^{33}S ANOMALY IN ACAPULCOITES AND LODRANITES.

Rai V. K., Jackson T. L. and Thiemens M. H., Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA, 92093-0356, USA.

Introduction: Sulfur is a significant constituent of all meteorites. It is not only present in appreciable amounts in meteorites but also has the added advantage of having multiple valance states. Because of its multiple valance states, it occurs in various chemical forms, such as sulfide, sulfate, elemental sulfur, and organic sulfur. Like oxygen, it has more than two stable isotopes that are produced in different stellar environments [1]. Therefore any mass dependent processes (melting, recrystallization, differentiation *etc*.) can be estimated and corrected for, leaving the scope for detection of any isotopic anomaly produced either due to incomplete mixing of different nucleosynthetic components or mass independent chemical processes in the early solar nebula. Recently, it has been shown that the gas phase photochemical reactions, involving CS_2, SO_2 and H_2S, either in planetary atmospheres or in laboratory experiments, fractionate S isotopes mass independently [2-5]. The laboratory studies of photochemical reactions has shown that the sign of mass independent fractionation depends upon the wavelength of UV light [2-5]. Since meteorites have accreted from grains condensed directly from a cooling nebular gas, potentially in the presence of strong UV light from the proto sun, it is possible that sulfur phases in meteorites might capture a photochemical signature. Therefore, precise measurements of S isotopic compositions of sulfur containing phases in differing meteorites might provide insight into the physicochemical conditions, as well as the photochemical environment in meteorite forming regions. A mass independent sulfur isotopic fractionation has been reported in meteorites such as ureilites [6], oldhamite in the Norton county aubrite [7] and in a few isolated components in Allende and Murchison [3, 8]. Here we present the sulfur isotopic data for all three sulfur isotopic ratios (δ^{33}S, δ^{34}S and δ^{36}S) for five meteorite samples from the acapulcoite-lodranite group of achondrites.

Based upon mineralogy, chemical and oxygen isotopic composition, acapulcoites and aodranites are believed to have originated from a common parent body and are classified as primitive achondrites. Various studies have suggested a very rapid cooling of the acapulcoite-lodranite parent body. Acapulcoite is a fine grained meteorite with approximately chondritic abundance of olivine, pyroxene, plagioclase, metals and troilite, while lodranites are coarse grained meteorites, depleted in troilite and plagioclase [9 and

orites, depleted in troilite and plagioclase [9 and references therein]. In this study we have analyzed three acapulcoites, one lodranite and LEW86220 (unusual, linked to acapulcoite-lodranite) for all four isotopes of sulfur in sulfides phases.

Experimental: Sulfur isotopic composition in this study has been measured as SF_6 by Finnigan Mat 252 isotope ratio mass-spectrometer following the procedure of [10]. The acid volatile S is converted to Ag_2S by the reaction with 6N HCl for 3 hour at 120°C. H_2S evolved as a result of reaction with HCl, converted to CdS by passing it through 0.2M cadmium acetate using high purity nitrogen gas as carrier. CdS is further converted to Ag_2S by the reaction with silver nitrate followed by fluorination in Ni tube with BrF_5 at 580°C for 12 hours. SF_6, the product of fluorination is collected in a sample tube after cryogenic separation from BrF_5 through three cold traps at -119°C in steps and this is repeated again in order to get cent percent recovery of SF_6. SF_6 is further purified by gas chromatography. The amount of sulfate present in these meteorites are too small to be analyzed for isotopes, here we present isotopic data from sulfide phases only.
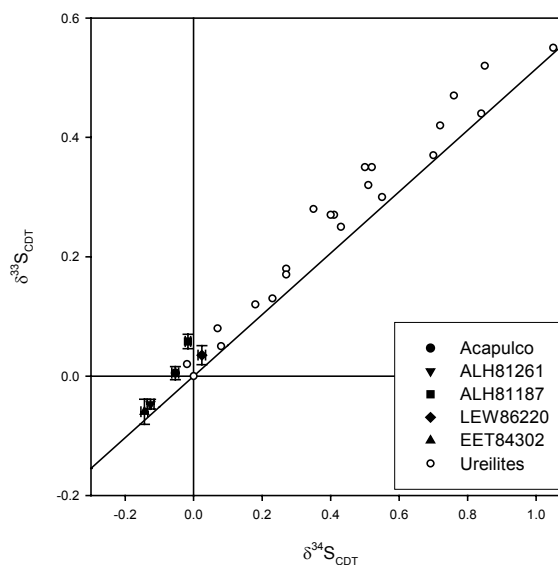

Fig 1. Three isotope plot of sulfur (δ^{33}S and δ^{34}S in ‰) in acapulcoite-lodranites plotted along with ureilites [6].

