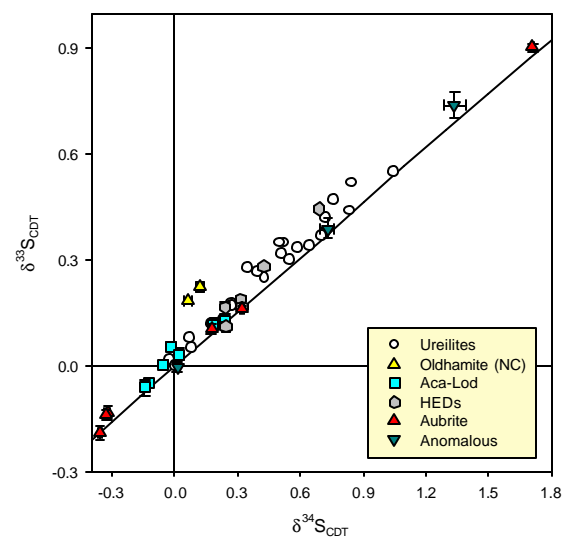


**MASS INDEPENDENT SULFUR IN ACHONDRITES: POSSIBLE EVIDENCE OF PHOTOCHEMISTRY IN THE SOLAR NEBULA** V. K. Rai<sup>1</sup>, T. L. Jackson and M. H. Thiemens, Chemistry and Biochemistry, University of California San Diego, La Jolla, 92093-0356, CA, <sup>1</sup>email: [rai@chem.ucsd.edu](mailto:rai@chem.ucsd.edu).

**Introduction:** In our continuing effort to resolve and interpret the sulfur isotopic heterogeneity of meteorites [1-5], we analyzed a number of achondritic meteorites. Like oxygen, sulfur has more than two stable isotopes and therefore it is feasible to deconvolute the isotopic anomaly from the mass dependent isotopic fractionation that occurred during parent body processes. Any non-mass dependent fractionation process produced due to mass independent photochemical or physicochemical processes in the presolar nebula may be characterized by a nonzero (or variable)  $\delta^{33}\text{S}$  or  $\delta^{36}\text{S}$ . It has been shown that the gas phase photochemical reactions, involving  $\text{CS}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{S}$ , either in the Earth's Archean as well as present day atmosphere, Mars, or in laboratory experiments, fractionate S isotopes mass independently [6-12]. Lab studies of photochemical reactions have shown that the sign of mass independent fractionation (MIF) depends upon the wavelength of UV light [7], presumably due to the energetics of intersystem, electronic state crossings. In light of these observations, it is important to investigate S in various meteorites as other than oxygen, sulfur is the only multi-isotopic element that could potentially record early mass independent processes, both self shielding, as first hypothesized by [13], photochemical, or mass independent chemical reactions.

Sulfur exists in a variety of valence states in meteorites its composition is remarkably constant [1,2] with exceptions for isolated phases in Allende and Murchison [14,5]. Unlike primitive chondrites where the anomalous isotopic composition of various elements has been observed, in achondrites, these primitive signatures were lost during parent body differentiation. For sulfur, this scenario differs as  $^{33}\text{S}$  enriched components have been observed in ureilites and oldhamite from the Norton County aubrite [16,4]. In order to resolve the origin of the  $^{33}\text{S}$  anomaly and to investigate whether it is present in other achondrite, we have analyzed sulfur from six HEDs, five aubrites, two acapulcoite-lodranite and anomalous Weatherford, Bencubbin meteorites for bulk S isotopic composition. For HEDs, sulfur data has been reported for the first time whereas we have analyzed two more samples from the unique acapulcoite-lodranite group. Bencubbin and Weatherford are interesting as they have been shown to possess very heavy nitrogen [17]. Despite several detailed studies, the origin of heavy nitrogen is still unexplained. The study of S in these meteorites may be helpful in understanding the origin of anomalous nitrogen.



**Fig. 1** Plot of  $\delta^{34}\text{S}$  vs  $\delta^{33}\text{S}$  for aubrites, HEDs and Bencubbin and Weatherford meteorite. Data for Norton County oldhamite, ureilites and acapulcoite-lodranites are from [4,5,16].

**Experimental.** The experimental procedure is described in [5]. In some of the samples sulfate extraction was attempted though most of the samples have too small sulfates to be analyzed for isotopic composition. New analytical developments at UCSD will make such measurements possible in the future.

**Results and Discussions:** In Fig. 1,  $\delta^{34}\text{S}$  is plotted against  $\delta^{33}\text{S}$  for achondrites analyzed here.

**HEDs.** In this study we analyzed one howardite (EET87503,95), three eucrites (EET90020, PCA82502 and Moor County) and two diogenites (LAP91900, ALH77256). They generally have low S content, between 0.01-0.2 % (by wt.). The average  $\delta^{34}\text{S}_{\text{CDT}}$  of the six analyses are  $0.37 \pm 0.17\text{‰}$  with a range from 0.24 to  $0.69\text{‰}$ . The average value of  $\delta^{33}\text{S}$  is  $0.036 \pm 0.039\text{‰}$  with a standard error of  $0.016\text{‰}$ . The average value of  $\delta^{36}\text{S}$  is  $-0.259 \pm 0.622\text{‰}$  with a standard error of  $0.254\text{‰}$ .

