

NASA NAGW-3551FINAL REPORT

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Our program has focused upon several new aspects.

These include 1) search and identification of the carriers of isotopically anomalous sulfur compositions recently detected 2) characterization of meteoritic bulk sulfur isotopic compositions, testing the possible link between bulk sulfur and oxygen isotopic compositions 3) measurement of mineral and chondrule sulfur isotopic compositions, including, for example, oldhamite and troilite separates 4) Determination of spallogenic ^{33}S , ^{36}S yields from high energy proton irradiation of iron, to resolve the source of observed anomalous iron meteorite isotopic composition. These measurements are important as the measured (presumed) spallogenic ^{33}S , ^{36}S excesses in iron meteorites do not conform to theoretical predictions. Precise measurements are needed as there is evidence for a second, non-spallogenic isotopically anomalous component present in iron meteorites. This species may not be identified until a precise correction for spallogenic ^{33}S , ^{36}S is applied. Extensive proton irradiations are proposed 5) Further development of the ability to measure smaller samples, was achieved. With the documentation in the past 10 months of isotopically anomalous sulfur in bulk ureilites, a search for carrier phase(s) is needed. With the exception of oldhamite and some troilites, most sulfides are small (sub milligram) and it is imperative that the ability to measure sub-microgram quantities of sulfur at high precision for all 4 stable isotopes continually be improved.

There have been significant accomplishments in all proposed areas. In addition, based upon recent observations and opportunities we have incorporated at least two new research components. The accomplishments of the past 10 months' funding is presented in some detail as the proposed research is, in large part, driven by these results.

(1) SEARCH FOR ISOTOPICALLY ANOMALOUS SULFUR COMPONENTS

In our last proposal, a major motivation for searching for isotopically anomalous sulfur components was the possibility that there may be small, nucleosynthetic grains present. For example, Clayton and Ramdurai (1977) suggested that TiS could serve as an interstellar carrier of isotopically anomalous sulfur. Rees and Thode (1977) reported a $\sim 1\%$ excess in ^{33}S from an acid residue extract from Allende, but the observation was never duplicated. Cameron (1979), in a model calculation, demonstrated that ^{36}S is produced in neutron-rich equilibrium burning, a process demonstrated to produce isotopically anomalous compositions in other elements, such as titanium and calcium. These observations lead us to propose, and pursue, sulfur isotopic measurements of different meteorites and their internal constituents.

Our first detection of an isotopically anomalous component was on an oldhamite separate from the Norton county meteorite (Thiemens, et al., 1994), where ^{33}S excess was observed. The measured isotopic composition was $\delta^{33}\text{S} = 0.225$, $\delta^{34}\text{S} = 0.119$ and $\delta^{36}\text{S} = 0.268$. From measurement of more than 50 meteorites, and an equally large data base of terrestrial samples, the sulfur mass fractionation line is given by the relation $\delta^{33}\text{S} = 0.5 \delta^{34}\text{S}$ and $^{33}\Delta = \delta^{33}\text{S} - 0.50 \delta^{34}\text{S}$ defines the deviation from the mass fractionation line. The average $^{33}\Delta$ is $+0.018 \pm 0.015$. In the case of the Norton County oldhamite separate, $^{33}\Delta = 0.17\%$, well beyond experimental error. In the last 10 months we have reanalyzed the oldhamite separate (~ 70 mg total sample). In three additional re-analysis of this oldhamite sample, the $^{33}\Delta$ is found to be $0.17 \pm 0.02\%$. These re-measurements were complete in that each sample went through the reduction chemistry, conversion to silver sulfide, fluorination to SF_6 , gas chromatographic purification/separation and mass spectrometry. In all analysis, $\delta^{36}\text{S}$ is found to be normal, within error ($\pm 0.15\%$). In between each re-analysis, we measure several terrestrial standards, such as commercial silver sulphide and Cañon Diablo troilite. In every analysis we find that the $^{33}\Delta = 0$ to within $\pm 0.02\%$. The greatest deviation found in any of our terrestrial standards in the past two years is $^{33}\Delta =$

