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THE ISOTOPIC ABUNDANCE AND CONTENT OF SULFUR IN METEORITES *

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UNPUBLISHED PRELIMINARY DATA

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ABSTRACT

Twenty meteorites were studied in the iron (Hexahedrites and Octahedrites) and stony (Enstatite achondrite, Carbonaceous, Enstatite and Olivine chondrites) families. The iron meteorites contain troilite as the chief sulfur component and the δS^{34} ranges from 0 to + 0.6°/oo with respect to Canyon Diablo troilite. Stony meteorites demonstrate a wide variety of sulfur compounds including water and acid soluble sulfides, elemental sulfur, water and acid soluble sulfates and unidentified components soluble only in aqua regia. The δS^{34} content of the isolated compounds varies from +2.5 to -5.5°/oo with respect to Canyon Diablo. The weighted average for all components of each meteorite, however, falls within ±1°/oo of Canyon Diablo. The S^{33} distribution closely follows S^{34}. The data suggest that differentiations have occurred in the meteorites starting from a single source

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of sulfur. There is no evidence for biological activity having occurred in the meteorite, either from the distribution of sulfur compounds or from the isotope abundance data. author

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INTRODUCTION

Sulfur is a common and often important constituent of many meteorites, and since it is found in a number of minerals and sometimes occurs in various valence states in one meteorite specimen, its distribution may closely reflect the history of the meteorite. Isotope studies in the past on meteoritic sulfur have generally shown very constant values for the S^{34}/S^{32} ratio (Macnamara and Thode, 1950; Vinogradov, Chupaskin and Grinenko, 1957; Ault and Kulp, 1959; Thode, Monster and Dunford, 1961; Jensen and Nakai, 1962). Most reliable results fall within δS^{34} $\pm 1.0^{\circ}/oo$ of an average value. As a consequence, it has been realized that meteoritic sulfur can be used as a primary standard for sulfur isotope studies and all such results are now usually expressed relative to the meteoritic sulfur being used as the standard by the particular investigator. As slight variations do exist, it has been suggested (Ault & Jensen, 1962) that only Canyon Diablo troilite be chosen as the primary standard.

Isotope studies on meteoritic sulfur have been conducted either with the troilite nodules of iron meteorites, or the total components in the stony meteorites from which sulfur dioxide was separated by combustion. Small significant variations in the isotope ratios of the order of 0.2°/oo were detected by Thode, Monster and Dunford (1961) whereas larger variations are generally thought to result from experimental errors.

The significance of this fact goes beyond the use of meteoritic sulfur as merely a suitable standard for mass spectrometry, and indicates that sulfur had undergone no fractionation in its extra-terrestrial history and should therefore also depict the original sulfur isotope ratio of the earth prior to the formation of a hydrosphere. All subsequent processes on earth from igneous activity to biological processes, in which sulfur compounds are involved, must therefore relate back to the average S^{34}/S^{32} ratio of meteorites.

Isotopic measurements by Dufresne and Thode (Anders, 1963) on sulfate and elemental sulfur from the carbonaceous chondrite Orgueil, indicated the former to be δS^{34} - 1.3°/oo and the latter +3.04°/oo. Jensen and Nakai (1962) found an average of δS^{34} - 2.1°/oo for a magnesium sulfate sample provided them by Dr. Brian Mason and isolated by Lawrence Smith (1876), presumably about eighty years ago.

As little attempt had been made to separate the various sulfur constituents from meteorites for analytical and isotope measurements, the study was initiated in this direction. It was hoped to characterize some of the major sulfur constituents and at the same time separate them. These compounds were then prepared for isotope analysis by mass spectrometry. A preliminary report of the results has been given elsewhere (Kaplan & Hulston, 1963). The investigation attempts to answer (a) whether individual sulfur compounds are fractionated relative to each other and to the weighted average, (b) if any large fractionations exist similar to these found on earth, (c) if there is a trend in the fractionation pattern which might indicate biological activity, and (d) what evidence exists that isotopic variations may have occurred during nucleogenesis.

Over twenty meteorites were investigated, representing types in which sulfur is often an important constituent.

METHODS

Pre-analytical treatment

Since most of the meteorites were obtained from museum or university collections, their history during storage was generally not accurately known except for the most recent falls. Whenever possible specimens were chosen not to include any fusion crust or identification markings, which are quite common on museum samples. Any obvious impurities were removed with a clean steel chisel and the specimen wiped carefully with glazed paper to remove adhering particles. Stony meteorites were ground to a fine powder with an alumina mortar and pestle.

Chondrules were removed from chondrites by gently crushing the meteorite, picking out the larger spheres and rolling out the smaller ones on an inclined sheet of glazed paper. When spherical particles no longer separated easily from the matrix, the material was studied with a low power binocular reflecting microscope and chondrules or sections of chondrules selected with fine-tipped forceps. The specimen was further crushed and the process repeated several times until the matrix was of a fine silt size. The chondrules were cleaned of loosely adhering matrix with a low powered ultrasonic disintegrator.

Troilite nodules were removed from the iron meteorites with a dental drill.

Sulfur analysis

Carbonaceous chondrites were generally dried over phosphorous pentoxide under vacuum prior to analysis, other meteorites were not because of their low water content, but a separate fraction was dried in order to present all values relative to the dry weight.

Iron meteorites.--The sulfide was removed from the troilite chips by action of hot 4N hydrochloric acid in a closed vessel. Oxygen-free nitrogen was continuously blown in to remove the liberated hydrogen sulfide which was absorbed in a 5N silver nitrate solution. The resulting silver sulfide was filtered on a sintered glass filter, washed with water, then with a 1:1 solution of ammonium hydroxide and then water again. It was dried at 105°C and was then stored in preparation for combustion to sulfur dioxide.

In the case of Coahuila the residue left after HCl reaction was oxidized with aqua regia and the sulfate precipitated as barium sulfate from the filtrate.

Carbonaceous and other chondrites.--An attempt was made to characterize as many of the groups of sulfur compounds as possible. The sequential steps generally followed were:

1. Extraction with 60:40 benzene-acetone. The extraction was generally carried out for 24 hours either in a Soxhlet apparatus or by refluxing the meteorite powder directly in the solvent. Since the sample weight was almost always under 10 grams, this method was considered sufficiently efficient.

The solvent was then either directly evaporated, to yield elemental sulfur, as in the case of Orgueil 2 (HU 4), Richardton and Karoonda, or else passed down a colloidal copper column (Blumer, 1957) which preferentially removed the sulfur as copper sulfide. The sulfur and copper sulfide were oxidized first with bromine and then aqua regia to sulfate. This was precipitated as barium sulfate.

2. Extraction of water-soluble sulfates. In the carbonaceous chondrites an attempt was made to extract water-soluble sulfates by refluxing the specimens, after organic solvent extraction, with deoxygenated water from 8 to 24 hours. At this stage a few drops of 10% cadmium acetate were added to the extract to detect any soluble sulfides; none was detected except in the enstatite meteorites. Soluble sulfate was precipitated as barium sulfate from the solution.

