SULFUR ISOTOPIC ANALYSIS OF SULFIDES FROM 20 SHERGOTTITES. H. B. Franz[1], N. Wu[2], J. Farquhar[2,3], and A. J. Irving[4], [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, [4]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195.

Introduction: Sulfur in extraterrestrial materials is a high-priority target for analysis because its abundance and isotopic composition can provide constraints of both planetary and cosmochemical scope. Previous work involving phase-specific extraction of sulfur from numerous shergottites revealed similarities in the sulfur isotopic compositions of terrestrial mid-ocean ridge basalts (MORB), the Moon, the martian mantle, and non-magmatic iron meteorites. At the same time, isotopic anomalies in igneous sulfides from several of these shergottites suggested that atmospherically processed sulfur from the subsurface had been assimilated into their parent magmas [1]. Although this finding adds complexity to the interpretation of the sulfide isotopic composition, it also provides important information regarding the sulfur photochemical signal incorporated into the youngest class of martian meteorites and reflects operation of a surface process on Mars with implications beyond sulfur geochemistry. The present study extends our characterization of the isotopic composition of sulfur-bearing mineral phases in martian meteorites to 20 new shergottites. Here we report measurements of $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$[1] for sulfide phases in these samples, allowing an improved estimate of the isotopic composition of martian mantle sulfur. In addition, sulfides from two meteorites, NWA 7635 and NWA 11300, yielded negative anomalies in $\Delta^{33}S$ that are unique among shergottites analyzed to date, offering new insight into the long-term nature of sulfur photochemistry on Mars.

Methods: Because we are interested in sulfur from both reduced and oxidized mineral phases, we employed a sequential chemical extraction procedure, modified slightly from that described in ref. [1]. For each meteorite, ~300 mg of powdered whole-rock sample were pre-treated by sonicating in milli-Q water to extract water-soluble sulfate, which was converted to barium sulfate and dried for later reduction. Sulfide phases were then extracted by heating the sample powder with an acidic Cr(II) solution under flowing N_2 gas. Both monosulfides and disulfides present in the sample reacted with the reduction solution to evolve H_2S gas. The H_2S bubbled through a condenser, then through a milli-Q water trap, and finally into an acidic capture solution containing $AgNO_3$. Reaction between evolved H_2S and $AgNO_3$ in the capture solution produced Ag_2S, which was rinsed with milli-Q water and a 1 M NH_4OH solution, then dried. Samples of Ag_2S were reacted with ~10 times stoichiometric excess of pure F_2 at ~250 °C for at least 16 hours. Product SF_6 was purified by both cryogenic and gas chromatographic techniques, and sulfur isotope abundances were 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 in reported isotope ratios are generally better than 0.15‰, 0.008‰, and 0.15‰ (1σ) for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. Results are normalized to measurements of Cañon Diablo Troilite (CDT).

Results: Sulfide fractions of shergottites analyzed in this study yielded from -0.89 ± 0.15‰ to 0.54 ± 0.15‰ in $\delta^{34}S$, -0.030 ± 0.008‰ to 0.016 ± 0.008‰ in $\Delta^{33}S$, and -0.15 ± 0.15‰ to 0.73 ± 0.26‰ in $\Delta^{36}S$. Two shergottites, NWA 7635 and NWA 11300, revealed negative $\Delta^{33}S$ anomalies, further discussed below.Abundances of sulfide sulfur extracted from these meteorites ranged from 265 ± 5 to 3148 ± 63 ppm, although only two meteorites had abundances >1500 ppm. The average sulfide abundance was 1159 ± 23 ppm.

Discussion: As a primary goal of this work was to tighten constraints on the isotopic composition of juvenile martian sulfur, sulfide data from this study were combined with those obtained by Franz et al. (2017) [1], as shown in Figure 1. The weighted average composition was computed (gold symbols) by excluding data from samples showing evidence of mass-independent fraction (MIF), indicated by non-zero values of $\Delta^{33}S$ or $\Delta^{36}S$, or suspected instrument effects. We obtained average values of -0.24 ± 0.30‰ for $\delta^{34}S$, 0.0041 ± 0.0009‰ for $\Delta^{33}S$, and 0.043 ± 0.259‰ for $\Delta^{36}S$ (±2σ s.e.m.), relative to CDT.

Our results confirm the similarities between the isotopic compositions of juvenile martian sulfur, CDT, and bulk chondritic sulfur reported by Franz et al. (2017) [1]. The small difference between $\delta^{34}S$ of the martian mantle (-0.24 ± 0.30‰, this work) and

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

MORB (-1.28 ± 0.33‰ [3]) may reflect fractionation during core segregation on Earth that did not occur on Mars due to its smaller size [3].

