ACID VOLATILE SULFUR ISOTOPIC COMPOSITION OF SEVEN SHERGOTTITES FROM NORTHWEST AFRICA. 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 isotopic composition of acid volatile sulfur from several martian meteorites collected in Northwest Africa. This work represents the second stage of a comprehensive study to characterize the isotopic composition of both reduced and oxidized sulfur-bearing mineral phases in martian meteorites. These measurements will extend the dataset of shergottite sulfur isotopes and enable a comparison of the martian sulfur composition to that of other achondrites, primitive meteorites, and the Earth and Moon.

Methods: Acid volatile sulfur (AVS) was obtained from powdered whole rock samples during the first step of a sequential chemical extraction procedure that allows the measurement of sulfur isotopic ratios for different mineral phases. A sample powder 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 $AgNO_3$. 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. All results are reported relative to Cañon Diablo Troilite (CDT).

Results: Table 1 reports the newly acquired isotopic composition of the AVS fraction of seven shergottites. The results are depicted graphically in Figure 1, along with previous AVS measurements of shergottites reported by us [2]. New data are shown with triangular symbols, while previous measurements are indicated with circles. Error bars represent 2σ uncertainties estimated from repeated analyses of the sulfur isotopic ratios of IAEA reference materials, and are generally better than 0.4‰, 0.02‰, and 0.4‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively [1]. However, very small samples incur greater measurement uncertainty, so error bars for points in Figure 1 obtained from Ag_2S

samples smaller than 0.4 mg are larger to reflect greater variability in mass spectrometric measurements. These points are also depicted with open symbols for clarity.

TABLE 1. SULFUR MULTIPLE ISOTOPE ABUNDANCES FOR AVS FRACTIONS

Sample[a]	Mass (mg)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)[b]	$\Delta^{36}S$ (‰)[c]
Dhofar 019 (d)	278.5	-0.117	-0.016	0.14
NWA 2046 (d)	277.5	-0.086	-0.023	0.00
NWA 2800 (e)	273.1	0.383	-0.022	0.15
NWA 5718 (e)	273.0	-0.036	-0.032	0.45
NWA 2990 (i)	270.0	0.858	0.035	0.61
NWA 4925 (d)	260.5	1.030	-0.002	1.50
NWA 5789 (d)	283.5	0.475	-0.012	1.68

[a]Parenthetical labels denote source characteristics: (e) enriched, (d) depleted, and (i) intermediate
[b]$\Delta^{33}S = \delta^{33}S - 1000 \times ((\delta^{34}S/1000+1)^{0.515}-1)$
[c]$\Delta^{36}S = \delta^{36}S - 1000 \times ((\delta^{34}S/1000+1)^{1.9}-1)$

We obtained small negative values of $\Delta^{33}S$ for all samples except NWA 2990, which had low product yield from the AVS reduction. Given the large uncertainty on the NWA 2990 measurement, its $\Delta^{33}S$ lies within 2σ of zero, as do those of NWA 4925, NWA 5789, and Dhofar 019. The $\Delta^{33}S$ for NWA 2046, NWA 2800, and NWA 5718 are discernibly negative but show only small deviations from predicted mass-dependent fractionation. The $\Delta^{36}S$ measurements for these samples are all zero or slightly positive. Values for Dhofar 019, NWA 2046, and NWA 2800 all lie within 2σ of zero, while those of NWA 5718, NWA 2990, NWA 4925, and NWA 5789 are all discernibly positive. All values of $\delta^{34}S$ lie within 2σ of zero except those of the three smallest samples, NWA 2990, NWA 4925, and NWA 5789. This may indicate a measurement bias for extremely small samples, which is currently under investigation.

Discussion: Current results show fairly homogeneous sulfur isotopic composition for these seven shergottites, as well as RBT 04261, LAR 06319, ALH 77005, and EET 79001 [2]. The current data for $\Delta^{33}S$, which are primarily clustered at small negative values, differ somewhat from those reported in earlier shergottite studies that indicated predominantly positive val-

ues for Δ^{33}S [3,4]. The validity of direct comparison between the current data and the previous studies is unclear, however, as the earlier measurements were standardized in another laboratory. Work is underway to calibrate these differences so that direct comparisons can be made. The negative Δ^{33}S values reported here for the shergottites are consistent with the Δ^{33}S of -0.09‰ recently obtained for Nakhla AVS [1].