3. Reaction with 5N HCl. The meteorite specimen was then refluxed with about 100 ml 5N HCl for 24 hours with a current of oxygen-free nitrogen being passed through the system. The released hydrogen sulfide was captured in a 5N $AgNO_3$ solution as silver sulfide. It was assumed that this process liberated the sulfide from troilite.

4. Acid-soluble sulfate. The acid solution was then filtered or centrifuged and acid-soluble sulfate precipitated as barium sulfate.

5. Second elemental sulfur extraction with benzene. The washed meteorite residue was dried at room temperature under vacuum and re-extracted with benzene. The solvent extract was evaporated to a small volume (10 cc) and elemental sulfur separated on a colloidal copper column.

6. Third elemental sulfur extraction of meteorite residue with 60:40 acetone-methanol. The meteorite residue was next extracted with a 60:40 acetone-methanol mixture to remove the most polar organic components (Kaplan, Degens & Reuter, 1963). This sometimes resulted in a dark phenolic extract in which elemental sulfur was dissolved. The sulfur was separated on the colloidal copper column.

7. Aqua regia oxidation. The remaining meteorites residue was finally oxidized with aqua regia by prolonged slow boiling. In most cases this caused the solution of most of the metals with the decomposition of some of the silicates, leaving a white insoluble residue--probably silica with some silicates. The solution was evaporated to near dryness, 10 ml concentral HCl added, and boiling continued to almost complete evaporation to remove excess nitric acid; 50 ml water was then added and barium sulfate precipitated in the filtrate with barium chloride solution.

In some cases where the organic content seemed very low and there was no reason to suspect elemental sulfur, steps 1, 5 and 6 were omitted. The data given in the section on RESULTS include comments regarding which extract contained the elemental sulfur.

Chondrules.--The chondrules were crushed to a fine powder in an alumina mortar and reacted with 4N hydrochloric acid to remove sulfides, as with the troilite nodules.

The insoluble residue of Richardton and Bjurbole was further oxidized with aqua regia and the solution tested for sulfates.

Enstatite chondrites and achondrite.--Since there are reports that oldhamite (calcium sulfide) is present in enstatite meteorites (Wiik, 1956) and also alabandite (manganese sulfide; Dawson, Maxwell & Parsons, 1960) the procedure for analyzing these specimens was somewhat changed.

Norton County & Hvittis. To the powdered meteorite was added boiling oxygen-free water and a stream of oxygen-free nitrogen was passed through the reaction vessel. The mixture was heated to near boiling for 3 hours and evolved hydrogen sulfide captured in a solution of silver nitrate as silver sulfide. The aqueous extract of the meteorite was then filtered rapidly on a Büchner funnel and the filtrate allowed to run into a flask containing 1 ml of a concentrated cadmium acetate solution to trap the soluble sulfide. The cadmium sulfide was then decomposed with hydrochloric acid and the hydrogen sulfide absorbed in the first silver nitrate trap.

The residual meteorite was then refluxed with 4N HCl and acid-volatile sulfide removed with nitrogen and absorbed in silver nitrate solution.

The filtrates from the water and acid extracts were tested for soluble sulfates with barium chloride.

Following these reactions the meteorite residue was oxidized with aqua regia and sulfate precipitated from the filtrate with barium chloride.

Abee.--An attempt was made to separate oldhamite from alabandite by the following method. The ground meteorite was shaken for 10 minutes with 10 ml boiling water, filtered rapidly on a Büchner funnel and washed with 900 ml boiling water into a flask containing 30 ml of 10% cadmium acetate solution. The cadmium sulfide was later converted to silver sulfide. Elemental sulfur was noted to crystallize on the walls of the flask as the filtrate cooled. This was separated by filtration and extraction with toluene after which it was recrystallized. To the residual meteorite was added 100 ml cold deoxygenated water and carbon dioxide blown through the mixture--no evolution of hydrogen sulfide occurred. An addition of 0.25 ml acetic acid was made and evolution began slowly and increased on heating. Bubbling of CO_2 continued until no further evolution of hydrogen sulfide could be detected in the silver nitrate trap. The above two sulfides were combined and termed calcium sulfide.

To the meteorite was next added 100 ml of a 20% acetic acid solution and carbon dioxide was bubbled through the reaction vessel for about 20 hours until no further hydrogen sulfide was evolved.

Next 70 ml concentrated hydrochloric acid was added to the reaction mixture and a very rapid evolution of hydrogen sulfide occurred. The hydrogen sulfide was trapped in a silver nitrate solution.

The remaining meteorite residue was oxidized with aqua regia. All filtrates, after water, acid, and aqua regia reactions, were tested for sulfate.

Chemical differentiation between alabandite and troilite. Since presumably only small quantities of alabandite are present in the Abee meteorite (Dawson, Maxwell & Parsons, 1960), it was assumed that only a chemical method would effectively separate it from the troilite. Trials with troilite from Canyon Diablo showed that acetic acid did not react with it to liberate hydrogen sulfide, even when the reaction mixture was heated.

A terrestrial alabandite ore from French Mine, Arizona, reacted slowly with 5% acetic acid in the cold and more readily with 20% acetic acid. Heating the mixture accelerated the release of hydrogen sulfide.

Ehole.--Since elemental sulfur was suspected from this meteorite, it was first extracted with an 80:20 benzene-methanol mixture. It was then reacted with 0.5% hot acetic acid and the released hydrogen sulfide removed in a stream of nitrogen and captured. Next it was reacted with 5% acetic acid first in the cold and then by heating. The sulfide further released was captured. Finally, the meteorite residue was reacted with 4N hydrochloric acid. The three sulfide fractions obtained were kept separate. All acid filtrates were tested for sulfate.

The dry meteorite was re-extracted with benzene-methanol (20:80) and finally oxidized with aqua regia and sulfate in the filtrate as previously.

Isotope measurements

All barium sulfates were reduced to hydrogen sulfide with a hypophosphorous-hydroiodic acid mixture and converted to silver sulfide following the description of Thode, Monster and Dunford (1961).

Sulfur dioxide, for mass spectrometer measurement, was prepared by an adaptation of the method described by Rafter (1957) in which the silver sulfide was burnt at 1200°C in a stream of oxygen.

Some of the samples were measured on the mass spectrometer as the gas sulfur hexafluoride (SF_6) using an adaption of the method developed by Hoering (1962). This enabled small samples of the order of 1.0 mgm sulfur (8 mgm Ag_2S) to be studied. It also had the advantage of allowing S^{36} to be measured, since there was no interference by other overlapping isotopic ion species (e.g. oxygen isotopes in SO_2). The SF_6 was produced in an all-metal vacuum system by passing dry fluorine gas over Ag_2S at room temperatures for 30 minutes and collecting the SF_6 produced in a trap cooled by liquid oxygen. The SF_6 was then purified by gas chromatography using a colunn packed with molecular sieve type 5A heated to 150°C. The method is described in detail elsewhere (Hulston & Thode, 1965).