0.05‰, thus the observed, and replicated, Norton County measurement is taken to be a real, albeit small isotopic anomaly. An interesting aspect of the anomaly is its location in oldhamite. Lodders and Palme (1990), Lodders et al., (1990, 1993) have previously suggested that oldhamites in aubrites are quasi-relict. The preservation of an ^{33}S excess may be consistent with this hypothesis. The sulfide liquid/silicate rare earth element partition coefficients and measured aubrite REE compositions in CaS have been taken as evidence for an igneous origin (Dickinson et al., 1990a, b, c; 1991; Wheelock et al., 1994). Further sulfur isotopic measurements of separated oldhamites, which we propose, will be of importance in addressing this issue of primitiveness. The interesting aspect of the ^{33}S excess is the question as to its source. As will be discussed, there is the possibility that the anomaly is chemical, rather than nuclear in origin and thus of considerable interest.

The most interesting measurements we have made to date are those recently observed in bulk ureilites (Thiemens and Jackson, 1995). In the past 10 months we have performed sulfur isotopic measurements on the ureilites ALHA 81101, ALH 82130, ALH 84136, PCA 82506, EET 83225, EET 83309 and EET 87517. With the exception of ALH 82130, all have values of $^{33}\Delta$ which are significantly greater than zero. Though the excesses are small, as Figure 1 demonstrates, the excess ^{33}S is resolvable from the terrestrial sulfur fractionation line and clearly defines their own fractionation line with slope 0.55 and $R = 0.99$. A slope of 0.55 is greater than that attainable by any mass dependent fractionation process. The ureilites may be one of the best candidates for observation of pristine sulfur components. First, the ureilites are known to possess primitive characteristics, particularly the oxygen isotopic composition (Clayton and Mayeda, 1988) which is carbonaceous chondritic. High siderophilic elemental concentrations and planetary-type noble gas concentrations have also been taken as being reflective of their pristine character. The sulfur concentrations we observe in these samples are the lowest of any stony meteorite (~0.2 wt. %), which may be an important aspect in preserving the original character. The high sulfur concentrations in other meteorites, along with the diversity in sulfur mineralogy, either masks, or secondarily exchanges and removes the original sulfur isotopic composition. As will be presented in the proposal text, there is a possible relation between the $^{17}\Delta$ (oxygen) and $^{33}\Delta$ (sulfur). This observation, if verifiable, could be of importance in determining the importance of chemical reactions in the solar nebula. Laboratory experiments have demonstrated that chemically produced mass independent fractionations occur (Thiemens, 1992; Bains Sahota and Thiemens, 1989), thus an observed relation between the two elements could be of importance. Identification of the carrier of the sulfur anomaly, its magnitude, variability and pervasiveness warrants investigation.

2.) DETERMINATION OF THE BULK SULFUR ISOTOPIC COMPOSITIONS.

In Gao and Thiemens (1993a,b) we demonstrated that bulk sulfur isotopic compositions are resolvable in their group sulfur isotopic compositions. As observed in Figure 2, the enstatite chondrites have $\delta^{34}\text{S}$ values which range between -0.4 and -0.15‰, distinct from other meteoritic classes. The ordinary chondrites have also define a resolved group, with $\delta^{34}\text{S}$ values between -0.4 to -0.15‰. The carbonaceous chondrites possess the greatest heavy isotope enrichment, with observed variations in $\delta^{34}\text{S}$ between approximately 0 to 1‰, with large internal sulfur variations, as discussed in Gao and Thiemens (1993b). In the past month we have initiated analysis of ALH 84028, a CV3 meteorite. Measurement of a small fragment of our sample shows a $\delta^{34}\text{S} = -0.11‰$ and a hint of an excess $^{33}\Delta$ (0.057‰). As seen in Figure 2, the $\delta^{34}\text{S}$ is lighter than any of the other carbonaceous chondrites we have measured to date. The $^{33}\Delta = 0.057$ is not taken to be anomalous, however, given that a ^{33}S anomaly of ~1‰ has been previously reported in an Allende acid residue, it does suggest that further analysis of the internal isotopic components (acid residues, organic and CCl_4 extracts, density separates) is potentially interesting. The $\delta^{36}\text{S}$ for ALH 84028 was found to be normal.

