LARGE SULFUR ISOTOPIC ANOMALIES IN SHERGOTTITES GADAMIS 001 AND NORTHEAST AFRICA 011.

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Introduction: Photochemical reactions driven by UV light can distribute isotopes of certain elements in ways not predicted based on their masses, a process known as mass-independent fractionation (MIF). One such element is sulfur, which possesses four stable isotopes. Anomalies in ratios involving minor isotopes ^{33}S and ^{36}S represent MIF signatures that serve as particularly useful tracers for reactions between the atmosphere and surface minerals on Mars. Although sulfur from the vast majority of shergottites suggests that the sulfur isotopic composition of the martian mantle is similar to that of terrestrial mid-ocean ridge basalts (MORB), the Moon, and non-magmatic iron meteorites, MIF signatures have been observed in igneous sulfides of several shergottites, nakhlites, and ALH 84001, interpreted to reflect assimilation of UV-processed sulfur into erupting magmas [1]. In addition, MIF signatures have been observed in sulfate phases of several shergottites and nakhlites, indicating interactions between surface minerals and fluids carrying UV-processed sulfur [1-3]. Here we report measurements of $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$[1] for sulfide phases in shergottites Gadamis 001 and Northeast Africa (NEA) 011.

Methods: Because we are interested in sulfur from both reduced and oxidized mineral phases, we employed a sequential chemical extraction procedure, similar that described in ref. [4]. For each meteorite, ~300 mg of powdered whole-rock sample were pretreated 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 several times, 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‰, 0.004‰, 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: Results of isotopic analyses for the sulfide fractions of Gadamis 001 and NEA 011 are given in Table 1. Sulfides of both Gadamis 001 and NEA 011 possess significant isotopic anomalies, evident in large positive values of $\Delta^{33}S$ (0.19 ± 0.008‰ and 0.37 ± 0.008‰, respectively).

Table 1. Results of sulfur isotopic analyses

Sample	$\delta^{34}S$	$\Delta^{33}S$	$\Delta^{36}S$
Gadamis 001	0.03	0.19	-0.09
NEA 011	0.84	0.37	0.07

Discussion: The anomalous ^{33}S enrichments measured in Gadamis 001 and NEA 011 are among the largest observed in any martian meteorites to date. They are consistent with the pattern of MIF signatures observed in other martian meteorites, characterized by anomalous enrichments or depletions in ^{33}S with no detectable anomalies in ^{36}S [1-4]. Sulfide data for shergottites are displayed in Fig. 1, including all results reported in ref. [1,4] as well as those from the current study. The weighted average for sulfide fractions from shergottites that do not display isotopic anomalies (shown as gold diamonds in Fig. 1), which is assumed to reflect the isotopic composition of the martian mantle, has been updated to include additional meteorites analyzed since publication of ref. [1,4]. Several shergottites reported in ref. [1] were observed to carry anomalous enrichments in ^{33}S. These were most notable in monosulfide minerals (predominantly pyrrhotite) of NWA 2990 and its pair NWA 5960 and sulfate minerals of NWA 5718. The anomalies observed in Gadamis 001 and NEA 011 sulfides are similar to those of the above three meteorites.

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[1] We use the following definitions:

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

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

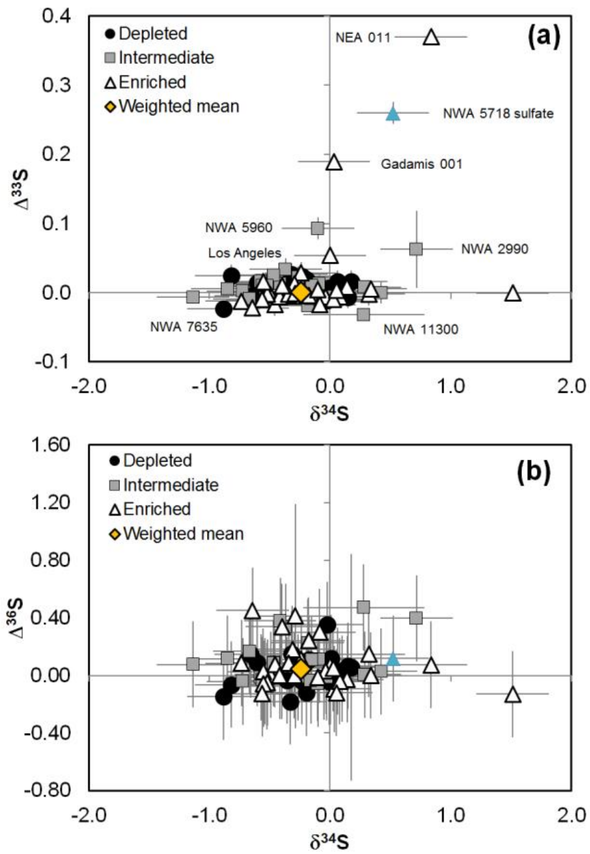

Figure 1. Sulfur isotopic composition of sulfides from shergottites in this study and ref. [1,4], (a) $\Delta^{33}S$ vs. $\delta^{34}S$ and (b) $\Delta^{36}S$ vs. $\delta^{34}S$. Sulfide data from meteorites with ^{33}S anomalies are labeled in panel (a): Gadamis 001 and NEA 011 (this study); NWA 2990/5960 and Los Angeles [1]; NWA 7635 and NWA 11300 [4]. The sulfate fraction of NWA 5718 is also shown for context [1]. Gold diamond indicates weighted mean for the martian mantle, updated from ref. [1,4]. Error bars show 2σ uncertainties. Error bars that are not visible are smaller than the symbols.

Because these anomalies are present in monosulfides presumed to represent igneous phases, they suggest that sulfur previously subjected to UV photochemistry in the martian atmosphere was introduced to the parent magmas of these meteorites. In the case of NWA 5718, in which the sulfide fraction showed no isotopic anomaly, the ^{33}S enrichment in the sulfate fraction was interpreted to indicate the presence of atmospherically-processed sulfur introduced during secondary alteration on Mars [1]. However, similarities in the MIF signatures of Gadamis 001, NEA 011, and NWA 5718, and to a lesser extent NWA 2990/5960 and Los Angeles, suggest that a common process likely produced the ^{33}S enrichments observed in these meteorites, which were incorporated into the parent rocks during different stages and potentially through different mechanisms.

The ^{33}S enrichments detected in Gadamis 001 and NEA 011 contrast with those reported for shergottites NWA 11300 and NWA 7635, which carry anomalous ^{33}S depletions [4]. Notably, sulfate fractions of Chassigny [1] and the nakhlite Lafayette [2] were also found to carry anomalous enrichments in ^{33}S, while anomalous depletions in ^{33}S have been found in sulfides and sulfates of other nakhlites and sulfide of ALH 84001 [1-4]. Laboratory experiments investigating UV photochemistry of SO_2 have found complementary ^{33}S enrichments and depletions in photolytic elemental sulfur products and residual SO_2, respectively [7-9]. Other work has suggested that similar complementary anomalous sulfur pools could arise through SO_3 photolysis driven by UV, which would incorporate ^{33}S-enriched sulfur into sulfate aerosols [10]. The exact photochemical pathway for the sulfur isotopic anomalies detected in martian meteorites remains an active area of research. Continuities observed in the sulfur MIF characteristics of meteorites of different classifications and formation ages suggest that the controlling sulfur cycle may have been similar from ancient Mars (~ 4 Ga) to relatively recent epochs (hundreds of Ma) [1].

Gadamis 001 and NEA 011 are both enriched mafic diabasic shergottites recovered from Libya in 2019 [5]. Major fragments of both were reported to be coated by fusion crusts [6], minimizing the possibility that sulfur in these meteorites could be compromised by terrestrial contamination. The small size of pyrrhotite grains in these meteorites suggests rapid cooling and may constrain the addition of sulfur to the parent magmas to relatively shallow depths within the crust, although the mechanism by which sulfur was incorporated cannot be determined without context provided by data for other elements. Given the significant sulfur isotopic anomalies observed in sulfides from these two meteorites, we suggest that they should be high-priority targets for other geochemical investigations focused on interactions between martian mantle and surface reservoirs.

References: [1] Franz et al. (2014) *Nature* 508, 364-368. [2] Farquhar et al. (2000) *Science* 404, 50-52. [3] Farquhar et al. (2007) *EPSL* 264, 1-8. [4] Franz et al. (2019) *Met. Planet. Sci.* 54, 3036-3051. [5] Irving (2021) http://www.imca.cc/mars/ martian-meteorites-list.htm. [6] Met. Soc. (2020) *Met. Bull.* 109. [7] Farquhar et al. (2001) *J. Geophys. Res.* 106, 32829-32839. [8] Franz et al. (2013) *Chem. Geol.* 362, 56-65. [9] Whitehill et al. (2015) *Atmos. Chem. Phys.* 15, 1843-1864. [10] Pavlov et al. (2005) *Geophys. Res. Lett.* 32, L12816.