The SO_2 and SF_6 samples were measured on a 6-inch mass spectrometer employing simultaneous collection and sample switching techniques as described by Wanless and Thode (1953). The ionic species SO_2^+ and SF_5^+ were used for these measurements. All results are quoted as δS^{34} values defined by:

$$\delta S^{34}(^{o}/oo) = (\frac{(S^{34}/S^{32})\text{ sample}}{(S^{34}/S^{32})\text{ Standard}} - 1) \times 1000$$

The standard SO_2 and SF_6 gases used were both prepared from the troilite phase of the Canyon Diablo meteorite. The δS^{34} value thus expresses the difference in parts per thousand between S^{34}/S^{32} ratio of the sample as compared to the S^{34}/S^{32} ratio of the Canyon Diablo troilite.

RESULTS

Description of meteorites

Some properties of the meteorites studied are given in Table 1. In general there does not appear to have been any extraneous addition of sulfur to the specimens during storage. Changes, especially oxidations, may well have occurred within the samples during storage. This is shown by the presence of sulfate in many meteorites (Table 2) and by ferric hydroxide often associated with lawrencite ($FeCl_2$) from which it is derived. Fresh surfaces often showed rust spots, especially if metallic iron was present. Troilite grains were sometimes covered with a yellow film suggesting slight oxidation at the exposed surfaces. In general, metallic iron appeared to oxidize more readily than the troilite. Inadequate protection of Type I carbonaceous chondrites results in efflorescence of white crystals on the surface during storage (M. H. Hey, personal communication).

Iron meteorites

The most abundant form of sulfur in the iron meteorites is troilite. Reports have been made for the presence of daubreelite ($FeCr_2S_4$), particularly in Coahuila (Prior, 1953), but only traces of a nonhydrochloric volatile sulfur component could be separated from this meteorite in the present study (Table 3). Since Nichiporuk and Chodos (1959) have shown that pyrrhotite is also a common constituent of many troilite nodules including Coahuila, the sulfur remaining after hydrochloric acid treatment may arise from various minerals.

A number of troilite nodules from iron meteorites were analysed inwhich the ratio of Fe:S was reported to be greater than usual (Nichiporuk and Chodos, 1959). These are the Toluca, Indian Valley and Ballinoo meteorites. Nichiporuk (personal communication) thought this enrichment in iron may indicate that sulfur had been preferentially removed and may indicate a fractionation process.

The isotope data in Table 3 show a remarkably constant value for the troilite sulfur of the iron meteorites. The δS^{34} results all fall within 0.0 to $+0.6^{\circ}/oo$ of Canyon

Diablo which is the standard; the average for the six samples being given as +0.2°/oo.

Carbonaceous and other chondrites

The distribution of sulfur in the chondrites appears to be quite complex. It is generally assumed that Types I and II carbonaceous chondrites have three valance states of sulfur demonstrated by sulfide, elemental sulfur, and sulfate; the other chondrites are thought to have only troilite. Mason and Wiik (1962), however, demonstrated that pentlandite $(Fe,Ni)_9S_8$ was the major sulfide mineral in Karoonda (olivine chondrite). They demonstrated the presence of traces of pyrite and chalcopyrite, existing as inclusions associated with the pentlandite. The presence of a number of sulfide minerals in traces was detected in polished thin section by Ramdohr ~~and Kullerud~~ (1962).

The variability of sulfur distribution in stony meteorites can be seen from the present results (Tables 2 and 3) and from Mason (1962, 1962-1963), and may in part reflect the uneven distribution of the solid phase as suggested by Wiik (1956).

The analytical procedure used to extract the sulfur was outlined in order to separate as many of the components as possible. In all meteorites, except the enstatite chondrites Norton County and Ehole, it was assumed that no water-soluble sulfide phase existed.

Carbonaceous chondrites were first extracted with an organic solvent mixture in order to remove elemental sulfur and then a series of other extractions, as outlined in the Methods to remove other components. The results seen in Table 2 seem to confirm Mason's (1962-1963) generalization that Type I carbonaceous chondrites are enriched in the sulfate phase, Type II in elemental sulfur, and Type III in troilite. There appears to be little doubt that Type III chondrites have troilite as the major, and perhaps only, phase in most stones. In the case of Type I carbonaceous chondrites insufficient evidence exists, since only one stone, Orgueil, was investigated in the present study and the results differ from those given by DuFresue and Anders (1962) for the same meteorite. The elemental sulfur seems to be distributed as a coating on the silicate mineral grains and is easily removed by organic solvent extraction. The most complex case was presented by the Type II carbonaceous chondrites. Here, sulfur seems to exist in numerous phases. Of the three specimens studied (Table 2) troilite was least abundant. The procedure used for extracting Mighei and Cold Bokkeveld was different from that used for Murray. In this latter case the meteorite was not re-extracted with organic solvents after hydrochloric acid treatment and this may account for the large component listed as residual sulfur (Table 2). A small specimen of a stone obtained from a separate source (Dr. E. P. Henderson, Smithsonian Institute, Washington, D. C.) was extracted later by the same procedure as for Mighei and Cold Bokkeveld and although no quantitative data are available, elemental sulfur was extracted by the second organic solvent extraction and no residual sulfur could be detected after aqua regia oxidation. It is therefore probable that the sulfur listed as residual sulfur in Table 2 is the organic solvent extractable sulfur. Due to lack of meteorite specimens, this could not be tested further quantitatively either in Murray or in Mokoia, where the same condition may pertain.

The ordinary chondrites contain troilite as the most abundant phase. Residual sulfur is most likely due to varying amounts of nickel sulfide as found in Karoonda, or even perhaps nonhydrochloric acid volatile iron sulfides. The presence of sulfates or elemental sulfur as found in Richardton (Table 3) is probably due to oxidation of reduced sulfur during storage of the sample after falling. This is especially true in the case of Richardton where marked oxidation was visible. However, it must be noted that elemental sulfur was detected in this meteorite by the second organic solvent extraction after hydrochloric acid treatment, similar to the case of Mighei and Cold Bokkeveld.

The enstatite chondrites are generally accepted as being highly reduced. This is confirmed by the presence of water soluble sulfide probably in the form of calcium sulfide (oldhamite). The occurrence of sulfate may be related to this unstable sulfur component. The residual sulfur in all cases may represent nickel sulfides, since the acid extracts of the meteorite were a deep green color. The presence of manganese sulfide, alabandite, has been suggested by Dawson et al. (1960) to exist in Abee. Its removal was attempted in this meteorite and in Ehole by reaction with weak acetic acid solution. This reaction was carried out on the basis that troilite extracted from Canyon Diablo iron meteorite did not liberate hydrogen sulfide by reaction with acetic acid, both dilute and concentrated, whereas terrestrial alabandite did so. The large discrepancy between the values found by Dawson et al. (1960) and the present work suggests that a more thorough investigation of this problem is necessary. Ramdohr (1963) suggests that the sulfides may be complex cationic forms eg (Ca, Mg, Fe, [illegible])S.

