequencies derived from the D_2S fundamental frequencies quoted by Haar et al (1955) and the more recent zero order H_2S frequencies determined by Allen and Plyler (1956).

TABLE A-1

FORCE CONSTANTS FOR SO_2 AND H_2S

Molecule	C_d	C_a	C_{dd}	C_{da}	Reference
SO_2	10.006	0.7933	0.0236	0.189	(f) - Kivelson (1954)
H_2S	4.4	0.55	-0.15	0.2	(f) - Smith, Linnett (1956)
H_2S	4.269	0.427	-0.042	0.15	(z) - Gamo (1955)
H_2S	4.282	0.439	-0.017	0.17	(z) - This work.

f = fundamental frequencies z = zero order frequencies

This last set of force constants has been used to calculate the H_2S partition function ratios shown in Table A-4 while Kivelson's data has been used to calculate the SO_2 partition function ratios in Table A-5. It will be noted that these results show some significant differences from the Q34/Q32 results of Cragg (1961). In the case of H_2S this appears to be due to his use of Smith and Linnett's force constants. These force constants are based on H_2S frequencies quoted by Herzberg (1945) which now appear to be in error. Cragg used Kivelson's force constants for SO_2 but obtained smaller frequency shifts than those shown in Table A-5, possibly due to an interchange of the zero order and fundamental frequencies of SO_2 in Table II of his thesis.

Tudge and Thode (1950) have calculated vibration frequencies for S^{32}, S^{34} and S^{36} atoms in sulphate ions and these frequencies have been used to calculate the partition function ratios shown in Table A-6. Pistorius (1958) has solved the secular equation of octahedreal molecules and has calculated the various constants for sulphur hexafluoride. After correction of an error in sign in this work pointed out by Chantry and Ewing (1962) this data has been used to calculate the partition function ratios of this molecule, see Table A-7. It will be seen from Tables A-2 to A-7 that the ratios D36/D34 and D34/D32 are essential constant at the values 1.90 and 1.94 for the above molecules.

TABLE A- 2 PARTITION FUNCTION RATIOS OF LEAD SULPHIDE

FREQUENCIES

32	426.94	1
33	421.31	1
34	415.96	1
36	405.92	1

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0	1.0051	5.11	1.0100	9.92	1.0190	18.78	1.945	1.941	1.902	1.894
50	1.0037	3.73	1.0073	7.23	1.0138	13.69	1.944	1.940	1.899	1.893
100	1.0028	2.83	1.0055	5.50	1.0105	10.40	1.943	1.940	1.897	1.892
150	1.0022	2.22	1.0043	4.31	1.0082	8.16	1.942	1.940	1.896	1.892
200	1.0018	1.79	1.0035	3.47	1.0066	6.57	1.941	1.940	1.895	1.892
250	1.0015	1.47	1.0029	2.85	1.0054	5.40	1.941	1.940	1.894	1.891
300	1.0012	1.23	1.0024	2.39	1.0045	4.51	1.941	1.939	1.893	1.891
350	1.0010	1.04	1.0020	2.02	1.0038	3.83	1.940	1.939	1.893	1.891
400	1.0009	0.90	1.0017	1.74	1.0033	3.29	1.940	1.939	1.893	1.891
450	1.0008	0.78	1.0015	1.51	1.0029	2.85	1.940	1.939	1.892	1.891
500	1.0007	0.68	1.0013	1.32	1.0025	2.50	1.940	1.939	1.892	1.891
550	1.0006	0.60	1.0012	1.17	1.0022	2.21	1.940	1.939	1.892	1.891
600	1.0005	0.54	1.0010	1.04	1.0020	1.96	1.940	1.939	1.892	1.891
650	1.0005	0.48	1.0009	0.93	1.0018	1.76	1.940	1.939	1.892	1.891
700	1.0004	0.43	1.0008	0.84	1.0016	1.58	1.940	1.939	1.891	1.891
750	1.0004	0.39	1.0008	0.76	1.0014	1.43	1.939	1.939	1.891	1.891
800	1.0004	0.36	1.0007	0.69	1.0013	1.30	1.939	1.939	1.891	1.891
850	1.0003	0.32	1.0006	0.63	1.0012	1.19	1.940	1.939	1.891	1.891
900	1.0003	0.30	1.0006	0.58	1.0011	1.09	1.939	1.939	1.891	1.891
950	1.0003	0.27	1.0005	0.53	1.0010	1.01	1.939	1.939	1.891	1.891
1000	1.0003	0.25	1.0005	0.49	1.0009	0.93	1.939	1.939	1.891	1.891

