SULFUR ISOTOPIC COMPOSITION OF MULTIPLE MINERAL PHASES IN SHERGOTTITES. H. B. Franz[1,2], J. Farquhar[2,3], and S. T. Kim[2], [1]NASA Goddard Space Flight Center, 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.

Introduction: We are measuring the sulfur multiple isotope abundances in both reduced and oxidized mineral phases of several shergottites, a subset of the SNC (Shergottite, Nakhlite, Chassignite) meteorites believed to be from Mars. Previous analyses of the sulfur isotopic composition of igneous sulfides in shergottites has suggested that the rocks may be representative of martian mantle material [1,2]. Recent measurements of sulfur isotopes in several classes of achondrites have shown that these meteorite groups exhibit small differences in their reference fractionation arrays, which are not colinear with those of the more primitive chondrites [3, 4]. These differences may derive from chemical or photochemical processes operating in distinct regions of the solar nebula [3, 4]. The existing SNC dataset is insufficient to evaluate the composition of martian mantle sulfur in the context of the achondrites or the meteorite population as a whole. The current study reexamines with improved precision two shergottites (ALHA77005 and EETA79001) for which sulfur data have already been reported and provides measurements of two recently discovered shergottites (RBT 04261 and LAR 06319), which have not been previously analyzed. These measurements will extend the dataset of shergottite sulfur isotopes and allow a comparison of the martian sulfur composition to that of other achondrites, primitive meteorites, and the Earth and Moon.

Methods: We performed sequential chemical extraction procedures on powdered whole rock samples that allow the measurement of sulfur isotopic ratios for different mineral phases. The method is similar to that described in Farquhar et al. (2007) [5]. Briefly, a sample powder is first heated with 5 N HCl under flowing N_2 gas. Acid volatile sulfur (AVS) 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 $AgNO_3$. After three hours, at which time the AVS reduction reaction is assumed complete (evidence that the reaction has ceased is also assessed by examining the capture solution), the capture solution is replaced, and a reduction solution containing HI, H_2PO_3, and 12 N HCl is added to the boiling flask [6,7]. During the next three hours, acid soluble sulfate in the sample is react ed 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.

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, estimated from repeated analyses of the sulfur isotopic ratios of IAEA reference materials, are generally better than 0.2‰, 0.01‰, and 0.2‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively [5]. All results are referenced to Vienna Cañon Diablo Troilite (VCDT).

Results: At the time of abstract submission, the multiple sulfur isotope abundances have been measured only for the AVS fraction of each meteorite. The sulfur isotopic compositions for each meteorite are reported in Table 1.

TABLE 1. SULFUR MULTIPLE ISOTOPE ABUNDANCES FOR AVS FRACTIONS

Sample	Mass (mg)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)[a]	$\Delta^{36}S$ (‰)[b]
ALHA77005.213	687.5	0.513	-0.022	0.13
EETA79001.624 (lithology B)	214.4	-0.019	-0.007	0.09
EETA79001.629 (lithology A)	187.3	-0.080	-0.012	0.18
RBT 04261.25	185.9	0.054	-0.028	0.13
LAR 06319.9	219.6	0.393	-0.021	0.19

[a]$\Delta^{33}S = \delta^{33}S - 1000 \times ((\delta^{34}S/1000+1)^{0.515}-1)$
[b]$\Delta^{36}S = \delta^{36}S - 1000 \times ((\delta^{34}S/1000+1)^{1.9}-1)$

Previous measurements of shergottites. The sulfur isotopic composition of ALHA77005 was previously reported by Gao and Thiemens (1990) for HCl-soluble and HCl-residue phases [8]. The HCl-soluble phase of

Gao and Thiemens is equivalent to the AVS fraction as reported in the current study. Based on sulfur chemistry for the same meteorite determined by Burgess et al. (1989) [9], Gao and Thiemens attributed the HCl-soluble phase to troilite. Using the equations shown beneath Table 1, the δ values given by Gao and Thiemens yield $\Delta^{33}S = 0.018‰$ and $\Delta^{36}S = 0.025‰$.

Farquhar et al. (2000) reported sulfur isotopic measurements of AVS in Shergotty, finding values of $\Delta^{33}S = 0.025‰$ and $\Delta^{36}S = 0.1‰$ [2]. Farquhar et al. (2000) also reported results for the H_3PO_4-volatile sulfur, presumed to consist of monosulfides, in Zagami and EETA79001 lithology A. These measurements yielded $\Delta^{33}S = 0.001‰$ and $\Delta^{36}S = 0.0‰$ for Zagami and $\Delta^{33}S = -0.012‰$ to 0.049‰ and $\Delta^{36}S = 0.1‰$ to 0.9‰ for EETA79001. However, due to the different techniques employed for these H_3PO_4 extractions versus the current study, the previously reported values are of lower precision, and direct comparison of the results may not be valid.

Comparison of current and previous results. We have obtained small negative $\Delta^{33}S$ values for all AVS samples, from -0.028 to -0.007‰. The $\Delta^{36}S$ values range from 0.09 to 0.19‰. The one sigma uncertainty envelopes of our measurements overlap with those of prior measurements of AVS from ALHA77005 and EETA79001.

The mean and standard deviation of our measurements for the five Shergottites are $\delta^{34}S = 0.17\pm0.26‰$, $\Delta^{33}S = -0.018\pm0.009‰$, and $\Delta^{36}S = 0.14 \pm 0.04‰$ which can be compared with our recent measurements of lunar basalts which yield a mean $\delta^{34}S = 0.57 \pm 0.10$ ‰, $\Delta^{33}S = 0.008 \pm 0.009$ ‰, and $\Delta^{36}S = 0.18 \pm 0.11$ ‰ [10].

Further analyses: The results presented here represent only the AVS fractions obtained via the sequential extraction process. The acid soluble sulfate and CRS fractions remain to be analyzed isotopically. Results for these sulfur phases will be presented at LPSC. Continued work is also planned to determine whether the mean values for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ are significant (i.e., whether they fall on a single mass fractionation array or carry an imprint from other non mass-dependent reservoirs) and whether they are distinct from the mass fractionation arrays of other solar system bodies and the moon.

References: [1] Greenwood et al. (1997) *GCA, 61,* 4449-4453. [2] Farquhar et al. (2000) *Nature, 404,* 50-52. [3] Rai et al. (2005) *Science, 309,* 1062-1065. [4] Farquhar et al. (2000) *GCA,* 64, 1819-1825. [5] Farquhar et al. (2007) EPSL*, 264,* 1-8. [6] Thode et al. (1961) *GCA, 25,* 159-174. [7] Mayer and Krouse (2004) in *Handbook of Stable Isotope Analytical Techniques, Vol 1*, 538-596. [8] Gao and Thiemens (1990) LPSC XXI, #402. [9] Burgess et al. (1989) *EPSL, 93,* 314-320. [10] Wing and Farquhar (in revision) GCA.