Sulfur in the chondrules of ordinary chondrites and Type III carbonaceous chondrites appears to be present largely in the form of troilite. No other component could be extracted. Adhering troilite grains were removed mechanically wherever possible. Microscopic observations clearly showed that the troilite content was variable. Photographs of chondrules by Anders and Goles (1961) demonstrate the variable distribution of the sulfide.

Achondrites

An unsuccessful attempt was made to separate troilite from Pasamonte meteorite--a pyroxene-plagioclase achondrite. From 1.4 g of a heavy mineral fraction separated from the meteorite by settling out in methylene iodide, only 0.001% S was removed.

Norton County, an enstatite achondrite, yielded no water-soluble sulfides but did produce a water-soluble sulfate which probably represents the oxidized phase of oldhamite. The acid extracts were green indicating the leaching of nickel. The residual sulfur is probably a hydrochloric acid insoluble iron nickel sulfide. Metal fragments up to 3 mm in diameter were separated, indicating the heterogeneous nature of this meteorite. This probably explains why the calculated total sulfur content which was measured using 16 g of meteorite differs from the total by direct analysis from 0.8 g meteorite.

Isotopic variation

Variation of δS^{34} in extracts of the meteorites studies varied from +2.6 to -5.6°/oo (Tables 2 and 3). A weighted average was taken for each meteorite and it can be seen to lie between +0.5 and -0.7°/oo. The direct total analysis falls close to 0. The data in Figure 1 and 2 clearly show that the isotopic ratio S^{34}/S^{32} is not constant for each compound and that the variation does not seem to follow any clear pattern, but that the average of the separate components falls close to zero. The discrepancy that exists between the calculated average and the direct measurement of the whole meteorite in the case of Norton County may reflect a heterogeneous distribution of components in the different fragments analyzed. The variation in δS^{34} from +1.0 to 3.3°/oo for elemental sulfur extracted from three separate fragments of Orgueil meteorite illustrates the spread.

From Figures 1 and 2 it can be seen that there are no definite trends for isotope variation of the different components. There may be some significance, however, to the fact that in the Type I and Type II carbonaceous chondrites the sulfide phase had a positive δS^{34} value and the sulfate a negative δS^{34} value relative to Canyon Diablo. In Mokoia (Type III) the reverse was measured. The negative value for sulfate may indicate that it was derived from a volatile sulfide phase in the meteorite through preferential diffusion and oxidation of the lighter molecule. This may also explain the very negative δS^{34} value for the sulfate isolated from Norton County (Table 3).

The values for δS^{34} in troilite from the chondrules of Richardton and Bjurbole (Table 3) were similar to the δS^{34} values of troilite in the matrix. This may indicate a common source for the sulfide phase.

The troilite of iron meteorites has a very constant value near δS^{34} 0.0°/oo. On the other hand a terrestrial troilite from Del Monte Country, California, one of the rare examples of such a mineral, gave a value of $\delta S^{34} =$ -2.3°/oo.(Table 3) showing that it was unlikely to have been derived in the past from a meteorite.

In addition to S^{34}, mass spectrometer measurements have also been made on S^{33} by using both the SO_2 and SF_6 techniques (Hulston and Thode, 1965). The data for the relative distribution are given in Figure 3.

DISCUSSION

Of particular interest is the presence of elemental sulfur in the carbonaceous meteorites. It appears that the distribution may be different in Type I and Type II. In the former, the sulfur is present on the surface of mineral grains, and can easily be removed by an organic solvent extraction. In the Type II chondrites, an organic solvent extraction alone could not remove the sulfur. It was only after the meteorite was hydrolyzed in hydrochloric acid that organic solvent extraction was successful. After hydrolysis, the organic residues seemed more soluble in polar than nonpolar organic solvents (Kaplan, Degens and Reuter, 1963) and the nature of these compounds suggests that they may have heterocyclic structure. The elemental sulfur may therefore be organically bound in such a case. Alternatively the sulfur is captured within crystal grains and only liberated when these have been partially destroyed by acid treatment. Since it is difficult to envisage a complete removal of organically bound sulfur as elemental sulfur by acid treatment, it may be assumed for the present, that elemental sulfur exists only in a relatively unavailable form in Type II carbonaceous chondrites.

The data presented in Tables 2 and 3 and Figures 1 and 2 show that the δS^{34} for the total meteorite agrees to within ±0.7 of the value derived by computation. This value was derived by multiplying the isotope ratio of each component by its proportion of the total sulfur content and summing. The general close agreement indicates that no important components could have been lost during the laboratory separation.

One factor that may produce anomalous fractionation factors is the analytical procedure. If, during the separation of the components, there was partial separation only, this may account for discrepancies. The fact that the iron meteorites, however, showed constant S^{34}/S^{33} ratios after release of sulfide from troilite would tend to argue against this. In addition, it is difficult to see how solid phases such as sulfate or elemental sulfur could be fractionated by solvent extraction, since there are no kinetic or equilibrium phenomena involved.

The data show no clear evidence for microbiological sulfate reduction of the type known in terrestrial deposits or laboratory experiments. In such a case the sulfate is invariably enriched in the heavier isotope. Mokoia may be the only exception to the other data, since here sulfate showed an enrichment in the heavier isotopes. The results do not, however, eliminate the possibility of a microbial sulfur oxidation of sulfides and elemental sulfur to sulfate. Other lines of evidence would have to be brought forward to support this contention.'

The constant average of S^{34}/S^{32} composition of the total sulfur in meteorites studied, strongly indicate that the sulfur incorporated into the planetary body or bodies during their formation arose from a common source.

The presence of isotopic variation and the averaging out of the values to a constant for any single meteorite fragment strongly suggests that reactions have occurred in a closed system without any appreciable losses of individual components. The data also argue against addition of sulfur from external sources.

Further support for in situ fractionation by chemical processes comes from the study by Hulston and Thode (1965) of the other stable isotopes of sulfur (S^{33} and S^{36}) relative to S^{32} and S^{34}. The results indicate no anomalous enrichment of either of these isotopes. Data plotted in Figure 3 showing the relationship between δS^{33} and δS^{34} yield a straight line with a slope of 0.51, identical with that proposed by theory.

The factors outlined above are strong evidence against the formation or accretion of any significant amounts of sulfur in the meteorite parent body through processes that may cause the anomalous enrichment of S^{33} or S^{36} (Hulston and Thode, 1965).

