CLUES TO THE MARTIAN SULFUR CYCLE REVEALED THROUGH ISOTOPIC ANALYSIS OF SHERGOTTITES, NAKHLITES, AND CHASSIGNY. H. B. Franz[1,2], J. Farquhar[2,3], and A. J. Irving[4], [1]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, [2]Department of Geology, University of Maryland, College Park, MD, 20742, [3]Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, [4]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195.

Introduction: We report here the results of an extensive study to characterize the isotopic composition of both reduced and oxidized sulfur-bearing mineral phases in Martian meteorites. Our study has generated new measurements of $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$[1] for 27 shergottites, the Y000593 nakhlite, and Chassigny, providing a basis for evaluating the homogeneity of Martian mantle sulfur and evidence of photochemical processes recorded in the sulfur isotopes. These measurements will be compared with the sulfur composition of other solar system bodies.

Methods: We employed a sequential chemical extraction procedure that allows the measurement of sulfur isotopic ratios for different mineral phases in powdered whole-rock samples. The general procedure is as follows. A sample powder is pre-treated by sonicating in milli-Q water to extract water-soluble sulfate, which is converted to barium sulfate and dried for later reduction. The sample powder is then processed with a series of three acidic solutions to extract different sulfur-bearing phases [1]. In the first step, the sample is heated with 5 N HCl under flowing N_2 gas. Acid volatile sulfur in the sample, presumed to consist primarily of monosulfides, reacts with the HCl to evolve H_2S gas. The H_2S bubbles through a condenser, then through a milli-Q water trap, and finally into an acidic capture solution containing $AgNO_3$. Upon completion of this reaction, the capture solution is replaced, and a reduction solution containing HI, H_2PO_3, and 12 N HCl (commonly called "Thode's solution") is added to the boiling flask [2]. During this step, acid soluble sulfate in the sample is reacted to form H_2S, which is captured in the manner described above. Upon completion of this reaction, the capture solution is replaced again, and an acidic Cr(II) solution is injected into the boiling flask. In this final reduction step, the Cr-reducible sulfur minerals, presumed to be disulfides and elemental sulfur, are converted to H_2S and captured in $AgNO_3$ solution. In a separate analysis, the water-soluble sulfate extracted during pre-treatment is reduced with Thode's solution to produce H_2S in a similar manner.

The H_2S evolved in each step of the extraction process reacts with the $AgNO_3$ in the capture solution to form Ag_2S, which is rinsed with milli-Q water and a 1 M NH_4OH solution, then dried. Samples of Ag_2S are reacted with ~10 times stoichiometric excess of pure F_2 at ~250 °C. Product SF_6 is purified by both cryogenic and gas chromatographic techniques, and sulfur isotope abundances are measured by monitoring m/z = 127, 128, 129, and 131 ($^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$, and $^{36}SF_5^+$) with a ThermoFinnigan MAT 253 mass spectrometer. Uncertainties are estimated from repeated measurements of IAEA reference standards and are generally better than 0.2‰, 0.01‰, and 0.2‰ (1σ) for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. We normalized our data to measurements of Cañon Diablo Troilite (CDT) to facilitate comparison with results of previous studies.

Results: Figure 1 shows our results for shergottite AVS sulfur isotopic composition, with 2σ error bars. Individual meteorite measurements are displayed as red symbols. The weighted average composition was computed (blue symbols) by excluding the points lying outside the main clusters, which are shown as open symbols in the figure. We obtained average values of -0.07 ± 0.2‰ for $\delta^{34}S$, 0.005 ± 0.01‰ for $\Delta^{33}S$, and 0.18 ± 0.2‰ for $\Delta^{36}S$, relative to CDT. Results for other shergottite mineral fractions, Y000593, and Chassigny will be presented at the conference.

Discussion: The sulfur isotopic compositions for shergottite AVS generally fall within tight clusters close to the origin, as seen in Figure 1. The average composition is identical within errors to CDT, suggesting a similarity between sulfur in the Martian mantle and that of the Group IAB iron meteorites. This average composition is not ^{33}S-enriched as seen in some achondrite groups (aubrites, HED and ureilites), components of chondrites, and IIIAB and IVA iron meteorites [3-6].