TABLE A- 3 PARTITION FUNCTION RATIOS OF SILICON SULPHIDE

FREQUENCIES

32	746.94	1
33	741.64	1
34	736.66	1
36	727.39	1

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0	1.0074	7.40	1.0144	14.32	1.0275	27.13	1.944	1.937	1.906	1.894
50	1.0056	5.56	1.0108	10.77	1.0206	20.39	1.941	1.936	1.902	1.893
100	1.0043	4.32	1.0084	8.37	1.0160	15.83	1.940	1.936	1.899	1.892
150	1.0035	3.44	1.0067	6.67	1.0127	12.62	1.939	1.936	1.898	1.892
200	1.0028	2.81	1.0054	5.43	1.0103	10.27	1.938	1.936	1.896	1.892
250	1.0023	2.33	1.0045	4.50	1.0086	8.52	1.937	1.935	1.895	1.891
300	1.0020	1.96	1.0038	3.79	1.0072	7.17	1.937	1.935	1.894	1.891
350	1.0017	1.67	1.0032	3.23	1.0061	6.11	1.937	1.935	1.894	1.891
400	1.0014	1.44	1.0028	2.79	1.0053	5.27	1.936	1.935	1.893	1.891
450	1.0013	1.25	1.0024	2.43	1.0046	4.59	1.936	1.935	1.893	1.891
500	1.0011	1.10	1.0021	2.13	1.0040	4.03	1.936	1.935	1.892	1.891
550	1.0010	0.98	1.0019	1.89	1.0036	3.57	1.936	1.935	1.892	1.890
600	1.0009	0.87	1.0017	1.68	1.0032	3.18	1.936	1.935	1.892	1.890
650	1.0008	0.78	1.0015	1.51	1.0029	2.85	1.936	1.935	1.892	1.890
700	1.0007	0.70	1.0014	1.36	1.0026	2.57	1.935	1.935	1.891	1.890
750	1.0006	0.64	1.0012	1.23	1.0023	2.33	1.935	1.935	1.891	1.890
800	1.0006	0.58	1.0011	1.12	1.0021	2.12	1.935	1.935	1.891	1.890
850	1.0005	0.53	1.0010	1.03	1.0019	1.94	1.935	1.935	1.891	1.890
900	1.0005	0.49	1.0009	0.94	1.0018	1.78	1.935	1.935	1.891	1.890
950	1.0004	0.45	1.0009	0.87	1.0016	1.64	1.935	1.935	1.891	1.890
1000	1.0004	0.41	1.0008	0.80	1.0015	1.52	1.935	1.935	1.891	1.890

TABLE A- 4 PARTITION FUNCTION RATIOS OF HYDROGEN SULPHIDE

FREQUENCIES

32	2614.46	1	1182.51	1	2627.19	1
33	2613.55	1	1181.90	1	2625.97	1
34	2612.70	1	1181.31	1	2624.83	1
36	2611.14	1	1180.24	1	2622.73	1