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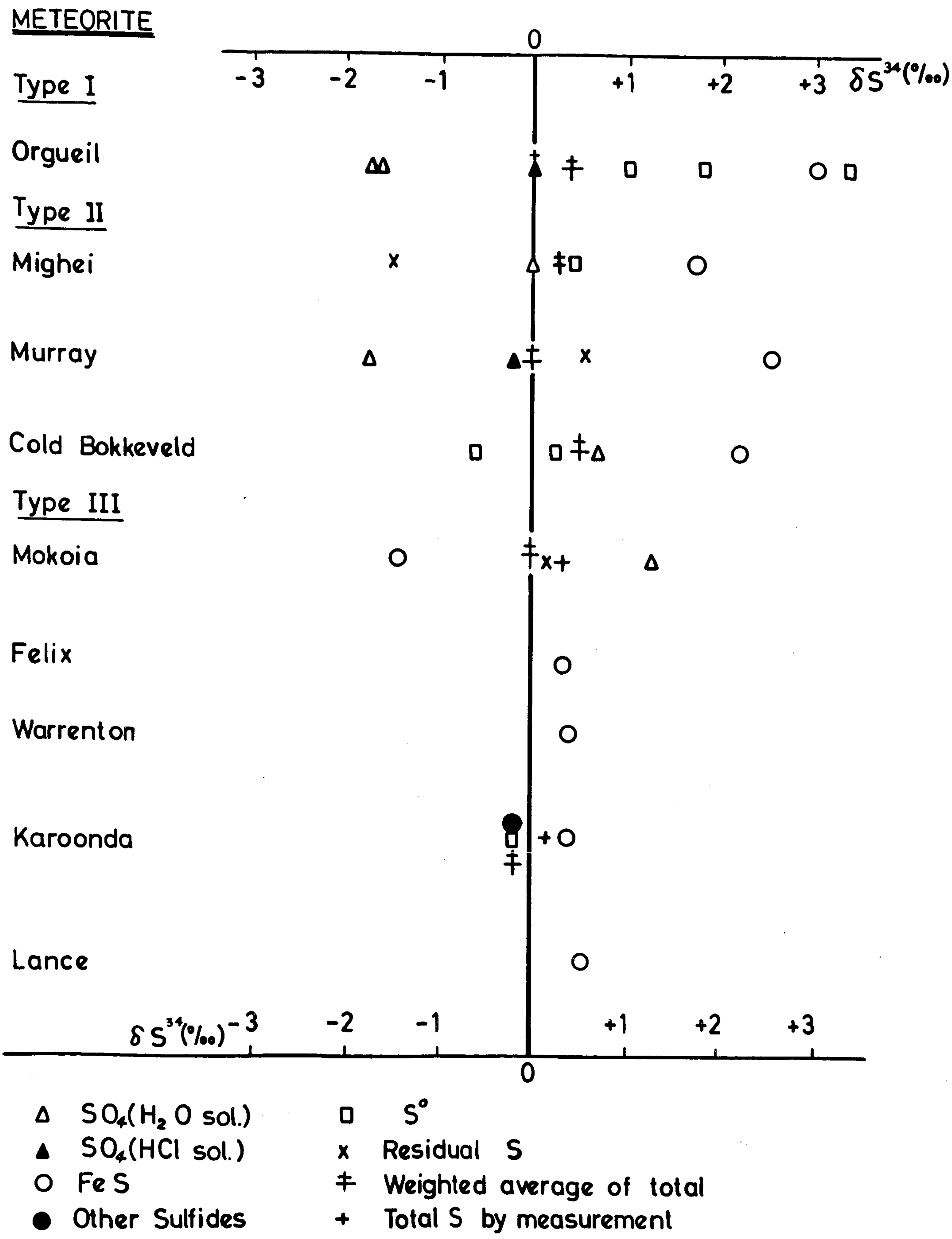
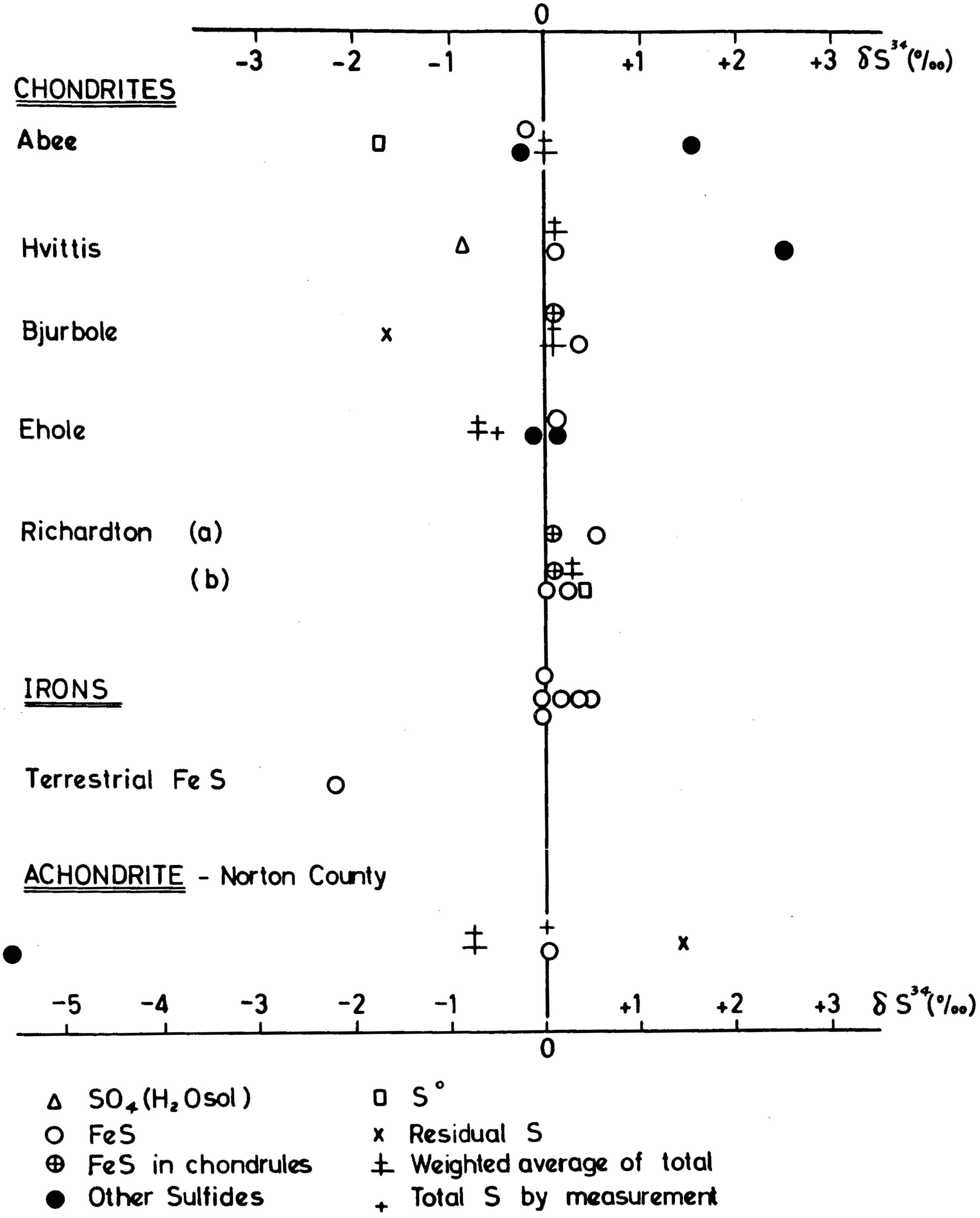
Legend to Figures

Figure 1. Distribution of S^{34}/S^{32} among the different sulfur constituents in carbonaceous chondrites.