Assuming that sulfur in the Martian mantle was homogenized by convection prior to shergottite formation, the points that lie outside the main cluster in the plot of $\Delta^{33}S$ vs. $\delta^{34}S$ would indicate incorporation of anomalous sulfur into monosulfide minerals during magmatic processes. This is analogous to a mechanism that has been suggested as a possible source of anomalous oxygen isotopic compositions in shergottites [7]. The positive sign of the $\Delta^{33}S$ anomaly in the shergottite AVS is notable, as it contrasts the negative $\Delta^{33}S$ devia-

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[1] We use the following definitions:
$\Delta^{33}S = \delta^{33}S - 1000 \times [(\delta^{34}S/1000+1)^{0.515}-1]$
$\Delta^{36}S = \delta^{36}S - 1000 \times [(\delta^{34}S/1000+1)^{1.9}-1]$

tions previously obtained for Nakhla sulfate that have been attributed to atmospheric photochemical processing of sulfur-bearing gases prior to sulfate formation [8, 9]. Our positive $\Delta^{33}S$ values for shergottite AVS may reflect sulfur complementary to that of the nakhlites, produced by the same photochemical processes on Mars, or they may derive from different photochemical processes on that planet.

Alternatively, it is possible that the sulfur isotope variations in shergottite AVS reflect heterogeneity of sulfur in the Martian mantle, as the observed variation lies within the range of anomalous sulfur compositions previously reported for other types of achondritic and chondritic meteorites [3-6]. In this case, the anomalous sulfur would preserve evidence of photochemical processing in the solar nebula.

The values of $\Delta^{36}S$ that lie outside the main cluster are of less certain origin, since measurements of the rare ^{36}S isotope are particularly prone to errors from contamination during the analysis process. If the single point with the highest value of $\Delta^{36}S$ were affected in this manner, then the shergottites would display apparent homogeneity in ^{36}S with significant deviations only in ^{33}S contents. This result would be consistent with those obtained for Nakhla and would carry potential implications for the mechanism responsible for producing the anomalous sulfur that is observed [9].

The isotopic compositions of other sulfur-bearing phases, in conjunction with these AVS data, provide further insight into the cycling of sulfur that may have occurred on Mars and the possible means by which sulfur of mass-independent composition was emplaced in various mineral fractions. These topics will be discussed at the conference.

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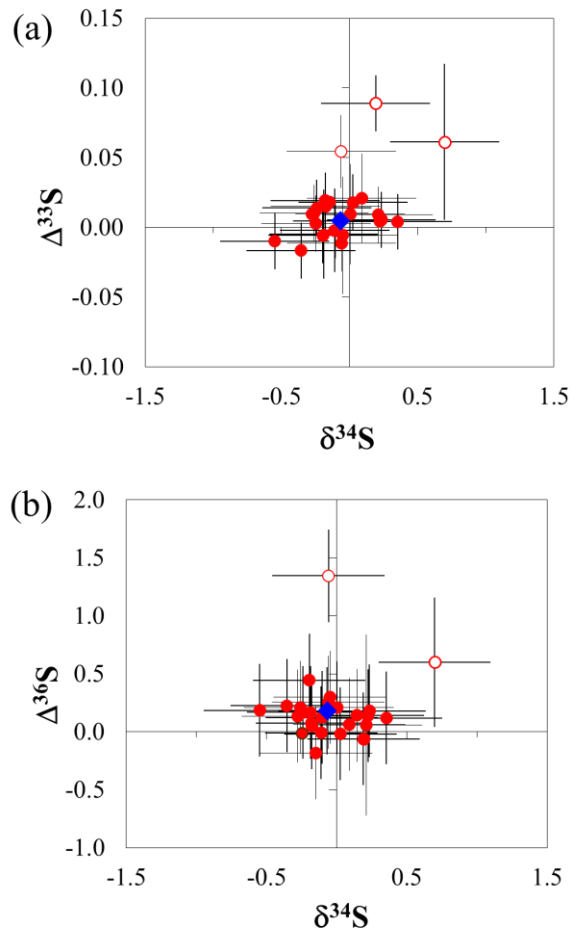

Figure 1. Our measurements of (a) $\Delta^{33}S$ vs. $\delta^{34}S$ and (b) $\Delta^{36}S$ vs. $\delta^{34}S$ for the acid volatile sulfur fraction of 27 shergottites, displayed with red symbols. Open symbols were not included in weighted average calculations. Blue symbols indicate average values for data clusters.