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0	1.0059	5.89	1.0115	11.44	1.0218	21.60	1.946	1.940	1.898	1.889
50	1.0048	4.79	1.0093	9.28	1.0177	17.54	1.944	1.940	1.897	1.889
100	1.0040	3.98	1.0077	7.72	1.0147	14.58	1.943	1.940	1.895	1.889
150	1.0034	3.37	1.0066	6.53	1.0124	12.34	1.943	1.940	1.894	1.889
200	1.0029	2.89	1.0056	5.61	1.0106	10.59	1.942	1.939	1.893	1.889
250	1.0025	2.51	1.0049	4.87	1.0092	9.20	1.942	1.939	1.893	1.889
300	1.0022	2.20	1.0043	4.27	1.0081	8.06	1.941	1.939	1.892	1.889
350	1.0019	1.94	1.0038	3.77	1.0071	7.12	1.941	1.939	1.892	1.888
400	1.0017	1.73	1.0034	3.35	1.0064	6.33	1.940	1.939	1.891	1.888
450	1.0015	1.55	1.0030	3.00	1.0057	5.67	1.940	1.939	1.891	1.888
500	1.0014	1.39	1.0027	2.70	1.0051	5.10	1.940	1.939	1.891	1.888
550	1.0013	1.26	1.0024	2.44	1.0046	4.61	1.940	1.939	1.890	1.888
600	1.0011	1.14	1.0022	2.22	1.0042	4.19	1.939	1.938	1.890	1.888
650	1.0010	1.04	1.0020	2.02	1.0038	3.82	1.939	1.938	1.890	1.888
700	1.0010	0.95	1.0019	1.85	1.0035	3.49	1.939	1.938	1.890	1.888
750	1.0009	0.88	1.0017	1.70	1.0032	3.21	1.939	1.938	1.890	1.888
800	1.0008	0.81	1.0016	1.56	1.0030	2.95	1.939	1.938	1.890	1.888
850	1.0007	0.75	1.0014	1.44	1.0027	2.73	1.939	1.938	1.889	1.888
900	1.0007	0.69	1.0013	1.34	1.0025	2.53	1.939	1.938	1.889	1.888
950	1.0006	0.64	1.0012	1.24	1.0023	2.35	1.939	1.938	1.889	1.888
1000	1.0006	0.60	1.0012	1.16	1.0022	2.18	1.939	1.938	1.889	1.888

TABLE A- 5 PARTITION FUNCTION RATIOS OF SULPHUR DIOXIDE

FREQUENCIES

32	517.56	1	1151.37	1	1360.33	1
33	515.30	1	1147.63	1	1351.48	1
34	513.13	1	1144.13	1	1343.13	1
36	508.91	1	1137.75	1	1327.63	1

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0	1.0262	25.87	1.0515	50.23	1.1000	95.29	1.966	1.942	1.941	1.897
50	1.0204	20.21	1.0400	39.24	1.0772	74.40	1.960	1.941	1.930	1.896
100	1.0163	16.20	1.0319	31.45	1.0614	59.60	1.956	1.941	1.922	1.895
150	1.0133	13.25	1.0261	25.72	1.0499	48.73	1.953	1.940	1.917	1.895
200	1.0111	11.02	1.0216	21.38	1.0413	40.50	1.950	1.940	1.912	1.894
250	1.0093	9.30	1.0182	18.03	1.0347	34.15	1.948	1.940	1.909	1.894
300	1.0080	7.94	1.0155	15.39	1.0296	29.14	1.947	1.940	1.906	1.893
350	1.0069	6.85	1.0134	13.28	1.0255	25.13	1.946	1.940	1.904	1.893
400	1.0060	5.96	1.0116	11.56	1.0221	21.88	1.945	1.939	1.902	1.893
450	1.0052	5.23	1.0102	10.15	1.0194	19.21	1.944	1.939	1.901	1.892
500	1.0046	4.63	1.0090	8.98	1.0171	16.99	1.943	1.939	1.900	1.892
550	1.0041	4.12	1.0080	7.99	1.0152	15.12	1.943	1.939	1.899	1.892
600	1.0037	3.69	1.0072	7.16	1.0136	13.54	1.942	1.939	1.898	1.892
650	1.0033	3.33	1.0065	6.45	1.0123	12.20	1.942	1.939	1.897	1.892
700	1.0030	3.01	1.0059	5.84	1.0111	11.04	1.942	1.939	1.896	1.892
750	1.0027	2.74	1.0053	5.31	1.0101	10.04	1.941	1.939	1.896	1.891
800	1.0025	2.50	1.0049	4.84	1.0092	9.16	1.941	1.939	1.895	1.891
850	1.0023	2.29	1.0044	4.44	1.0084	8.40	1.941	1.939	1.895	1.891
900	1.0021	2.11	1.0041	4.08	1.0078	7.72	1.941	1.939	1.895	1.891
950	1.0019	1.94	1.0038	3.77	1.0071	7.12	1.940	1.939	1.894	1.891
1000	1.0018	1.80	1.0035	3.49	1.0066	6.59	1.940	1.939	1.894	1.891