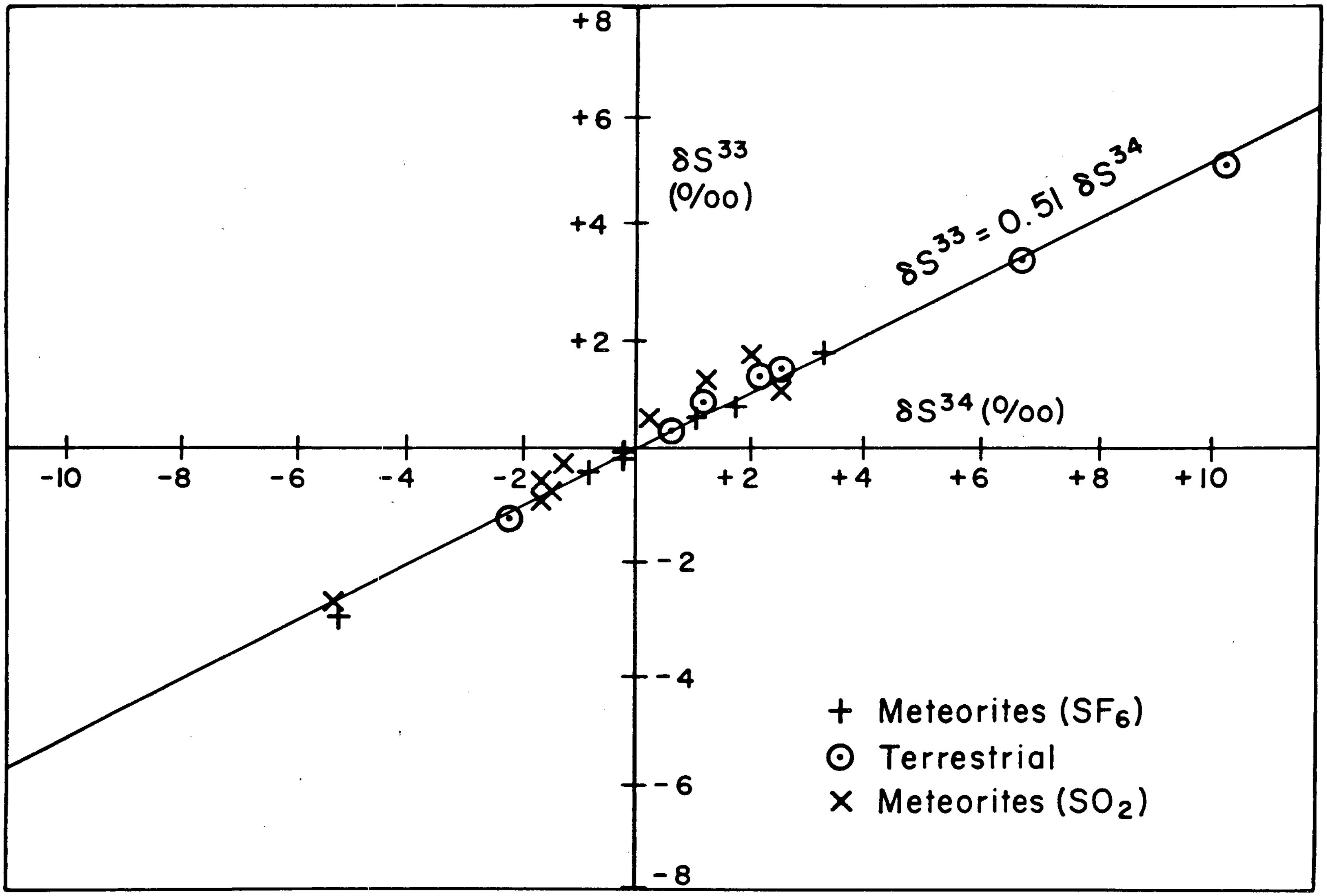
Figure 2. Distribution of S^{34}/S^{32} among the different sulfur constituents in chondrites, achondrites, iron meteorites and terrestrial troilite from Del Norte County, California.

Figure 3. Variation in S^{34} relative to S^{33} in meteorites and terrestrial sulfur compounds used as standards. The meteoritic samples were measured either in the form of SO_2 or SF_6.


METEORITE
Type I
Orgueil
Type II
Mighei
Murray
Cold Bokkeveld
Type III
Mokoia
Felix
Warrenton
Karoonda
Lance
0
-3
-2
-1
+1
+2
+3
δS34(‰)
△ SO4(H2O sol.)
▲ SO4(HCl sol.)
○ FeS
● Other Sulfides
□ S°
x Residual S
‡ Weighted average of total
+ Total S by measurement



0
-3
-2
-1
+1
+2
+3
δS³⁴(‰)
CHONDRITES
Abee
Hvittis
Bjurbole
Ehole
Richardton (a)
(b)
IRONS
Terrestrial Fe S
ACHONDRITE - Norton County
-5
-4
-3
-2
-1
+1
+2
+3
δS³⁴(‰)
0
△ SO₄(H₂O sol)
○ FeS
⊕ FeS in chondrules
● Other Sulfides
□ S°
x Residual S
‡ Weighted average of total
+ Total S by measurement



+8
+6
+4
+2
-2
-4
-6
-8
-10
-8
-6
-4
-2
+2
+4
+6
+8
+10
δS³³ (0/00)
δS³⁴ (0/00)
δS³³ = 0.51 δS³⁴
+ Meteorites (SF₆)
⊙ Terrestrial
× Meteorites (SO₂)

TABLE 1 coT (1)

TABLE 1 - DESCRIPTION C

Meteorite		Type	Ori
Orgueil	(a)	Carbonaceous Chondrite Type I	B. Mason, Am. Mus. N.Y.
Orgueil	(b)		
"	(c)		
"	(d)		
Mighei		Carbonaceous Chondrite Type II	K.K. Ture Yale Univ Dept. of
Murray		Carbonaceous Chondrite Type II	Californi Techno
Cold Bokkeveld		Carbonaceous Chondrite Type II	K.K. Ture Univ.
Mokoia		Carbonaceous Chondrite* Type III	C.B. Moor Univ. of (Ninninger Coll^{n}.)
Felix		Carbonaceous Chondrite* Type III	Californi Techn
Warrenton		Carbonaceous Chondrite* Type III	K.K. Ture Universit Geology.
Karoonda		Carbonaceous Chondrite* Type III	B. Mason, Am. Mus. N.Y.
Lance		Carbonaceous Chondrite* Type III	K.K. Ture Yale Univ
Abee		Enstatite Chondrite	G.G. Gole U.C.S.D.,
Hvittis		Enstatite Chondrite	K.K. Ture Yale Univ
Bjurbole		Olivine-Hypersthene Chondrite	B. Mason, Am. Mus. N.Y.

