

**ACID-VOLATILE SULFUR ISOTOPIC COMPOSITION OF SIX SHERGOTTITES.** H. B. Franz<sup>1,2,3</sup>, J. Farquhar<sup>3,4</sup>, and A. J. Irving<sup>5</sup>, <sup>1</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, [Heather.B.Franz@nasa.gov](mailto:Heather.B.Franz@nasa.gov), <sup>2</sup>Goddard Earth Sciences and Technology Center, University of Maryland Baltimore County, Baltimore, MD 21228 <sup>3</sup>Department of Geology, University of Maryland, College Park, MD, 20742, <sup>4</sup>Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, <sup>5</sup>Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195.

**Introduction:** We report here new measurements of the isotopic composition of acid-volatile sulfur from several shergottites. This work represents part 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<sub>2</sub> gas. Acid-volatile sulfur in the sample, presumed to consist primarily of monosulfides, reacts with the HCl to evolve H<sub>2</sub>S gas. The H<sub>2</sub>S bubbles through a condenser, then through a milli-Q water trap, and finally into an acidic capture solution containing AgNO<sub>3</sub>. The H<sub>2</sub>S evolved in each step of the extraction process reacts with the AgNO<sub>3</sub> in the capture solution to form Ag<sub>2</sub>S, which is rinsed with milli-Q water and a 1 M NH<sub>4</sub>OH solution, then dried. Samples of Ag<sub>2</sub>S are reacted with ~10 times stoichiometric excess of pure F<sub>2</sub> at ~250 °C. Product SF<sub>6</sub> is purified by both cryogenic and gas chromatographic techniques, and sulfur isotope abundances are measured by monitoring m/z = 127, 128, 129, and

131 (<sup>32</sup>SF<sub>5</sub><sup>+</sup>, <sup>33</sup>SF<sub>5</sub><sup>+</sup>, <sup>34</sup>SF<sub>5</sub><sup>+</sup>, and <sup>36</sup>SF<sub>5</sub><sup>+</sup>) with a Thermo-Finnigan 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 six shergottites. The results are depicted graphically in Figure 1. 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 δ<sup>34</sup>S, Δ<sup>33</sup>S, and Δ<sup>36</sup>S, respectively [1].

**TABLE 1. SULFUR MULTIPLE ISOTOPE ABUNDANCES FOR AVS FRACTIONS**

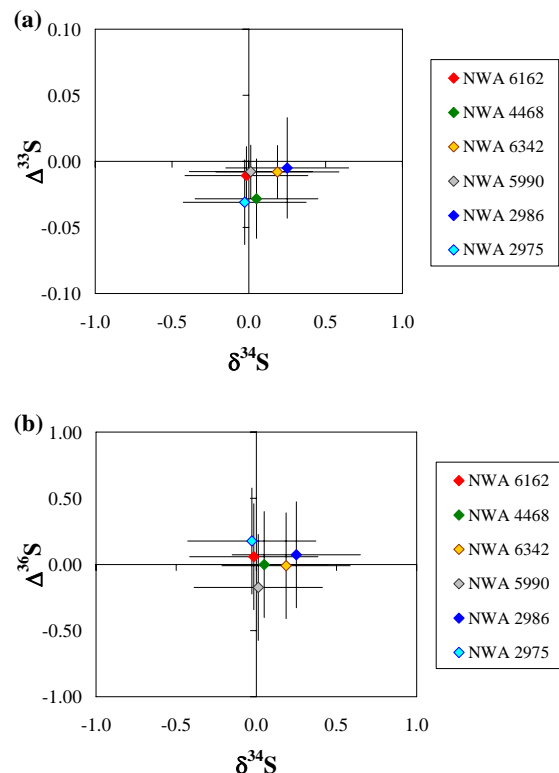
| Sample <sup>a</sup> | Mass (mg) | δ <sup>34</sup> S (‰) | Δ <sup>33</sup> S (‰) <sup>b</sup> | Δ <sup>36</sup> S (‰) <sup>c</sup> |
|---------------------|-----------|-----------------------|------------------------------------|------------------------------------|
| NWA 2975 (e)        | 277.1     | -0.030                | -0.031                             | 0.177                              |
| NWA 2986 (e)        | 598.8     | 0.249                 | -0.005                             | 0.073                              |
| NWA 4468 (e)        | 600.6     | 0.049                 | -0.028                             | -0.001                             |
| NWA 5990 (d)        | 442.4     | 0.012                 | -0.008                             | -0.173                             |
| NWA 6162 (d)        | 606.0     | -0.016                | -0.011                             | 0.058                              |
| NWA 6342 (e)        | 355.2     | 0.186                 | -0.008                             | -0.009                             |