Values of Δ^{33}S and Δ^{36}S that we measured are consistent with those of the previous study [1] in indicating that the sulfur photochemical cycle on Mars has produced a MIF signature characterized by variations in Δ^{33}S but Δ^{36}S values close to zero. This relationship between Δ^{33}S and Δ^{36}S is distinct from that of ancient Earth, providing evidence that a different photochemical fractionation mechanism has dominated the atmosphere of Mars throughout geologic time [1].

Two shergottites in this study yielded sulfide with clearly-resolved negative anomalies in ^{33}S: NWA 7635 (Δ^{33}S = -0.023 ± 0.016‰) and NWA 11300 (Δ^{33}S = -0.030 ± 0.73‰) (±2σ). These signatures are unique among shergottites analyzed to date, as all previous MIF detected in shergottites has been characterized by positive Δ^{33}S anomalies [1, 4]. This impact of this observation is enhanced by certain unusual aspects of NWA 7635. This meteorite contains maskelynite but no phosphate and reflects fractionation well beyond the stage evident in QUE 94201 [5]. It is the most evolved of the known depleted shergottites, with the most depleted Sm-Nd and Lu-Hf compositions yet identified for shergottites [6]. With crystallization age ~2.3 Ga [7], NWA 7635 is about four times older than other depleted shergottites and about a billion years older than the nakhlites and chassignites [8]. Its launch age of 1.1 Ma, similar to that of 10 other depleted shergottites, suggests that it may have been launched in the same event as other, much younger meteorites of the same classification, implying the possibility that prolonged magmatic activity may have occurred in the depleted shergottite source region [7].

Comparison of data for depleted shergottites sharing ejection ages of ~1 Ma does not indicate the presence of a crustal signature displaying a distinct (positive or negative, but not both) MIF signature that might characterize a local sulfur reservoir. Instead, the range of Δ^{33}S values, from -0.023 ± 0.008‰ to 0.027 ± 0.008‰, includes meteorites with the most enriched (NWA 6162) and depleted (NWA 7635) Δ^{33}S values for all shergottites. Interestingly, NWA 7635 and Tissint share similar depletions in ^{34}S compared to other depleted shergottites with similar ejection ages. The values of Δ^{33}S and crystallization ages of these two meteorites are significantly different, suggesting that the similarity in δ^{34}S is coincidental, but their sulfur phases may reflect that a similar type process depleted the ^{34}S in both meteorites.

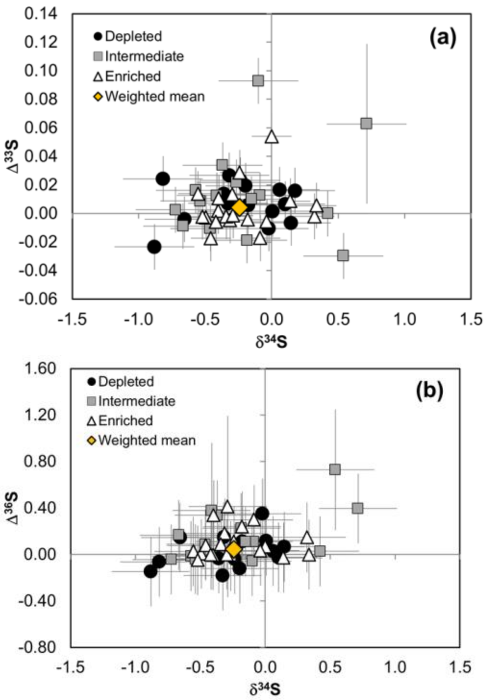

Figure 1. Sulfur isotopic composition of sulfide fractions for data from this study and ref. [2], used to calculate a revised estimate for the juvenile martian sulfur composition: (a) Δ^{33}S vs. δ^{34}S and (b) Δ^{36}S vs. δ^{34}S. Gold diamonds indicate weighted mean composition,. Error bars show 2σ uncertainties.

Two meteorites in our study that are most likely launch paired, NWA 10761 and NWA 11300, revealed distinct sulfur isotopic compositions between them. This may suggest heterogeneous distribution of sulfur MIF-bearing components at a highly local scale, in keeping with observations of sulfur isotopes in sulfides at Gale crater by the Curiosity rover [9]. Comparison of other geochemical data for meteorites we analyzed, such as Cl isotopes and rare earth elements, with sulfur isotopic data also carries potential implications for martian surface processes.

References: [1] Franz et al. (2014) *Nature* 508, 364-368. [2] Irving (2017) http://www.imca.cc/mars/ martian-meteorites-list.htm. [3] Labidi et al. (2013) *Nature* 501, 208-212. [4] Farquhar et al. (2000) *Nature* 404, 50-52. [5] Irving et al. (2013) 76th Met. Soc. Mtg., 5274. [6] Andreasen et al. (2014) LPSC XLV, 2865. [7] Lapen et al. (2017) *Sci. Adv.* 3, 31600922. [8] Nyquist et al. (2001) *Space Sci. Rev.* 96, 105-164. [9] Franz et al. (2017) *Nature Geosci.* 10, 658-662.