TABLE 1 CUT②

F [illegible]TEORITES STUDIED

gi	Condition and Description of Specimens
of Nat. History,	Small fragments without fusion crust. White efflorescence present (3 g).
"	Same (0.23g)
"	
"	Isolated sulfate obtained from B. Mason extracted by J.L. Smith (1876).
kian, ersity, Geology.	Black chondrite with few chondrules. White salt on surfaces. Specks of brown Fe_2O_3 visible (4.3 g).
a Inst. of logy	Crushed specimen as powder stored in glass vial (6.2 g).
kian, Yale	Sample broken from larger specimen. Some magnetic particles appearing to contain sulfides. White salt visible (6.8 g).
e, Arizona, Meteorite	Single fragment, fracture planes containing white crystals, some brown spots of iron oxide visible. Chondrules dominant (6.14 g).
a Inst. of ology	Crushed specimen as powder stored in glass vial (1.8 g).
kian, Yale y, Dept. of	Single fragment. Magnetic. Some oxidation. White salt visible under low power magnification (1.7 g).
of Nat. History,	Black easily fragmented specimen. Sulfides easily visible under low power magnification (3.4 g).
kian, ersity	Single fragment. Magnetic. Some oxidation (2.5 g).
s, La Jolla.	Dense and hard. Polished surfaces show free metal and metal sulfide surfaces. Magnetic. No oxidation apparent (7.9 g).
kian, ersity	As above (5.3 g).
of Nat. History	Grey chondrite containing 25% chondrules. Sulfides present in abundance. Some oxidation evident (5.2 g).

Ehole		Olivine-Bronzonite Chondrite	H. Suess, U.C.S.D.,
Richardton	(a)	Olivine-Bronzite Chondrite	Californi Technol
Richardton	(b)		K.K. Turel Yale Unive
Norton County		Enstatite Achondrite (calcium poor)	Californi Technol
Canyon Diablo	(a)	Iron - coarse octahedrite	W. Nichipo California Technol
	(b)		"
	(c)		American M
Toluca	(a)	Iron - medium octahedrite	W. Nichipo California Technol
Toluca	(b)		American M
Merceditas		Iron - medium octahedrite	W. Nichipo California
Indian Valley		Iron - hexahedrite	
Ballinoo		Iron - fine octahedrite	
Coahuila		Iron - hexahedrite	K.K. Turek Yale Unive
Terrestrial Troilite		Del Norte County California	L. Silver, California Technol

TABLE I
cut ③

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*Described by Mason (1962) as Olivine - Pi

La Jolla.	Highly magnetic. Fresh surfaces showed little oxidation or tarnishing. Some encrustations of salt. No chondrules (3.8 g).
Inst. of ogy.	Fragmented specimen. Obvious evidence of oxidation. Chondrules dominant (3 g).
ian, rsity	Some fusion crust still present (7.5 g).
Inst. of ogy.	Sample broken from larger specimen. Metal (Fe or Ni) fragments up to 3 mm diameter present. Oxidation evident (16.1 g).
ruk, Inst. of ogy.	Fresh surface cut and troilite removed from nodule by drill.
	- Same -
eteorite Co.	- Same -
ruk, Inst. of ogy.	- Same -
eteorite Co.	- Same -
ruk, Inst. of Technology.	- Same -
"	- Same -
"	- Same -
ian, rsity	- Same -
Inst. of ogy.	Removed by drill from clean surface of troilite.

---

geonite Chondrites.

TABLE 1
CUT ④

TABLE 2 CUT ①

TABLE 2 - EXPERIMENTAL RESULTS OF CHEMICAL AND

Meteorite and Type	Compound Extracted	Probable Component	Sample No.
Type I			
Orgueil (a)	S° 1st extract	S°	CM53
	S° 2nd extract	S°?	CM54
	$SO_4^=$ (H_2O sol)	$MgSO_4$	CM19
	$SO_4^=$ (HCl sol)	$CaSO_4$	CM22
	$S^=$ (HCl vol)	FeS	CM20
	Residual S (aqua regia)	-	-
	Total S		HU2/69
Orgueil (b)	S°	S°	HU4/93
Orgueil (c)	S°	S°	M/203
Orgueil (d)	$SO_4^=$(Smith, 1876)	$MgSO_4$	
Type II			
Cold Bokkeveld	S° 1st extract	-	-
	S° 2nd extract	S°?	CM55
	S° 3rd extract	S°?	CM56
	$SO_4^=$ (H_2O sol)	$(Mg,Ca)SO_4$	CM43
	$SO_4^=$ (HCl sol)	-	-
	$S^=$ (HCl vol)	FeS	CM45
	Residual S (aqua regia)	-	-
	Total S		
Mighei	S° 1st extract	-	-
	S° 2nd extract	S°?	
	S° 3rd extract	S°	CM57

TABLE 2 CUT ②

ISOTOPIC MEASUREMENTS OF CARBONACEOUS CHONDRITES

S Content %	Calc Total S (%)	δS^{34} (°/oo)	Calc Av δS^{34} (°/oo)
1.35		+ 1.8	
0.09		-	
2.47		- 1.6	
0.13		+ 0.0	
0.04		+ 3 ± 1	
Trace		-	
5.96	5.54	+ 0.0	+ 0.35
1.5		+ 1.0	
-		+ 3.3	
		- 1.7	
0.00			
0.03		- 0.6	
0.53		+ 0.2	
1.05		+ 0.7	
0.00			
0.01		+ 2.2	
0.00			
-	1.62		$+0.5_2$
0.00		-	
Trace			
1.58		+ 0.4	