<sup>a</sup>Parentetical labels denote source characteristics:

(e) enriched and (d) depleted

$$^b \Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times ((\delta^{34}\text{S}/1000 + 1)^{0.515} - 1)$$

$$^c \Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times ((\delta^{34}\text{S}/1000 + 1)^{1.9} - 1)$$



**Figure 1.** New measurements of (a) Δ<sup>33</sup>S vs. δ<sup>34</sup>S and (b) Δ<sup>36</sup>S vs. δ<sup>34</sup>S for the acid volatile sulfur fraction of six shergottites.

We obtained small negative values of Δ<sup>33</sup>S for all six samples. The Δ<sup>33</sup>S for NWA 2986, NWA 5990, NWA 6162, and NWA 6342 are discernibly negative but show only small deviations from predicted mass-dependent fractionation. The Δ<sup>33</sup>S for NWA 2975 and NWA 4468 are slightly more negative but lie within

the range of previous measurements of AVS from shergottites [2, 3]. The  $\Delta^{36}\text{S}$  measurements for these samples range from -0.173 to +0.177‰, but all lie within  $2\sigma$  of zero, as do all values of  $\delta^{34}\text{S}$ .

**Discussion:** Current results show fairly homogeneous sulfur isotopic composition for these six shergottites, as well as those previously reported by us [2,3]. These data for  $\Delta^{33}\text{S}$  are primarily clustered at small negative values, slightly more positive than the  $\Delta^{33}\text{S}$  of -0.06‰ recently obtained for Nakhla AVS [1].

Note that NWA 2975 and NWA 2986 are paired stones. As Table 1 indicates, the mass of raw material processed for NWA 2986 was approximately twice that of NWA 2975. The AVS yield from NWA 2975 was much smaller than expected, yielding slightly higher mass spectrometric measurement errors than usual and prompting analysis of a larger sample of NWA 2986 to verify the results. An AVS concentration of 120 ppm was estimated for NWA 2975, compared to 287 ppm for NWA 2986. This difference is attributed to sample heterogeneity. While their data plot as distinct points in Figure 2, the sulfur isotopic composition of these two meteorites is identical within  $2\sigma$  error.

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 [5,7]. 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 [6]. 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 [6]. Source characteristics for these six meteorites are denoted in Table 1 [8-11]. The shergottite sulfur isotopic measurements reported here do not reveal a clear correlation between sulfur isotope systematics and degree of trace element enrichment, in agreement with our earlier data [2,3].

**References:** [1] Farquhar et al. (2007) *EPSL*, 264, 1-8. [2] Franz et al. (2008) LPSC XXXIX, #2433. [3] Franz et al. (2010) LPSC XLI, #2341. [4] Gao and Thiemens (1990) LPSC XXI, #402. [5] Farquhar et al. (2000) *Nature*, 404, 50-52. [6] Rumble and Irving (2009) LPSC XL, #2293. [7] Greenwood et al. (1997) *GCA*, 61, 4449-4453. [8] Irving et al. (2007) LPSC XXXVIII, #1526. [9] Wiitke et al. (2010) 73rd Met. Soc. Mtg., #5313. [10] Irving et al. (2010) PSC XLI,

#1833. [11] Irving et al. (2011) LPSC XLII (this meeting).