The possible existence of bulk sulfur isotopic systematics has been further supported by our analysis of aubrites (Jackson, Bobias and Thiemens, 1994). Norton County, ALH 84009 and Cumberland Falls, are observed to have $\delta^{34}\text{S}$ which vary between -0.26 and -0.33. As seen in Figure 3, this data falls precisely within the enstatite chondrite's isotopic region. This suggests an affinity for oxygen which a) also defines systematic group isotopic compositions and b) reveal that enstatite chondrites and aubrites have identical isotopic compositions (Mayeda and Clayton, 1980; Clayton et al., 1984; Clayton, 1993). In the past several months we have initiated studies of the potential internal isotopic variability in Norton County. In a series of successive acid dissolutions it is observed that there is, within error, no isotopic variation, implying that the sulfur isotopic composition has been equilibrated. The extent of homogenization of the isotopes has not yet been established. As we reported, (Thiemens et al., 1994) oldhamite from Norton County is significantly heavier ($\delta^{34}\text{S} = 0.119$) compared to bulk ($\delta^{34}\text{S} = -0.269\text{‰}$). At present, the sulfur isotopic measurements of the enstatite chondrites and aubrites suggest a genetic link, as in the case of oxygen isotopes, chemistry, mineralogy and trace elemental composition (Wheelock et al., 1994; Watters and Prinz, 1979). It is known that the enstatite chondrites, while isotopically constant in their bulk $\delta^{34}\text{S}$, exhibit considerable internal variability between CaS and troilite, greater than 1.9‰ in the case of Indarch (Gao and Thiemens, 1993a); It is not known what the variability is for the same phases in aubrites. This information could potentially be of importance in establishing the source of the sulfur isotopic composition.

Another case for a possible link between the bulk sulfur and oxygen isotopic systematics is provided by the ureilite isotopic measurements. As Figure 4 demonstrates, the bulk oxygen isotopic composition of ureilites lies along the Allende mixing line. This, as well as other measures, e.g. siderophile abundances and noble gas compositions, have been taken as indications of the primitive character of these objects. As Figure 5 displays, the ureilites sulfur isotopic composition lie in the $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ region exclusively occupied by the carbonaceous chondrites. This data set includes the measurements we have made within the past half year. Thus, as was the case for the aubrite-enstatite chondrite relation, there is a ureilite-carbonaceous chondritic sulfur and oxygen isotopic relation. The low sulfur concentrations in ureilites optimizes the opportunity to observe primordial components, devoid of extensive secondary alterations. Determining the variability of both the $\delta^{34}\text{S}$ and $^{33}\Delta$ in ureilites is of importance, as well as determining the carriers. This will be a major component of the proposed research.

3.) DETERMINATION OF SPALLOGENIC ^{33}S , ^{36}S YIELDS BY THE INTERACTION OF COSMIC RAYS WITH IRON

It is known that iron meteorites of sufficient cosmic ray exposure age possess excess ^{33}S and ^{36}S from spallation of iron (Hulston and Thode, 1965a,b; Gao and Thiemens, 1991). The spallogenic excess amounts of ^{33}S and ^{36}S was determined to be approximately 6 for the $^{33}\text{S}/^{36}\text{S}$ ratio. Using the energy dependent excitation functions of Honda (1962), Silberberg and Tsao (1973) calculated the cross sectional yields for the $^{33}\text{S}/^{36}\text{S}$ to be 3.1 for the relevant cosmic rays energies. The difference between predicted ^{33}S , ^{36}S excesses, and observed, is outside the range of theoretical and analytical uncertainties. In an effort to resolve the paradox, we have, in conjunction with Dr. Bob Reedy of Los Alamos, initiated analysis of the yields by proton irradiation of iron foils at energies of ~ 800 MeV. In the first series of irradiations there were 10 irradiated foils, which we analyzed in the past year. A second irradiation of 50 foils was completed and which are presently being analyzed. The results at present, have, within measurement error, indicated no excess ^{33}S or ^{36}S . Measurement of ^{46}Sc and ^{54}Mn in the foils demonstrate that the irradiations were equivalent to less than a billion years cosmic ray exposure time and energy. The results are paradoxical, though potentially important. If the cross section for spallogenic yields are significantly lower than calculated, then the measured iron meteoritic anomalies derive, at least in part, from the presence of a second, isotopically anomalous

