

SULFUR ISOTOPIC SYSTEMATICS OF SULFIDES FROM OLIVINE-PHYRIC SHERGOTTITES LARKMAN NUNATAK (LAR) 12095/12240 and LAR 12011. H. B. Franz¹, J. Dottin III², and J. Farquhar^{2,3}, ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²Department of Geology, University of Maryland, College Park, MD, 20742, ³Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742.

Introduction: Sulfur is a multivalent element that is abundant on Mars and may be found in a variety of mineral phases at the martian surface. Ratios of its four stable isotopes provide valuable tracers of geochemical and atmospheric processes recorded in sulfide and sulfate minerals on both Earth and Mars. 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 [1]. However, anomalies in ratios involving minor isotopes ³³S and ³⁶S, known as mass-independent fractionation (MIF) signatures that were likely introduced during UV processing of sulfur-bearing gases in the atmosphere, document a history of atmosphere-surface interaction and help discern formation mechanisms of relevant phases. In addition, some martian melts assimilated surface materials as they rose through the crust or extruded onto the surface, imparting MIF signatures to igneous sulfides. Such signatures, when present, can facilitate understanding of magmatic history, including potential sources of variability in other elements. Here we report measurements of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ ¹ for sulfide phases in three shergottites recovered from Antarctica, LAR 12095, its pair LAR 12240, and LAR 12011.

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. [2]. 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 N₂ gas. Both monosulfides and disulfides present in the sample reacted with the reduction solution to evolve H₂S gas. The H₂S bubbled through a condenser, then through a milli-Q water trap, and finally into an acidic capture solution containing AgNO₃. Reaction between evolved H₂S and AgNO₃ in the capture solution produced Ag₂S, which was rinsed with milli-Q water several times, then dried. Samples of Ag₂S were reacted with ~10 times stoichi-

ometric excess of pure F₂ at ~250 °C for at least 16 hours. Product SF₆ was purified by both cryogenic and gas chromatographic techniques, and sulfur isotope abundances were measured by monitoring m/z = 127, 128, 129, and 131 (³²SF₅⁺, ³³SF₅⁺, ³⁴SF₅⁺, and ³⁶SF₅⁺) 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 $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, respectively. Results are normalized to measurements of Cañon Diablo Troilite (CDT).

Results: Results of isotopic analyses for the sulfide fractions of shergottites analyzed in this study are given in Table 1. Observed values ranged from $-0.01 \pm 0.15\text{‰}$ to $0.08 \pm 0.15\text{‰}$ in $\delta^{34}\text{S}$ and $-0.006 \pm 0.008\text{‰}$ to $0.007 \pm 0.008\text{‰}$ in $\Delta^{33}\text{S}$, while all three samples showed $-0.04 \pm 0.15\text{‰}$ for $\Delta^{36}\text{S}$. All values match those of CDT within error.

Table 1. Results of sulfur isotopic analyses

Sample	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
LAR 12095	0.00	0.006	-0.04
LAR 12240	-0.01	0.007	-0.04
LAR 12011	0.08	-0.006	-0.04

Discussion: LAR 12095 and its pair LAR 12240 are fractured, porphyritic depleted olivine-phyric shergottites with large mm-sized olivine grains in a matrix of pyroxene, smaller and more Fe-rich olivines, and maskelynite [3-5]. Accessory minerals include phosphates, ilmenite, and Cr-rich spinels that are associated with sulfides [5]. The sulfides in LAR 12095/12240 are mostly Fe-rich pyrrhotite, but some high-Ni pyrrhotites are present, unlike most shergottites. The sulfide composition is most similar to that of SaU 005/094, but LAR 12095/12240 contain sulfides with higher Ni content [3]. The presence of troilite has also been reported [4]. These meteorites crystallized from a magma with relatively low oxygen fugacity, similar to DaG 476, but show evidence for a difference of ~3.1 log units between early and late redox estimates for the melt [4-6]. Possible mechanisms for changes to $f\text{O}_2$ during crystallization include open-system behavior as suggested for the Tissint meteorite [4] and outgassing of volatiles, including reduced sulfur (H₂S), that left the residual magma more oxidized, as proposed by Shearer et al. for the enriched olivine-phyric shergottite Northwest Africa (NWA) 1183 [4, 7]. Analysis of sulfur isotopes in Tissint during our

¹ We use the following definitions:

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

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

previous study showed its sulfide fraction to have a notably negative $\delta^{34}\text{S}$ signature ($-0.82 \pm 0.15\%$) compared to the shergottite population (average $-0.24 \pm 0.05\%$), with $\Delta^{33}\text{S}$ ($0.024 \pm 0.008\%$) at the upper edge of the range observed for the same population [2]. Degassing of H_2S would be expected to preferentially remove light sulfur isotopes, leaving the remaining melt relatively enriched in ^{34}S . However, our analyses of LAR 12095/12240 sulfides did not show depletion in ^{34}S , leaving open the question of late-stage outgassing.