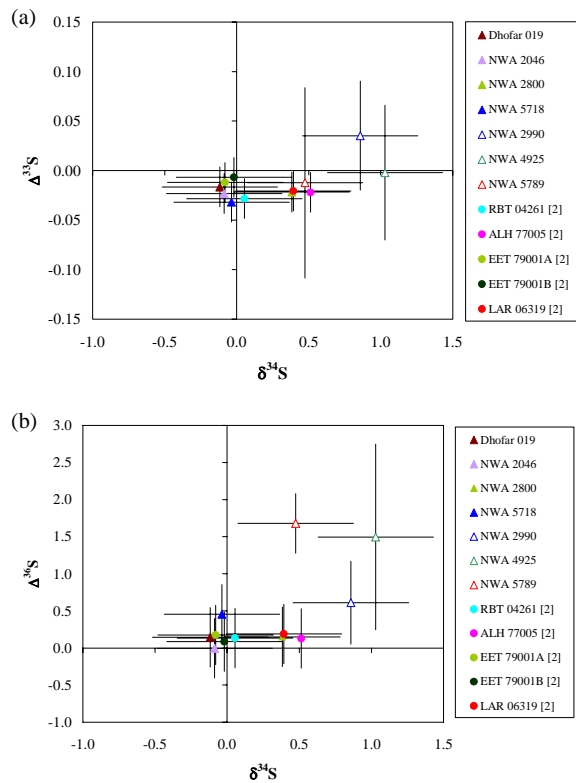**Figure 1.** New measurements of (a) Δ^{33}S vs. δ^{34}S and (b) Δ^{36}S vs. δ^{34}S for the acid volatile sulfur fraction of seven shergottites, displayed with triangular symbols. Data from previous measurements of shergottite monosulfides, indicated with circular symbols, are included for comparison.

Previous analyses of igneous sulfides in shergottites have supported the hypothesis that these rocks are derived from the martian mantle and thus may carry a juvenile martian sulfur imprint [4,6]. A recent survey by Rumble and Irving (2009) of oxygen isotopes in 42 martian meteorites revealed a surprising degree of heterogeneity in shergottite oxygen composition [5]. Rumble and Irving (2009) suggested that this heterogeneity could derive either directly from the mantle source regions or from variable assimilation of altered crustal rocks by ascending shergottite magmas, and that the latter process might manifest as "enriched" and "depleted" shergottite groups [5]. The shergottite sulfur isotopic measurements reported here suggest that

sulfur is invariant at the level of analytical uncertainties. Results obtained for the shergottites analyzed so far do not indicate significant variations in the sulfur composition of their mantle source regions, nor do they reveal a clear correlation between sulfur isotope systematics and degree of trace element enrichment.

Previous shergottite studies have suggested a similarity between the sulfur isotopic composition of the martian and terrestrial mantles [4,6]. Detection of excess ^{33}S in ureilites as well as smaller sulfur isotopic anomalies in other classes of achondrites and chondrites have revealed that different chemical or photochemical processes may have operated in distinct regions of the solar nebula [7-11]. Figure 2 shows the variation in Δ^{33}S and δ^{34}S among different types of extraterrestrial materials. While there are some variations in Δ^{33}S, comparison of meteoritic and lunar sulfur with the AVS fraction of martian meteorites shows that the sulfur composition of most solar system bodies analyzed to date is remarkably similar, with a few outlying groups (e.g., ureilites, aubrites [7,8]), but without the clear distinctions between meteorite classes or wide range of values characteristic of bulk oxygen isotopic composition. Interlaboratory comparisons of standardization and further analyses will allow us to determine if the present data for Martian meteorites suggests a significant difference from other populations.
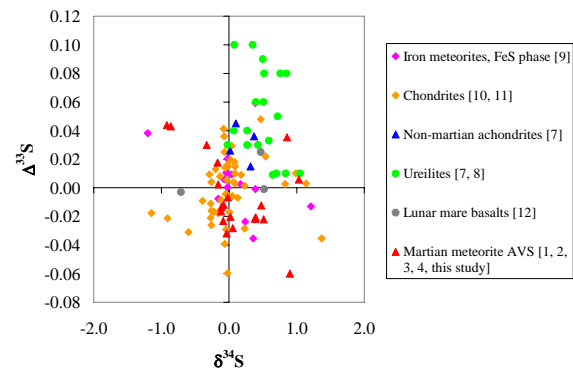

Figure 2. Comparison of Δ^{33}S vs. δ^{34}S for extraterrestrial samples. Error bars are omitted for clarity.

References: [1] Farquhar et al. (2007) *EPSL, 264,* 1-8. [2] Franz et al. (2008) LPSC XXXIX, #2433. [3] Gao and Thiemens (1990) LPSC XXI, #402. [4] Farquhar et al. (2000) *Nature, 404,* 50-52. [5] Rumble and Irving (2009) LPSC XL, #2293. [6] Greenwood et al. (1997) *GCA*, *61,* 4449-4453. [7] Rai et al. (2005) *Science, 309*, 1062-1065. [8] Farquhar et al. (2000) *GCA,* 64, 1819-1825. [9] Gao and Thiemens (1991) *GCA, 55,* 2671-2679. [10] Gao and Thiemens (1990) LPSC XXI, #401. [11] Rai and Thiemens (2007) *GCA, 71,* 1341-1354. [12] Farquhar and Wing (2005) LPSC XXXVI, #2380.