**Aubrite.** Aubrites are a group of achondrites formed from enstatite chondrite-like parental material. Oldhamite separates from Norton County were shown to have significantly enriched in  $^{33}\text{S}$  though bulk sample analysis did not show any enrichment of  $^{33}\text{S}$  [4]. Here the five bulk samples (ALH8409,14; ALH84023,9; Cumberland Falls, ALH78113; ALH84010) have been analyzed in which two of them are paired. Aubrites contain S between 0.3–0.6%. They exhibit a relatively large range in  $\delta^{34}\text{S}$ : from  $-0.58\text{‰}$  to  $1.7\text{‰}$  (Fig.1) with average  $\delta^{34}\text{S}$  value of six analyses including Norton County [4] is  $0.32$

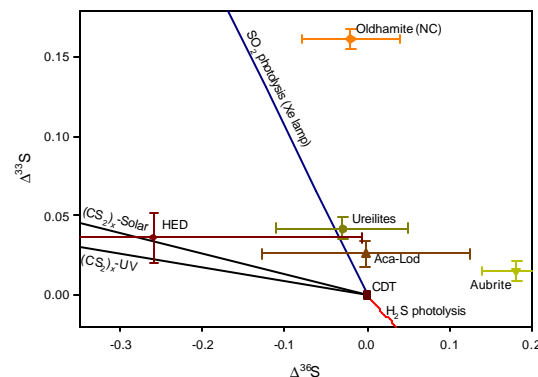
$\pm 0.75\%$  with standard error of  $0.31\%$ . The mean values of  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  are  $0.015 \pm 0.015\%$  and  $0.182 \pm 0.106\%$  respectively, with corresponding standard error values (of six analyses) are  $0.006$  and  $0.043\%$ .

**Bencubbin and Weatherford.** These samples were analyzed after separating into magnetic and nonmagnetic fractions. Because of small concentrations of S combined with availability of small sample size, for nonmagnetic fractions of both the meteorites, only the three more abundant isotopes of S (*i.e.*,  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$ ) could be measured. It can be seen from the Fig.1 that there is wide range of  $\delta^{34}\text{S}$  of these two anomalous meteorites but most of the data points are very close to the mass dependent fractionation line (MFL) indicating that sulfur, unlike nitrogen in these meteorites is normal. It should be noted that the terrestrial mass fractionation line has been extraordinarily well defined and has been established by measurements of hundreds of terrestrial samples and other meteorites, such as carbonaceous, enstatite and ordinary chondrites.

**Acapulcoite-Lodranites.** After inclusion of data of two new samples to the previous analysis of [5], the value of  $\delta^{34}\text{S}$  is changed to  $0.015 \pm 0.147\%$  with standard error of seven measurements of  $0.056\%$ . The average value of  $\Delta^{33}\text{S}$  is  $0.026 \pm 0.020\%$  with standard error of  $0.008\%$ .

Based on S content, HEDs are similar to ureilites, they both have low S concentration. In Fig.1, it can be seen clearly that ureilites, HEDs and acapulcoite-lodranites lie above MFL, the deviation though small, is resolvable at the high precision of the measurements. The average  $\Delta^{33}\text{S}$  value of HEDs is higher than that of acapulcoite-lodranites and close to, but lower than that of ureilites (Fig. 2). It is clear that all the three achondrite groups have resolvable excesses of  $^{33}\text{S}$ , beyond the experimental uncertainty. Aubrites, on the other hand contain relatively higher concentration of S compared to ureilites and HEDs. Despite the observation of  $^{33}\text{S}$  enriched oldhamite and a relatively larger range of  $\delta^{34}\text{S}$  than that of other achondrites, most of the bulk aubrites fall very close to the MFL (Fig. 1) indicating that the larger proportion of normal S along with anomalous oldhamite dilutes the anomaly. Origin of this anomalous  $^{33}\text{S}$  enrichment is not cosmic ray spallation or stellar nucleosynthesis [5,15]. In the case of cosmic rays, there is insufficient exposure age and iron target, for nucleosynthesis, there is not an accompanied  $^{36}\text{S}$  anomaly.

In laboratory experiments, it has been shown that photochemical reactions of S compounds enrich  $^{33}\text{S}$  mass independently but also produce changes in  $^{36}\text{S}$  [7,8] though there remain a number of experiments that need to be done. The observed mass independent S



**Fig.2** Plot of average  $D^{33}\text{S}$  vs  $D^{36}\text{S}$  various achondrites. The lines show the directions of fractionation observed in various photochemical reactions in the laboratory experiments.

anomaly most closely matches that observed in  $\text{SO}_2$  photolysis experiment with high pressure Xe arc lamp in the spectral region ( $>220\text{nm}$ ) [7] (Fig 2).  $\text{SO}_2$  photolysis might be the more appropriate for observed mass independent S in Archean sediments but not for the  $^{33}\text{S}$  anomaly in meteorites as  $\text{SO}_2$  is unlikely to be present in the early solar nebula. Photopolymerization of  $\text{CS}_2$  or CS and photochemical reactions of  $\text{H}_2\text{S}$  are more appropriate for nebular settings but the sign of fractionation is opposite to that is observed in the latter case while the former also shows a relatively large depletion in  $^{36}\text{S}$  along with enrichment  $^{33}\text{S}$  [8,6] (Fig 2). It has been shown that mass independent fractionation is strongly wavelength dependent [7] and most of the laboratory experiments have been performed at higher UV wavelengths. It is now critically important to study these reactions at shorter wavelengths that are appropriate for presolar nebular conditions

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