TABLE A- 6 PARTITION FUNCTION RATIOS OF SULPHATE IONS

FREQUENCIES

32	1113.60	3	618.90	3
33	0.	3	0.	3
34	1097.56	3	615.55	3
36	1083.21	3	612.30	3

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0			1.1011	96.28	1.2006	182.81			1.985	1.899
50			1.0772	74.32	1.1515	141.03			1.963	1.897
100			1.0607	58.94	1.1183	111.78			1.948	1.896
150			1.0489	47.77	1.0948	90.54			1.937	1.896
200			1.0402	39.42	1.0775	74.69			1.929	1.895
250			1.0336	33.02	1.0646	62.56			1.923	1.894
300			1.0284	28.04	1.0545	53.10			1.918	1.894
350			1.0244	24.08	1.0466	45.59			1.914	1.893
400			1.0211	20.88	1.0403	39.54			1.911	1.893
450			1.0184	18.28	1.0352	34.60			1.908	1.893
500			1.0163	16.12	1.0310	30.51			1.906	1.893
550			1.0144	14.32	1.0275	27.10			1.905	1.892
600			1.0129	12.80	1.0245	24.22			1.903	1.892
650			1.0116	11.51	1.0220	21.78			1.902	1.892
700			1.0105	10.40	1.0199	19.68			1.901	1.892
750			1.0095	9.44	1.0180	17.87			1.900	1.892
800			1.0086	8.61	1.0164	16.29			1.899	1.892
850			1.0079	7.88	1.0150	14.91			1.898	1.892
900			1.0073	7.24	1.0138	13.70			1.898	1.892
950			1.0067	6.68	1.0127	12.63			1.897	1.892
1000			1.0062	6.17	1.0117	11.68			1.897	1.892

TABLE A- 7 PARTITION FUNCTION RATIOS OF SULPHUR HEXAFLUORIDE

FREQUENCIES

32	946.94	3	614.93	3
33	938.11	3	613.33	3
34	929.81	3	611.72	3
36	914.54	3	608.47	3

T	Q33/Q32	D33	Q34/Q32	D34	Q36/Q32	D36	δ34/δ33	D34/D33	δ36/δ34	D36/D34
0	1.0497	48.50	1.0989	94.28	1.1960	178.99	1.989	1.944	1.983	1.899
50	1.0377	37.02	1.0746	71.93	1.1462	136.45	1.977	1.943	1.960	1.897
100	1.0295	29.09	1.0581	56.49	1.1130	107.09	1.969	1.942	1.945	1.896
150	1.0237	23.39	1.0465	45.42	1.0899	86.06	1.963	1.942	1.934	1.895
200	1.0194	19.18	1.0379	37.24	1.0731	70.53	1.959	1.941	1.926	1.894
250	1.0161	15.99	1.0315	31.04	1.0605	58.77	1.956	1.941	1.920	1.894
300	1.0136	13.52	1.0266	26.24	1.0509	49.67	1.953	1.941	1.916	1.893
350	1.0116	11.57	1.0227	22.46	1.0434	42.50	1.951	1.940	1.912	1.893
400	1.0101	10.01	1.0196	19.42	1.0374	36.75	1.949	1.940	1.909	1.892
450	1.0088	8.74	1.0171	16.96	1.0326	32.08	1.948	1.940	1.907	1.892
500	1.0077	7.69	1.0150	14.93	1.0286	28.24	1.947	1.940	1.905	1.892
550	1.0068	6.82	1.0133	13.24	1.0254	25.04	1.946	1.940	1.903	1.892
600	1.0061	6.09	1.0119	11.81	1.0226	22.35	1.945	1.940	1.902	1.892
650	1.0055	5.47	1.0107	10.61	1.0203	20.07	1.945	1.940	1.900	1.891
700	1.0049	4.94	1.0096	9.58	1.0183	18.11	1.944	1.940	1.899	1.891
750	1.0045	4.48	1.0087	8.69	1.0166	16.43	1.944	1.940	1.899	1.891
800	1.0041	4.08	1.0079	7.91	1.0151	14.97	1.943	1.940	1.898	1.891
850	1.0037	3.73	1.0073	7.24	1.0138	13.69	1.943	1.940	1.897	1.891
900	1.0034	3.43	1.0067	6.65	1.0127	12.57	1.943	1.939	1.897	1.891
950	1.0032	3.16	1.0061	6.13	1.0117	11.58	1.942	1.939	1.896	1.891
1000	1.0029	2.92	1.0057	5.66	1.0108	10.71	1.942	1.939	1.896	1.891