Results: Acapulcoites contain S between 0.7% to 2%, which is comparable to ordinary chondrites [10]. It is heterogeneously distributed in the samples (on cm

scales). The lowest amount of S obtained in EET84302 is 0.2 wt% which is transitional between acapulcoites and lodranites. The average value of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ are -0.002 ± 0.051 (standard error of 0.023), -0.063±0.071 (standard error: 0.032) and 0.120±0.397 (standard error: 0.178) respectively for five acapulcoite-lodranites and the corresponding ranges in δs are –0.06 to 0.06, -0.144 to 0.024 and –0.428 to 0.562 respectively. In Fig 1, $\delta^{33}S$ values have been plotted against $\delta^{34}S$ for acapulcoite-lodranites along with ureilite data [6] and the reference line for the mass dependent fractionation. It can be seen that all the data points lie above the reference line on a three isotope plot to an extent similar to that observed in ureilites. The average $\Delta^{33}S=0.031\pm0.020$ with standard error of 0.001 and $\Delta^{36}S=0.001\pm0.407$ with standard error of 0.182. All the $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ fall within the ranges shown by sulfides and sulfates from meteorites. But the average value of $\Delta^{33}S$ (0.031±0.001) is significantly higher by more than the standard error as compared to other meteorite groups [10,11] except ureilites [6] while the average $\Delta^{36}S$ (=0.001±0. 182) falls within the range of other meteorites. The case for acapulcoites-lodranites is very much similar to that of ureilites except that the $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ values are closer to) per mil CDT. This implies that like ureilites, acapulcoites-lodranites contains a ^{33}S enrichment.

Discussion: Cosmic ray induced spallation of iron is well known to produce ^{33}S enrichments, but in this instance is unlikely in that most of the acapulcoite-lodranites have low cosmic ray (<7 Ma) exposure ages and spallation also produces ^{36}S enrichments, which are not observed [12]. This also does not seem to be nucleosynthetic anomaly because, with present knowledge, none of the stellar nucleosynthetic sources are known that produce ^{33}S without co-producing other isotopes of S [13,14]. In laboratory experiments, it has been shown that photochemical reactions of S compounds enrich ^{33}S mass independently but also produce changes in ^{36}S [3-5] though there remain a number of experiments that need to be done. The observed mass independent S anomaly most closely matches with that observed in SO_2 photolysis experiment with high pressure Xe arc lamp[4] (see Fig 2). SO_2 photolysis might be the more appropriate for observed mass independent S in Archean sediments [3, 4] but not for the ^{33}S anomaly in meteorites because SO_2 is unlikely to be present in the early solar nebula. Photopolymerization of CS_2 or CS and photochemical reactions of H_2S 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}S along with enrichment ^{33}S [5] (Fig 2).

It has been shown that mass independent fractionation is strongly dependent on wavelength [3, 4] and most of the laboratory experiments have been performed at higher wavelengths of UV. It is now desirable to study these reactions on lower wavelengths that will be more appropriate for presolar nebular conditions.
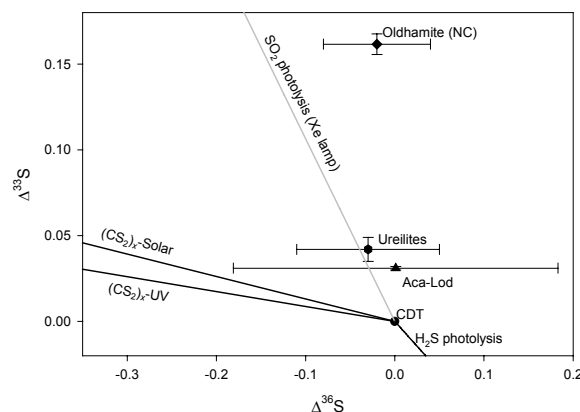

Fig 2. Plot showing the $\Delta^{36}S$ and $\Delta^{33}S$ observed in acapulcoite-lodranites, ureilites and oldhamite from Norton county aubrite. The lines show the directions of fractionation observed in various photochemical reactions in laboratory experiments [4, 5]. Mass dependent S component fall at (0,0) on this plot.

At present, the observation of ^{33}S enrichment in ureilites and acapulcoite-lodranites and their very similar average $\Delta^{17}O$ is intriguing [15] and a more extensive data set is required. Consideration of other possible sources of the anomaly is presently under consideration.

References:

[1] Clayton R. N. and Ramadurai S. (1977) *Nature, 265,* 427–428. [2] Colman et al. (1996) *Science, 273,* 774-776. [3] Cooper et al. (1997) *Science, 277,* 1072-1074. [4] Farquhar J. et al. (2001) *JGR, 106,* 32829–32839. [5] Farquhar J. et al. (2000) *Nature, 404,* 50–52. [6] Farquhar et al. (2000) *GCA, 64,* 1819-1825. [7] Thiemens et al. (1994) *Meteoritics, 29,* 540-541. [8] Rees C. E. and Thode (1977) *GCA, 41,* 1679-1682. [9] Mittlefehldt et al. (1998) In *Planetary Materials,* (ed. J.J. Papike) Mineralogical Society of America, 4-64–4-73. [10] Gao X. and Thiemens (1993) *GCA, 57,* 3171-3176. [11] Gao X. and Thiemens (1993) *GCA, 57,* 3159-3169. [12] Gao X. and Thiemens (1991) *GCA, 55,* 2671-2679. [13] Wooslay S. E. et al. (1973) *Astrophy.s J. Supp., 26,* 231-312. [14] Cameron A. G. W. (1979) *Ap. J., 230(1,pt.2),* L53-L59. [15] Clayton R. N. and Mayeda T. K. (1996) *GCA, 60,* 1999-2017.