Multiple Sulfur Isotopic Analysis of Eucrites and Angrites. N. Wu[1], J. Farquhar[1], N. Magalhaes[1], J.W. Dottin III[1], and J. Labidi[2]. [1]Department of Geology, University of Maryland, College Park, MD, 20742, [2]Department of Geosciences, Universität Tübingen, Tübingen Germany. wunanping@gmail.com.

Introduction: Studies of meteoritic sulfur undertaken in the past 15 years have revealed evidence for heterogeneity in the relative abundances of ^{34}S, ^{33}S, and ^{36}S of achondrites [1-2], iron meteorites [3], stony irons [4], and some primitive meteorites [5-6]. Part of this isotopic heterogeneity may be linked to processes associated with melting and separation of silicate liquids, metallic liquids and sulfide melts during the planetesimal evolution. The origin of this heterogeneity also appears to be related to nebular sulfur chemistry and primary signatures derived from the material from which differentiated parent bodies accreted [2,3].

Here, we report sulfur isotopic data for 7 eucrites and 4 angrites. We aim to characterize the sulfur isotopic compositions of the two groups, determine processes that lead to the observed fractionations, and evaluate the relationships between sulfur isotope data and geochemical tracers of the history of the differentiation within the parent bodies.

Methods: Chromium-reducible sulfur was extracted from crushed meteorite samples and converted to silver sulfide (Ag_2S). The dried Ag_2S, wrapped in aluminum foil, was loaded into a nickel metal vessel, which was subsequently filled with tenfold excess of fluorine gas and heated at ~250 °C overnight. The product SF_6 gas was purified by cryogenic distillation and a gas chromatography system. The purified SF_6 gas was then analyzed for multiple sulfur isotopes using a Thermo-Fisher MAT 253 gas source isotope ratio mass spectrometer at the Stable Isotope Laboratory in University of Maryland at College Park. Four collectors simultaneously detect ion beams with mass/charge ratios of 127($^{32}SF_5^+$), 128($^{33}SF_5^+$), 129($^{34}SF_5^+$), and 131($^{36}SF_5^+$). The uncertainties associated with sample measurements are estimated on basis of external precisions of IAEA-S1 measurements, and the 2σ errors for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ are estimated at 0.30‰, 0.008‰ and 0.30‰, respectively.

Results: We report multiple sulfur isotopic data for eucrites and angrites in both table 1 and figure 1. The data are normalized to Canyon Diablo Troilite (CDT) and reported in per mil using $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ notation.

Sulfur isotope data for the eucrites show a cluster of measurements with $\delta^{34}S$ of 0.30 ‰, $\Delta^{33}S$ of 0.010 ‰, and $\Delta^{36}S$ of -0.26 ‰ with one measurement (GRA 98098) having $\delta^{34}S$ of 0.81 ‰ and another measurement (CMS 04049) displaying a $\delta^{34}S$ of -0.22 ‰ and $\Delta^{33}S$ of 0.024‰. The variation of $\delta^{34}S$ is interpreted to be real, and the difference in $\Delta^{33}S$ may be real, but needs to be reproduced, allowing statistical confirmation about this low-level heterogeneity in $\Delta^{33}S$.

Sulfur isotope data for the angrites reveals 2 samples (NWA 4590 and SAH 99555) with $\Delta^{33}S$ of 0.008‰, $\delta^{34}S$ of 0.45‰, and $\Delta^{36}S$ of -0.24‰ and 2 samples (Angra Dos Reis and NWA 4801) with negative $\delta^{34}S$ (-0.35 ‰ and -0.72 ‰, respectively), $\Delta^{33}S$ of 0.014‰ and $\Delta^{36}S$ of -0.35‰. The $\Delta^{33}S$ and $\Delta^{36}S$ variation falls within 2σ estimates of uncertainties. The difference for $\delta^{34}S$ is outside the 2σ uncertainty and is considered to be real, reflecting isotopic heterogeneity in angrites.

Table 1. S isotopic data for eucrites and angrites

	$\delta^{34}S$	$\Delta^{33}S$	$\Delta^{36}S$	Concentration (ppm)
BTN 00300	0.34	0.009	-0.38	1264
MIL 11290.14	0.23	0.006	-0.25	1759
QUE 97014.40	0.33	0.013	-0.35	1641
EET 90020.71	0.35	0.007	-0.09	1269
PCA 82502.110	0.27	0.016	-0.23	110
CMS 04049.28	-0.22	0.024	-0.17	472
GRA 98098.110	0.81	0.010	0.01	277
NWA 4801	-0.38	0.014	-0.39	2527
Angra Dos Reis	-0.72	0.014	-0.30	1427
NWA 4590	0.42	0.007	-0.25	4105
SAH 99555	0.49	0.009	-0.24	3302

Discussion: The data presented in figure 1 reveal small but statistically resolvable enrichments in ^{33}S (positive $\Delta^{33}S$) relative to CDT, especially for CMS 04049, PCA 82502, NWA 4801, and Angra Dos Reis, and sub-permil variation of $\delta^{34}S$ for both the eucrites and angrites.