KINETIC ISOTOPE EFFECTS - Kinetic isotope effects are normally described in terms of Eyring's absolute reaction rate theory (Glasstone, Laidler and Eyring, 1941). This theory considers that in the reaction

$$A + BC \longrightarrow AB + C$$

an activated complex state (ABC)* is formed which is in quasi-equilibrium with the reactants. The vibrational mode of the activated complex state along the reaction coordinate is imaginary in frequency and is therefore removed from the partition function expression and treated as a translational motion. The remaining terms of the partition function are designated by Q'^{+}_{ABC}. By this means the rate of reaction k' is calculated as

$$k' = \frac{kT}{h} \quad \frac{Q'^{+}_{ABC}}{Q'_A \; Q'_{BC}} \; \kappa$$

where k is Boltzmann's constant

h is Plánck's constant

and κ is the transmission coefficient.

Although other equations have been used in the past for isotopic work (Bigeleisen, 1948) the above equation is now accepted (Bigeleisen and Wolfsberg, 1958) as the starting point for the consideration of kinetic isotope effects.

If A in the above reaction has two isotopes A_1 and A_2 then assuming κ to be identical for both isotopes the ratio of the rate constants k_1' and k_2' is

$$\frac{k_1'}{k_2'} = \frac{Q'^{+}_{1ABC} \cdot Q'_{2A}}{Q'^{+}_{2ABC} \cdot Q'_{1A}}$$

Application of the Teller Redlich product rule as in the equilibrium isotope calculations yields

$$\frac{k_1'}{k_2'} = \frac{v^+_{1L}}{v^+_{2L}} . \left[\frac{Q^+_1}{Q^+_2}\right]_{ABC} \cdot \left[\frac{Q_2}{Q_1}\right]_A$$

Where $Q^{+\cdot}$ is defined similarly to Q but does not contain the term corresponding to the imaginary vibrational frequency v^+_L which now appears as a separate term. Expressed in terms of the Bigeleisen approximation this equation becomes

$$\frac{k_1'}{k_2'} = \frac{s_2}{s_1} \frac{v^+_{1L}}{v^+_{2L}} \left[1 + \sum_i^{3N-6} G(u_i)\Delta u_i - \sum_i^{3N-7} G(u_i^+)\Delta u_i^+ \right]$$

The imaginary frequencies are normally evaluated either by assuming their ratio to be some function of the reduced masses or by considering the activated complex in the same way as the central atom of a linear triatomic molecule (Rees, 1964). Thus relationships between δS^{33}, δS^{34} and δS^{36}, resulting from fractionation due to kinetic isotope effects are seen to rely on the same basic arguments as those used in the consideration of isotopic equilibrium fractionation and the same results may be expected.

The velocity of a molecule in diffusion processes is proportional to the inverse square root of its mass and thus fractionation due to diffusion processes will yield essentially similar relationships between δS^{33}, δS^{34} and δS^{36} as was obtained for the frequency shifts of isotopic diatomic molecules.

We thus conclude that independent of the mechanism of fractionation the following relationships should hold within 1% for δS^{34} values less than 15‰

$$\delta S^{36} = 1.90 \quad \delta S^{34}$$
$$\delta S^{34} = 1.94 \quad \delta S^{33}$$

For δS^{34} values greater than 15‰ the logarithmic form of the δ-value allows this relationship to be used at higher levels of fractionation.

APPENDIX B

CALCULATION OF δ-VALUES FROM MASS SPECTROMETER RESULTS

SULPHUR DIOXIDE - With the collector system used in this work the ratios obtained in SO_2^+ measurements are

$$R(65) = \frac{\text{mass } 65}{\text{mass } 64}$$

$$R(66) = \frac{\text{mass } 66}{\text{mass } 64 + \text{mass } 65}$$

$$R(68) = \frac{\text{mass } 68}{\text{mass } 64 + \text{mass } 65 + \text{mass } 66}$$