	$SO_4^=$ (H_2O sol)	(Mg,Ca)SO_4	CM44
	$SO_4^=$ (HCl sol)	-	-
	$S^=$ (HCl vol)	FeS	CM46
	Residual S (aqua regia)	?	CM51
	Total S		
Murray	S^o	-	-
	$SO_4^=$ (H_2O sol)	(Mg,Ca)SO_4	CM12
	$SO_4^=$ (HCl sol)	$CaSO_4$	CM14
	$S^=$ (HCl vol)	FeS	CM13
	Residual S (aqua regia)	?	CM17
	Total S		
Type III			
Mokoia	S^o	-	-
	$SO_4^=$ (H_2O sol)	$CaSO_4$?	CM15
	$SO_4^=$ (HCl sol)	-	-
	$S^=$ (HCl vol)	FeS	CM16
	Residual S (aqua regia)	?	CM18
	Total S		HU3/71
Mokoia chondrules	$S^=$ (HCl vol)	FeS	-
Felix	$S^=$ (HCl vol)	FeS	CM11
Lance	$S^=$ (HCl vol)	FeS	CM39b
Warrenton	$S^=$ (HCl vol)	FeS	CM40b
	Residual S (aqua regia)		-
Karoonda	$S^=$ (HCl vol)	FeS	-
	$SO_4^=$ (HCl sol)	-	-
	S^o	S^o?	HU6/91
	Residual S	$(Fe,Ni)_9S_8$	HU7/90
	Total S		HU1/70

TABLE 2
CUT ③

0.46		+ 0.0	
0.00		-	
0.18		+ 1.7	
0.15		- 1.5	
-	2.37		+ 0.3
0.00			
0.39		- 1.7	
0.10		- 0.2	
0.06		+ 2.5	
1.71		+ 0.3	
	2.26		- 0.01
0.00		-	
0.14		+ 1.3	
0.00		-	
0.15		- 1.4	
1.82		+ 0.1	
1.95	2.11	+ 0.3	+ 0.07
< 0.01		-	
1.83	1.83	+ 0.3	
1.18	1.18	+ 0.5	+ 0.5
1.60	1.60	+ 0.4	+ 0.4
Trace		-	
0.02		+ 0.4	
0.00		-	
0.13		- 0.2	
1.25		- 0.2	
1.02	1.38	+ 0.2	- 0.2

TABLE 2
CUT ④

TABLE 3 cut ①

TABLE 3 - EXPERIMENTAL RESULTS OF CHEMICAL A

Meteorite and Type	Compound Extracted	Probable Component	Sam N
CHONDRITES (non Carbonaceous)			
Richardton (a) (matrix)	$S^=$ (HCl vol)	FeS	CM
	Total S		CM
(chondrules)	$S^=$ (HCl vol)	FeS	CM
Richardton (b) (matrix) - (i)	nonmagnetic fraction (61.8%)		
	S^o	S^o?	CM5
	$S^=$ (HCl vol)	FeS	CM2
(ii)	magnetic fraction (29.4%)		
	$S^=$ (HCl vol)	FeS	CM2
	Total S		
(chondrules)	$S^=$ (HCl vol) (8.8%)	FeS	CM2
Bjurbole (matrix)	$S^=$ (HCl vol) (75.4%)	FeS	CM3
	Residual S (aqua regia)	?	CM3
	Total S		
(chondrules)	$S^=$ (HCl vol) (24.6%)	FeS	CM3
Ehole	S^o	-	-
	0.5% Acetic acid vol	CaS?	HU
	5% Acetic acid vol	MnS?	HU1
	$S^=$ (HCl vol)	FeS	HU1
	SO_4	-	
	Residual S (aqua regia)	-	
	Total S		HU
Abee	$S^=$ (H_2O sol)	CaS	CM4
	S^o	CaS?	CM5

TABLE 3 CUT②

D ISOTOPIC MEASUREMENTS OF STONY AND IRON METEORITES

le .	S Content (%)	Calc Total S (%)	δS^{34} ($^o/_{oo}$)	Calc Av δS^{34} ($^o/_{oo}$)
	1.28		+ 0.5	
	0.88	1.28	+ 0.5	+ 0.5
	0.83		+ 0.1	
	0.12		+ 0.3	
	1.81		+ 0.2	
	0.79		+ 0.1	
		1.56		+ 0.2
	0.87		+ 0.1	
	2.17		+ 0.3	
	0.05		- 1.7	
		2.22		$+0.2_6$
	1.36		+ 0.1	
	0.00		-	
/79	0.06		- 0.1	
/80	0.11		+ 0.1	
/81	1.83		- 0.8	
	0.00		-	
	0.00		-	
/78	2.02	2.00	- 0.5	-0.7_3
	0.07		+ 1.6	
	0.06		- 1.7	

	20% Acetic acid vol (0-18 hrs.)	MnS?	CM4
	20% Acetic acid vol (18-20 hrs.)	MnS?	CM4
	$S^=$ (HCl vol)	FeS	CM5
	Residual S (aqua regia)		-
	Total S		
Hvittis	$S^=$ (H_2O sol)	CaS	CM3
	$SO_4^=$ (H_2O sol)	CaS?	CM3
	$S^=$ (HCl sol)	FeS	CM3
	$SO_4^=$ (HCl sol)	-	-
	Residual S (aqua regia)	$(Fe,Ni)_9S_8$?	CM3
	Total S		
ACHONDRITES			
Norton County	$SO_4^=$ (H_2O sol)	CaS?	CM3
	$S^=$ (HCl vol)	FeS	CM3
	$SO_4^=$ (HCl sol)	-	-
	Residual S (aqua regia)	$(Fe,Ni)_9S_8$?	CM3
	Total S		HU5
IRONS (Troilite Phase)			
Canyon Diablo (a)	$S^=$ (HCl vol)	FeS	CM
(b)	" "	FeS	CM
(c)	" "	FeS	M/1
Toluca (a)	" "	FeS	CM
(b)	" "	FeS	M/1
Merceditas	" "	FeS	CM
Indian Valley	" "	FeS	CM
Ballinoo	" "	FeS	CM
Coahuila	" "	FeS	CM2
	Residual S (aqua regia)	$FeCr_2S_4$	CM2
TERRESTRIAL TROILITE			
Del Norte County (Calif.)	$S^=$ (HCl vol)	FeS	CM2

TABLE 3
CUT ③

	1.86		- 0.2	
	0.06		+ 0.4	
	4.62		- 0.2	
	0.00			
		6.67		-0.0_6
a	0.06		+ 2.5	
b	0.04		- 0.8	
	0.12		+ 0.1	
	0.00		-	
	0.24		+ 0.2	
		3.46		-0.1_4
	0.13		- 5.6	
	0.34		+ 0.0	
	0.00		-	
	0.18		+ 1.4	
/92	0.35	0.65	+ 0.0	-0.7_6
	17.3		+ 0.0	+ 0.0
	25.8		+ 0.1	+ 0.1
38	-		+ 0.0	+ 0.0
	35.7		+ 0.1	+ 0.1
36	-		+ 0.1	+ 0.1
	31.8		+ 0.3	+ 0.3
	10.8		+ 0.0	+ 0.0
	14.4		+ 0.6	+ 0.6
	29.0		+ 0.4	+ 0.4
	0.07	-	-	
	25.8		- 2.3	

TABLE 3
CUT ④