component. The possibility, based upon our recent ureilite work, of ^{33}S excesses in ureilites, is consistent with this possibility. To quantitatively make this determination, it is essential that the spallogenic yields be precisely determined, as well as the energy dependence. In addition, as reported in Gao and Thiemens (1991), significantly variable $^{33}\text{S}/^{36}\text{S}$ ratios are observed, though are not expected from a purely spallogenic component.

CONTINUED ANALYTICAL DEVELOPMENT OF HIGH PRECISION SULFUR ISOTOPE RATIO MEASUREMENT TECHNIQUES

The observation in the past year of the anomalous isotopic behavior of sulfur in ureilites and oldhamite has been made possible only through the attainment of ultra high precision techniques. This has been achieved from continual improvements in the fluorination technique, cryogenic purification, gas chromatographic protocol and mass spectrometry. In the past 1-2 years we have made significant advances in each area. In the past, there have been difficulties in reliable ^{36}S measurements due to impurities in the reagent bromine pentafluoride. In the past year, we have re-built the fluorination manifold to permit a final stage in distillation of the BrF_5 . This purification has made a significant difference in our ^{36}S measurements and their reproducibility (at present, better than $\pm 0.13\text{‰}$ for $\delta^{36}\text{S}$).

Ultimately, the precision of our sulfur isotopic measurements is limited by the internal noise characteristics of the mass spectrometer, and particularly, its electrometer. In the past, we have had to externally switch electrometer boards, as we only have 3 cups for the isotope ratio measurements. The $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ measurements are made during one analysis and $\delta^{36}\text{S}$ made subsequently. We have now incorporated a new switching unit, which is noise free and permits us to maintain our high resistance (10^8 - 10^{12} ohm) Victoreen resistors under high vacuum, which has significantly decreased our noise level. In the past half year, the internal measurements (zero enriched) produce values typically:

$$\delta^{33}\text{S} = + 0.02 \text{‰}$$

$$\delta^{34}\text{S} = \pm 0.01$$

$$\delta^{36}\text{S} = \pm 0.1\text{‰}$$

The statistics quoted above are based upon data accumulated (>30 analysis) in the past half year, and reflect the combined advance in mass spectrometry and the ideal behavior of SF_6 as a measurement gas. The present precision for the entire sulfur analytical procedure is

$$\delta^{33}\text{S} = \pm 0.04, \delta^{34}\text{S} = \pm 0.03 \text{ and } \delta^{36}\text{S} = \pm 0.15\text{‰}$$

This is based upon measurement of more than 80 samples of Cañon Diablo troilite and a commercial silver sulfide. In the past year, we published a manuscript with collaborators (Dr. G. Beaudoin, B.E. Taylor and D. Rumble) which demonstrated that Cañon Diablo is not isotopically constant and, is variable by $\sim 0.4\text{‰}$ (Geochim. Cosmo. (1995) Acta 58, 4253-4255). This observation has emphasized the importance of development of a range of sulfur isotope standards. As discussed in last year's proposal, we developed and characterized a silver sulfide standard which we now routinely use. Since we propose to pursue isotopic measurements of sulfur in oxidized meteoritic sulfur phases we have most recently developed a sulfate isotopic standard. As will be presented, we propose to isotopically analyze the sulfur composition of alkyl sulfonates from Murchison. Our development of reliable high precision isotopic analysis of standard sulfates is an important component of this proposal.