The SO_2^+ ions which give peaks at these masses are

$$\text{mass } 64 = S^{32}O^{16}O^{16}$$

$$\text{mass } 65 = S^{33}O^{16}O^{16} + 2S^{32}O^{16}O^{17}$$

$$\text{mass } 66 = S^{34}O^{16}O^{16} + 2S^{32}O^{16}O^{18} + (S^{32}O^{17}O^{17} + 2S^{33}O^{16}O^{17})$$

$$\text{mass } 68 = S^{36}O^{16}O^{16} + 2S^{34}O^{16}O^{18} + (S^{32}O^{18}O^{18} + S^{34}O^{17}O^{17} + 2S^{33}O^{17}O^{18})$$

Since $S^{33}/S^{32} = 0.008$, $S^{34}/S^{32} = 0.045$, $S^{36}/S^{32} = 0.0015$ $O^{17}/O^{16} = 0.00039$ and $O^{18}/O^{16} = 0.00205$ it is seen that the species shown in parenthesis are sufficiently small to be neglected in the calculations. Some ions may occur in two ways e.g. $S^{32}O^{16}O^{17}$ and $S^{32}O^{17}O^{16}$ but for clarity these are shown as two ions of a single species.

Substituting these ions into the ratios above and dividing by $S^{32}O^{16}O^{16}$ we obtain

$$R(65) = S^{33}/S^{32} + 2O^{17}/O^{16} \tag{B.1}$$

$$R(66) = \frac{S^{34}/S^{32} + 2O^{18}/O^{16}}{1 + S^{33}/S^{32}} \tag{B.2}$$

$$R(68) = \frac{S^{36}/S^{32} + 2(O^{18}/O^{16})\,(S^{34}/S^{32})}{1 + S^{34}/S^{32} + (S^{33}/S^{32} + 2O^{18}/O^{16})} \tag{B.3}$$

These equations can all be expressed in the general form

$$R = \frac{A + B}{1 + C} \tag{B.4}$$

If we define

$$\delta R = \frac{R_x}{R_s} - 1 \tag{B.5}$$

i.e. $$R_x = R_s\,(1 + \delta R) \tag{B.6}$$

(x refers to the unknown sample and s to the standard sample)

and work in δ-units of parts per part then substitution of equation B.4 into equation B.5 gives

$$\delta R = \frac{(A_x + B_x)/(1 + C_x)}{(A_s + B_s)/(1 + C_s)} - 1$$

$$= \frac{A_x}{A_s} \cdot \frac{1 + B_x/A_x}{1 + B_s/A_s} \cdot \frac{1 + C_s}{1 + C_x} - 1$$

i.e. $$\delta R = (1+\delta A)\,\frac{\{1+B_s(1+\delta B)/A_s(1+\delta A)\}\{1+C_s\}}{\{1 + B_s/A_s\}\{1 + C_s\,(1 + \delta C)\}} - 1 \tag{B.7}$$

where δA, δB and δC are defined in the same way as δR (equation B.5)

Ignoring second order δ terms, equation B.7 may be expanded to give

$$\delta R = \delta A + \frac{B_s/A_s\ (\delta B - \delta A)}{1 + B_s/A_s} - \frac{C_s\ \delta C}{1+C_s} \qquad (B.8)$$

$$\text{i.e. } \delta A = (1+B_s/A_s)\delta R - (B_s/A_s)\delta B + C_s\left[(1+B_s/A_s)/(1+C_s)\right]\delta C \qquad (B.9)$$

δS^{33} EVALUATION

$$A = S^{33}/S^{32}, \quad B = 2O^{17}/O^{16}, \quad C = 0$$

Hence from equation B.9

$$\delta S^{33} = 1.098\ \delta(65) - 0.098\ \delta O^{17} \qquad (B.10)$$

If $\delta O^{17} = 0.5\ \delta O^{18}$ then

$$\delta S^{33} = 1.098\ \delta(65) - 0.05\ \delta O^{18} \qquad (B.11)$$

δS^{34} EVALUATION

$$A = S^{34}/S^{32}, \quad B = 2O^{18}/O^{16} \quad C = S^{33}/S^{32}$$

Hence from equation B.9

$$\delta S^{34} = 1.091\ \delta(66) - 0.091\ \delta O^{18} + 0.008\ \delta S^{33} \qquad (B.12)$$

For samples which approximately obey the relationship $\delta S^{33} = 0.51\,\delta S^{34}$ we may write this as

$$\delta S^{34} = 1.095\ \delta(66) - 0.091\ \delta O^{18} \qquad (B.13)$$

δS^{36} EVALUATION

$$A = S^{36}/S^{32}, \quad B = 2(O^{18}/O^{18})(S^{34}/S^{32}) \quad C = S^{34}/S^{32}$$