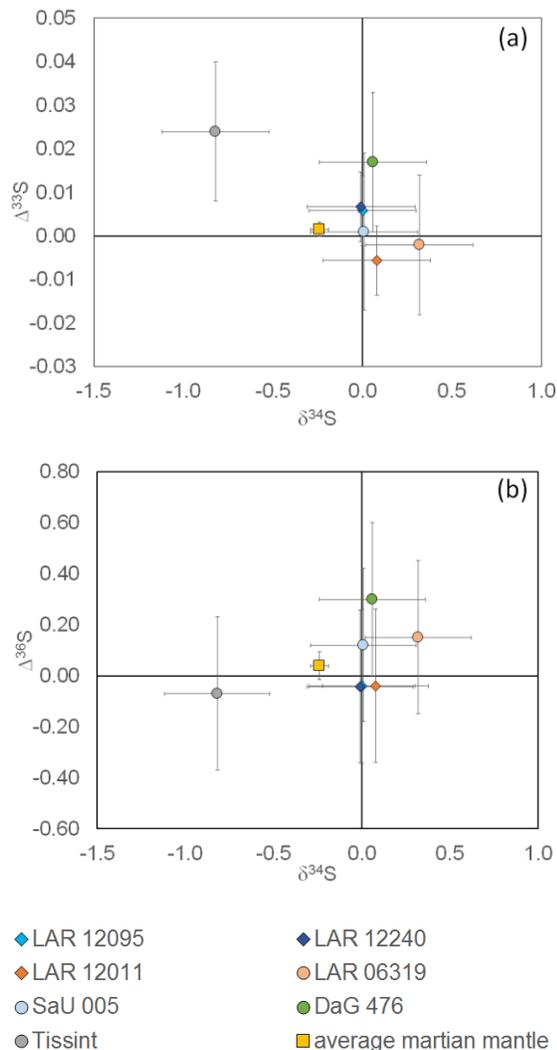


Figure 1. Sulfur isotopic composition of sulfide fractions for data from this study and ref. [1], discussed in the text: (a) $\Delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ and (b) $\Delta^{36}\text{S}$ vs. $\delta^{34}\text{S}$. Gold square indicates weighted mean for the martian mantle [2]. Error bars show 2σ uncertainties.

LAR 12011 is an olivine-phyric shergottite containing large olivine and occasional pyroxene phenocrysts in a groundmass of pyroxene, maskelynite, and minor phases that include spinel, merrillite, OH-rich apatite, and uniformly Fe-rich pyrrhotite [3]. It is most likely paired with LAR 06319 [6]. These meteorites crystallized from a more oxidized melt than other olivine-phyric shergottites such as DaG 476 and LAR 12095/12240, as discussed above [6]. Analysis of LAR 06319 during our previous study revealed the presence of sulfate with MIF composition, but the MIF signature was not detected in the sulfide fraction. This suggests deposition of surface sulfur into sulfate minerals during weathering that occurred on Mars [1]. The sulfide fraction of LAR 12011 yielded values matching within error those of our previous analysis of LAR 06319 [1], but sulfate fractions of LAR 12011 have yet to be analyzed and will be reported in a future contribution.

None of the meteorites analyzed in this study revealed MIF in their sulfide fractions, supporting (but not definitively proving) an absence of assimilation of surface sulfur into their parent magmas.

References: [1] Franz et al. (2014) *Nature* 508, 364-368. [2] Franz et al. (2019) *Met. Planet. Sci.* 54, 3036-3051. [2] Irving (2017) <http://www.imca.cc/mars/martian-meteorites-list.htm>. [3] Balta et al. (2015) LPSC, 2294. [4] Castle and Herd (2015) LPSC, 1975. [5] Funk et al. (2015) LPSC, 2830. [6] Dunham et al. (2015) 78th Met. Soc. Mtg., 5289. [7] Shearer et al. (2013) *Geochim. Cosmochim. Acta* 120, 17-38.