As outlined in last year's proposal, a sustained component of our program is the continual development of our ability to analyze, at high isotopic precision, progressively smaller samples. We have continued in that effort. In the past year, our chemical extraction procedure has been reduced in volume and we are able to chemical extract, convert to SF_6 and purify sub milligram sized sulfur samples. The modification and development of the mass spectrometer microinlet

system has reduced our sample size requirements for analysis by more than 2 orders of magnitude. In the past month, we have routinely analyzed prepared commercial SF₆ samples of less than 0.1×10^{-6} moles, which corresponds to 3.2 micrograms of sulfur. Our future analytical development will focus upon the chemical technique. This is an important aspect, as definition of the carrier phase of the ³³S excess will require analysis of progressively smaller samples.

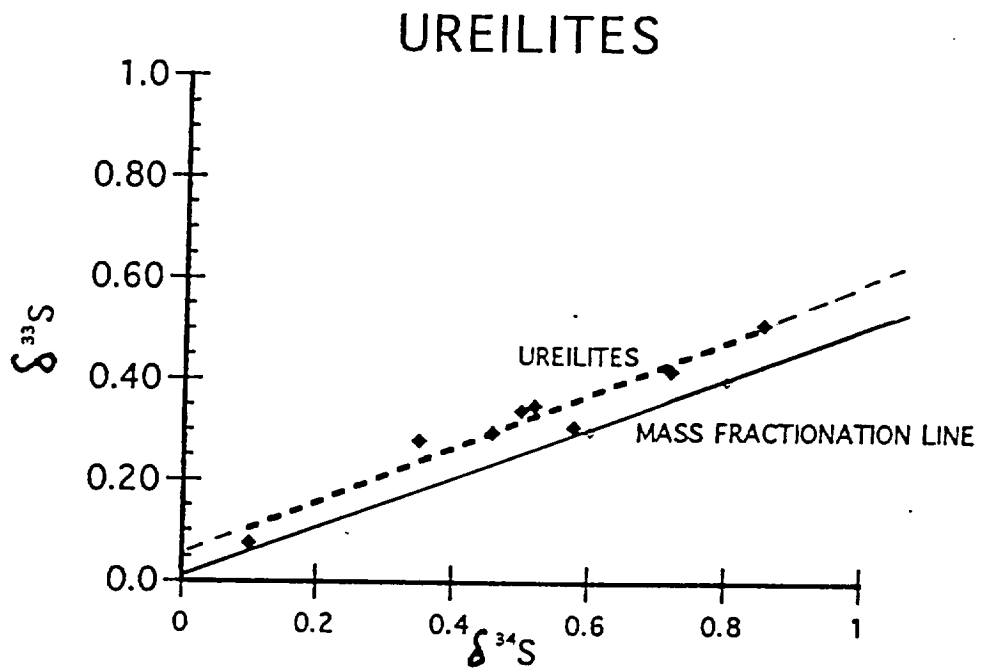


FIGURE 1. The $\delta^{33}\text{S}$ vs $\delta^{34}\text{S}$ values for ureilites. The line for all terrestrial and other meteorites is shown for comparison.

