A NEW ISOTOPE EFFECT AND ITS POSSIBLE ROLE IN THE PRODUCTION OF EXCESS METEORITIC $^{33}$S AND CARBONACEOUS MATERIAL (Q?); M. H. Thiemens, X. Xu, J. Colman, W. C. Trogler; DEPARTMENT OF CHEMISTRY, UCSD, LA JOLLA, CALIFORNIA. 92093.

There are several observations of sulfur isotopic anomalies in meteoritic material. This includes excess $^{33}$S in Allende acid residues (1), olivines from Norton County (2) and bulk ureilites (3). The source of these observed isotopic anomalies is at present, unresolved. Recently, excess $^{33}$S has been observed in an organic extract from Murchison (methane sulfonic acid) (4). This molecule also possesses deuterium excesses ranging from 660 to 2,730 per mil (5). Since sulfur, like oxygen, may be subject to symmetry dependent reaction chemistry, investigations exploring isotopic fractionations in astronomically relevant molecules may be of utility.

It has been demonstrated that the formation of the symmetric molecule $S_2F_{10}$ produces a mass independent isotopic fractionation, with enrichment of the heavy isotopes (6). While this provides additional evidence for the role of symmetry in the production of mass independent compositions, $S_2F_{10}$ is not a relevant molecule for nebular, molecular cloud or cometary conditions. For sulfur, thermochemical calculations show that $H_2S$, $CS_2$ and $S_2$ are important sulfur bearing molecules under solar or nebular conditions (7). Carbon disulfide ($CS_2$), may be of special importance due to its symmetry and accompanying isotopic effects. As a result of its position on the periodic chart and the possession of more than 2 stable isotopes, sulfur is the only element, besides oxygen, which could produce an observable symmetry dependent isotopic fractionation under nebular conditions. There are no studies of isotopic fractionations associated with $CS_2$ chemistry of relevance with respect to meteoritic material.

It was first demonstrated by Bridgman (8) that $CS_2$ may polymerize into a black solid. Recently, Colman and Trogler (9) have shown that irradiation of carbon disulfide vapor at 313 nm produces a solid aerosol with diameters typically nanosized. The elemental composition of this material has a composition of $CS_{1.98}$ and density of 1.92 g/cm$^3$. Spectroscopic studies of the aerosols suggest that the material is composed of chains of $(CS_2)_x$, cross linked by S-S bonds (9). The polymerization initiates with the promotion of $CS_2$ to an electronically excited state ($CS_2^*$) by absorption of UV light. The electronically excited $CS_2$ molecule possesses sufficient energy to initiate polymerization reaction:

$$CS_2 + CS_2^* \rightarrow \text{polymeric material}$$

The studies reported by Colman and Trogler (9) were repeated and the polymeric material collected for high precision sulfur isotopic analysis. The techniques used for isotopic analysis were identical to those reported by Gao and Thiemens (10). In the first experiment, the aerosol product from photolysis of gas phase $CS_2$ at 313 nm was collected by solvent extraction (acetone) of the residue in the photolysis vessel. The solution was centrifuged and brought to dryness. For this sample, the isotopic composition with respect to the initial $CS_2$ was:

$\delta^{33}S=28.0$, $\delta^{34}S=45.4$ and $\delta^{36}S = -16.6$ per mil. Gas chromatographic re-purification of the SF$_6$ did not alter the isotopic composition, thus the measurements are not a result of contamination. The results possess several remarkable features: 1) there is an excess $^{33}$S of more than 5 per mil with respect to a mass dependent fractionation. 2) The samples are enriched in $\delta^{33}S$ and $\delta^{34}S$, whereas a conventional reaction would predict a depletion. 3) The $^{36}$S is enormously depleted; the $\delta^{36}S$ isotopic composition deviates more than $100$ per mil from a mass dependent fractionation! In a repeat experiment, with the only difference that the polymeric material was simply scraped from the walls of the photochemical vessel, the $\delta^{34}S$ and $\delta^{33}S$ isotopic compositions were identical, however, the $\delta^{36}S$ was depleted with respect to mass fractionation by 130 per mil! It is not certain what the source of the difference is between
the two experiments. In the solvent extract, there will be a total collection of aerosols, whereas there may be a selection against smaller particles in the dry extraction. If this is the case, this may be evidence for different isotopic fractionations in solid aerosol formation. This could ultimately be of utility in understanding interstellar grain formation and the accompanying isotopic fractionations.

In a final experiment, the photolysis was done utilizing ground level solar radiation and dry extraction. In this case, the $\delta^{34}S$ is enriched by 56 per mil and $^{33}S$ is in excess of 10 per mil from a mass dependent fractionation. In the case of $^{36}S$, there is a 140 per mil deficit from mass fractionation.

The experimental results demonstrate that large mass independent isotopic fractionations accompany the formation of solid polymeric material from a gas phase reaction. The precursor molecule, CS$_2$, is a molecule which occurs in astrophysical environments, including the solar nebula, comets and interstellar molecular clouds. It is plausible that the source of the observed meteoritic $^{33}S$ excesses derive from similar gas phase photochemical chemical reactions. The ureilites possess excess $^{33}S$ at the bulk level. Large euhedral graphite crystals, intergrown with metal-sulfide intergrowths have been observed (11). If the precursor material were carbon polymeric material, such as that produced in the CS$_2$ experiments, this would provide a mechanism responsible for production of the observed $^{33}S$ excess. Condensation of black polymeric material, such as produced in the experiments, with incorporation into the meteorite parent body, followed by differentiation and/or shock could result in graphitization with preservation of the $^{33}S$ excess. While a $^{36}S$ deficiency is expected, this has not been observed. The typical ureilite $^{33}S$ excesses are 0.1 per mil, thus a $^{36}S$ deficiency would be expected at the per mil level. The present laboratory experiments demonstrate that the deficiency of $^{36}S$ highly is sensitive to the reaction conditions and are variable, whereas the $^{33}S$ excess are less so. It is therefore important to determine the dependency of the fractionation process upon relevant parameters, such as pressure, temperature, irradiation conditions and presence of other molecules. Secondary isotopic fractionations on the meteorite parent body may also alter the initial isotopic signature. The observation of a large $^{33}S$ excess in an organic molecule (4) also suggests a chemical origin for the anomaly as methane sulfonic acid is not a likely carrier of a nucleosynthetic component. In this case, the $^{33}S$ anomaly would be transferred from the CS$_2$ reaction network.

In summary, a large mass independent isotopic fractionation is observed in the photolysis of carbon disulfide which produces a black polymeric solid with a 5-10 per mil $^{33}S$ excess and as great as a 145 per mil deficiency in $^{36}S$. The solid is produced when CS$_2$ is submitted to ground level solar radiation. The present lab and meteoritic observations suggest that the polymerization reaction could have occurred in the early solar system and may account for the excess $^{33}S$ observed in ureilites and the carbonaceous Allende acid residues. A relation between noble gas anomalies in ureilites and acid residue Q-gases has also been proposed (12). This opens the possibility that this process could be a source of the carbonaceous material found in Allende. Future measurements of sulfur Q-components (acid residues), ureilite sulfur components and relevant laboratory experiments are needed to further resolve this hypothesis.