The ^{33}S enrichments in angrites and eucrites are small, slightly smaller than that seen for the IVA, IIIAB, IIAB groups of magmatic irons, pallasites, and ureilites [1-4], requiring a ^{33}S-enriched sulfur source. Such a source has been interpreted to be derived from photochemical reactions in the solar nebular [2-3, 6], but evidence also exists for possible nucleosynthetic variations of sulfur isotopes in solar system materials [7-8] which may also have contributed to isotopic variability. While further analyses are needed to confirm whether the eucrites and angrites define a subtly different mass fractionation line than other meteorite groups, our analyses suggest that they have a $\Delta^{33}S$ that is enriched by approximately 10 ppm relative to CDT and depleted relative to IIAB, IIIAB, and IVA irons as well as Pallasites. Only one IVB meteorite (Hoba) has been analyzed [3] and yielded a $\Delta^{33}S$ of 0.000‰, suggesting that the IVB have a different $\Delta^{33}S$ than both the angrites and the eucrites.

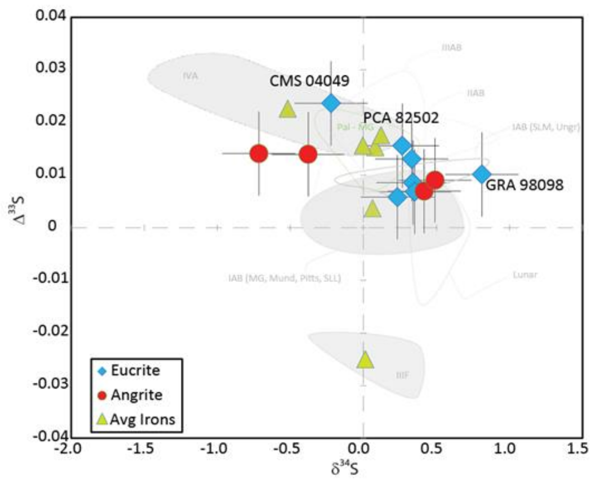

Figure 1. $\Delta^{33}S$ vs. $\delta^{34}S$ for eucrites and angrites. The error bars represent 2σ uncertainties associated with isotopic measurements. The plot also presents the averages (triangles) and ranges for iron meteorites [3], pallastites [4] and lunar samples [13] (normalized to CDT).

The sub-permil variation of $\delta^{34}S$ for eucrites and angrites is interpreted to reflect mass-dependent fractionations associated with processing within the respective planetesimals, but the detailed mechanisms that produced the $\delta^{34}S$ variations and the slightly positive $\delta^{34}S$ for eucrites have yet to be identified.

The two eucrites that define the variation in $\delta^{34}S$ relative to the average value are CMS 04049, which has a negative $\delta^{34}S$ value, and GRA 98098, which has a slightly higher positive $\delta^{34}S$ value. CMS 04049 has been documented to contain unusual mesostasis-like regions [9] that are rich in sulfides. Likewise, GRA 98098 contains unusual petrography, including silicate veins containing tridymite, plagioclase, and pyroxene [10]. Both CMS 04049 and GRA 98098 yielded lower sulfide (500 ppm & 280 ppm, respectively) compared to the other eucrites we studied. It is also noted that PCA 82502 which yielded the lowest sulfide (110ppm) in this study shows the most depletion in zinc isotopes and may be from a distinct asteroid [11]. GRA 98098 displays the most enrichment in ^{66}Zn and ^{68}Zn [11]; further work is required to elucidate possible co-variation of zinc isotopes and sulfur isotopes.

The slightly positive $\delta^{34}S$ of eucrites, relative to the mean $\delta^{34}S$ of iron meteorites is similar to, but less pronounced than that seen for lunar basalts [12-13]. It is difficult to reconcile the positive $\delta^{34}S$ directly with metal-silicate differentiation as isotopic fractionations between metal and silicate liquids [14-15] yield metals that are ^{34}S-enriched relative to silicate melts with greater fractionations predicted for higher pressure conditions at a given chemical composition. Generation and crystallization of sulfur saturated silicate melts could yield fractionations that enrich ^{34}S in the silicate, but also do not provide a ready explanation for the observations as it has been shown to produce only very small fractionations [16, $\alpha_{sulfide\text{-}melt} = 0.9995\pm0.0005$].

The analyses also do not reveal a correlation between the sulfur isotopes and geochemical indicators of continued accretion for the angrite parent body or Hf/W evidence for metal-silicate differentiation [17-18]. Presently, unknowns include identifying the processes that generate the variation of $\delta^{34}S$ and $\Delta^{33}S$ in these meteorites and whether relationships will emerge relating sulfur to differentiation processes. Further work to expand the measurements, validate the observations, and explore whether similar relationships exist for related meteorites, including diogenites is planned.

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