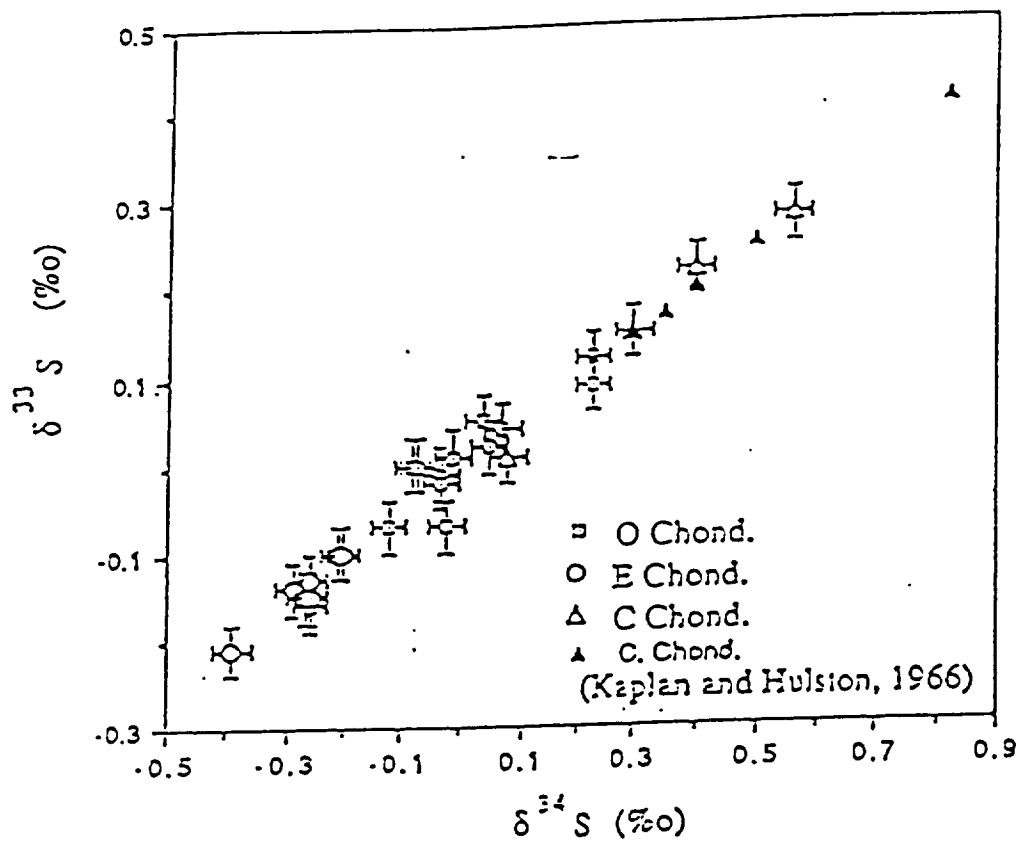


FIGURE 2. Bulk $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ for different meteorites.

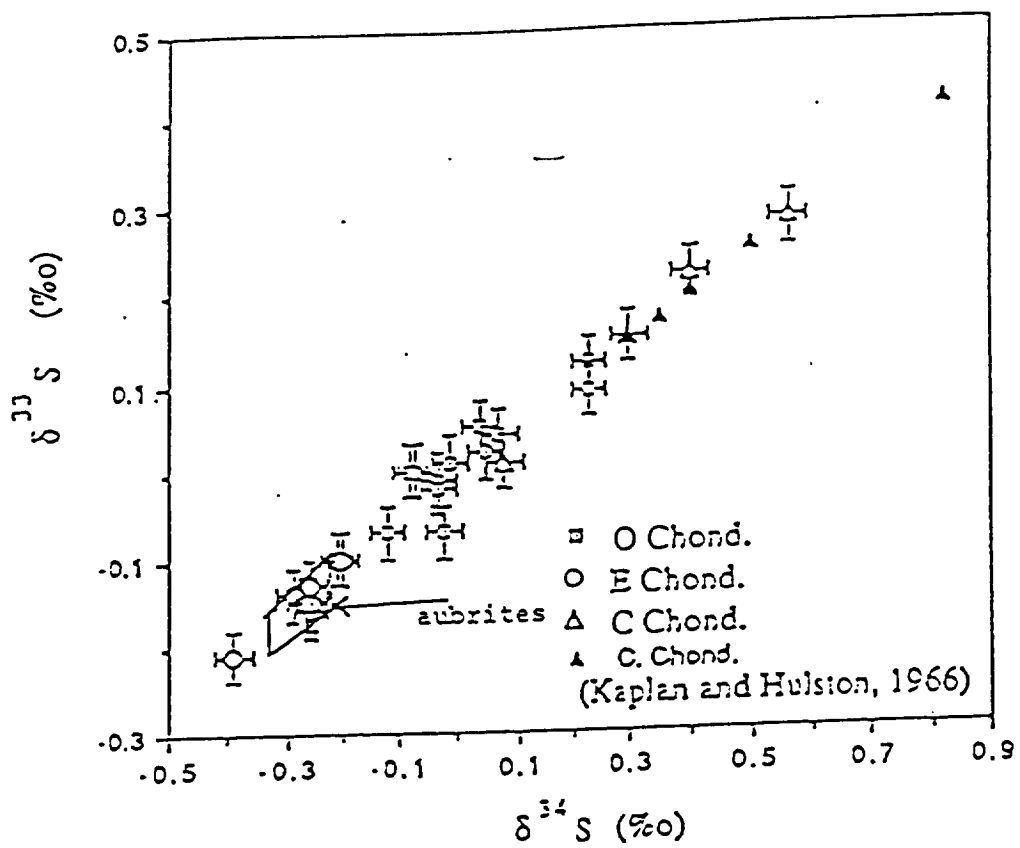


FIGURE 3. The bulk isotopic composition of meteorites showing the overlap of enstatite chondrites and achondrites.