Now $B_x = 2(O^{18}/O^{16})_x\,(S^{34}/S^{32})_x$

Hence $(1+\delta B)B_s = (1+\delta O^{18})(O^{18}/O^{16})_s(1+\delta S^{34})(1+S^{34}/S^{32})_s$

thus $\delta B = \delta O^{18} + \delta S^{34} \quad (+\delta O^{18}\,\delta S^{34})$

Substitution in equation B.9 gives

$$\delta S^{36} = 2.23\ \delta(68) - 1.13\ \delta S^{34} - 1.23\ \delta O^{18} \qquad (B.14)$$

For samples whose -values fit the relationship $\delta S^{36} = 1.9\ \delta S^{34}$ we may write this equation as

$$\delta S^{36} = 1.40\ \delta(68) - 0.78\ \delta O^{18} \qquad (B.15)$$

Corrections for the isotopic difference between the secondary standard used in the measurements and the primary Canyon Diablo standard were made using the method described by Hulston (1962).

SULPHUR HEXAFLUORIDE - The ratios measured in the analysis of sulphur hexafluoride samples are

$$R\ (128) = \frac{S^{33}(F^{19})_5}{S^{32}(F^{19})_5} = \frac{S^{33}}{S^{32}} \qquad (B.16)$$

$$R\ (129) = \frac{S^{34}(F^{19})_5}{S^{32}(F^{19})_5 + S^{33}(F^{19})_5} = \frac{S^{34}}{S^{32}+S^{33}} \qquad (B.17)$$

$$R\ (131) = \frac{S^{36}(F^{19})_5 + TS^{34}(F^{19})_5}{S^{32}(F^{19})_5 + S^{33}(F^{19})_5 + S^{34}(F^{19})_5}$$

$$= \frac{S^{36} + TS^{34}}{S^{32} + S^{33} + S^{34}} \qquad (B.18)$$

where T is the fraction of the mass 129 peak which is added to the mass 131 peak by "tailing".

δS^{33} EVALUATION

Obviously

$$\delta S^{33} = \delta\ (128) \tag{B.19}$$

δS^{34} EVALUATION

Again using the general form of these equations (equation B.4) we have

$$A = S^{34}/S^{32}, \quad B = 0, \quad C = S^{33}/S^{32}$$

Hence from equation B.9

$$\delta S^{34} = \delta\ (129) + 0.008\ \delta S^{33} \tag{B.20}$$

For samples which follow the relationship $\delta S^{33} = 0.51\ \delta S^{34}$ we have

$$\delta S^{34} = 1.004\ \delta\ (129) \tag{B.21}$$

For the meteorite samples analysed in this work it is adequate to use $\delta S^{34} = \delta\ (129)$ (B.22)

δS^{36} EVALUATION

$$A = S^{36}/S^{32}, \quad B = TS^{34}/S^{32}, \quad C = S^{34}/S^{32}$$

Substitution in equation B.9 gives

$$\delta S^{36} = (1+TS^{34}/S^{36})\delta(131) - TS^{34}/S^{36}\delta S^{34}$$
$$+0.043(1+TS^{34}/S^{36})\ \delta S^{34}$$

i.e. $$\delta S^{36} = (1+Z)\delta(131) - (0.96Z - 0.043)\delta S^{34} \tag{B.23}$$

where $Z = TS^{34}/S^{36}$ represents the "tailing" contribution of mass 129 to mass 131 as a fraction of the S^{36} peak.

If $Z = 0$ i.e. negligible tailing

$$\delta S^{36} = \delta(131) + 0.043\, \delta S^{34} \qquad (B.24)$$

or $$\delta S^{36} = 1.02\, \delta(131) \qquad (B.25)$$

for samples which fit the relationship $\delta S^{36} = 1.9\, \delta S^{34}$

If $Z = 0.04$ i.e. about 4% of the mass 131 peak is due to tailing then

$$\delta S^{36} = 1.04\, \delta(131) \qquad (B.26)$$

i.e. the term in δS^{34} becomes vanishingly small. As the tailing was estimated to be of the order of 4% of the mass 131 peak, equation B.26 was used for most of the samples analysed in this work.

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