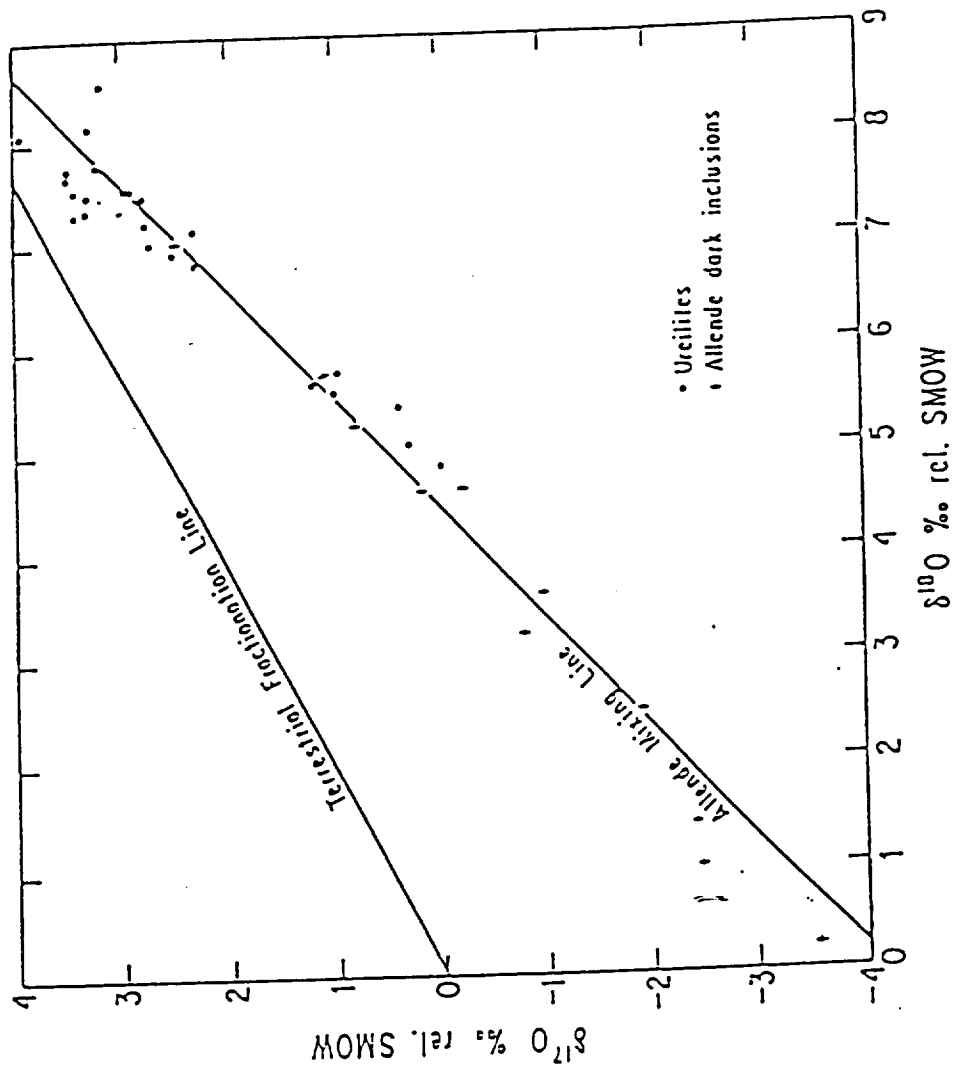


FIGURE 4. The oxygen isotopic composition of ureilites. Data from Clayton (1993).

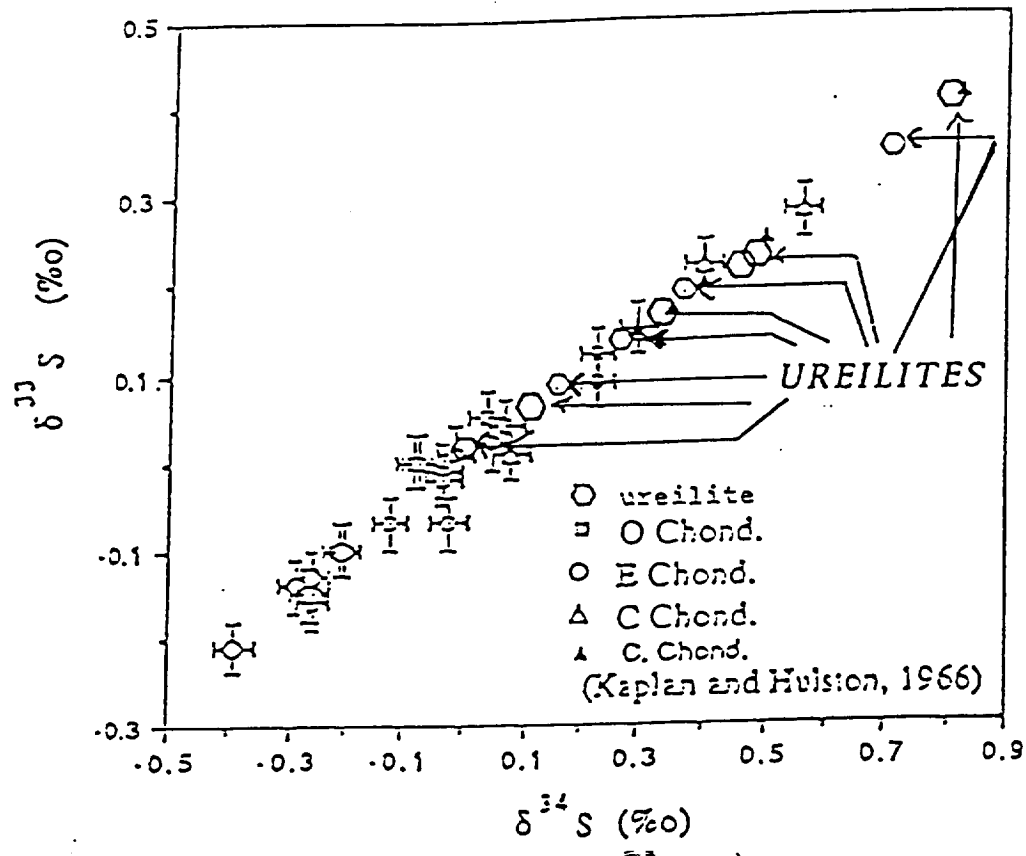


FIGURE 5. The sulfur isotopic composition of meteorites showing the overlap of carbonaceous chondrites and ureilites.

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13. ABSTRACT (Maximum 200 words) Funds were requested to continue our program in meteoritic sulfur isotopic analysis. We have recently detected a potential nucleosynthetic sulfur isotopic anomaly. We will search for potential carriers. The documentation of bulk systematics and the possible relation to nebular chemistry and oxygen isotopes will be explored. Analytical techniques for $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$ isotopic analysis were improved. Analysis of sub milligram samples is now possible. A possible relation between sulfur isotopes and oxygen was detected, with similar group systematics noted, particularly in the case of aubrites, ureilites and entstatite chondrites. A possible nucleosynthetic excess ^{33}S has been noted in bulk ureilites and an oldhamite separate from Norton County. High energy proton (1 GeV) bombardments of iron foils were done to experimentally determine ^{33}S , ^{36}S spallogenic yields for quantitation of isotopic measurements in iron meteorites. Techniques for measurement of mineral separates were perfected and an analysis program initiated. The systematic behavior of bulk sulfur isotopes will continue to be explored.				
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