

FRACTIONATION OF THE HIGHLY SIDEROPHILE ELEMENTS IN SHERGOTTITE SULFIDES.

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Introduction: The shergottite meteorites provide insights into the composition of the martian mantle and magmatic differentiation processes. The highly siderophile elements (HSE: Au, Re, Pd, Pt, Rh, Ir, Ru and Os) are dominantly found within sulfide assemblages in shergottites and these elements can be used to interrogate metal-silicate and sulfide melt-silicate melt processes on Mars [1,2]. Following initial work by Baumgartner et al. [1] to characterize sulfide assemblages in four shergottites, we have examined sulfide mineral assemblages in 12 martian shergottites using in-situ Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for HSE abundances, and report new whole-rock HSE abundance and ¹⁸⁷Os/¹⁸⁸Os data to complement our previous work [2,3]. It has been shown that shergottite sulfides preserve magmatic HSE signatures [1]. Furthermore, there are apparent depletions of Pt - and sometimes Ir - in sulfides, suggesting the presence of additional phases such as Pt-Fe-Ir alloys in shergottites [1].

Samples and Methods: Sulfides were characterized for major- and trace- element compositions (including highly siderophile elements) in 14 polished sections (Allan Hills (ALHA) 77005, Dar al Gani (DaG) 476, Elephant Moraine (EETA) 79001, Larkman Nunatak (LAR) 06319,28, LAR 06319,39, Northwest Africa (NWA) 3171, NWA 7397, NWA 7755, NWA 8679, NWA 10961A, NWA 10961B, NWA 11043, NWA 11065, Roberts Massif (RBT) 04262) using a *New Wave* UP-213nm Laser Ablation system coupled to a *Thermo Scientific* iCAP Qc Inductively Coupled Plasma Mass Spectrometer (ICP-MS). We measured between 11 and 37 sulfides in each section (Fig. 1). Powders for five of these shergottites were analyzed for major-, trace- and highly siderophile- element abundances, and Os isotope compositions (NWA 7397, NWA 7755, NWA 10961, NWA 11043, NWA 11065) using the methods given in [2].

Results and Discussion: Bulk rock REE data suggest that NWA 7397, 7755 and 11043 originated from a LREE-enriched mantle source whereas NWA 10961 and 11065 sampled a moderately depleted-LREE source [3]. Our new data for whole-rock samples (NWA 7397, NWA 7755, NWA 10961, NWA 11043, NWA 11065) are in agreement with previous work done on whole-rock shergottite samples in terms of relative and absolute HSE abundances (Fig. 2) and

¹⁸⁷Os/¹⁸⁸Os ratios [2]. Northwest Africa 7755, NWA 10961, NWA 11043 and NWA 11065 have homogeneous and broadly flat HSE patterns with abundances ~100 to 1000 times lower than CI-chondrite, with slight relative depletions in Re and enrichments in Pd. These HSE compositions are similar to those of the depleted shergottites described in [2]. Enriched shergottites like NWA 7397 show a similar range of Re abundances to the depleted shergottites, but tend to have highly variable Pd and Pt contents, and are depleted in Ru, Ir and Os. Abundances for Pd and Ir reported in this study for NWA 7397 are between 1.5 and 20 times higher, respectively, than those reported in Tait & Day [2]. The variability observed for the HSE patterns for NWA 7397 between our study and [2] suggests significant heterogeneity (“nugget effects”) due to the limited mass available for these shergottite samples. The ¹⁸⁷Os/¹⁸⁸Os ratios for the five new samples range from 0.11896 ±6 (2σ) and 0.14217 ±8 (2σ), overlapping values reported in [2] and [4].

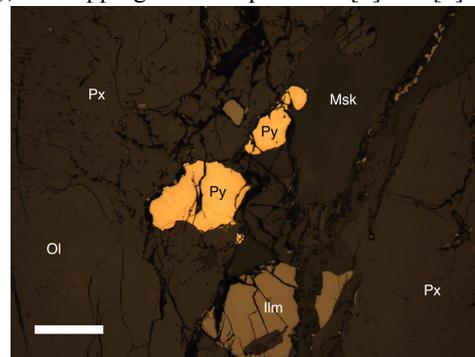


Figure 1. Example of pyrrhotite grains in NWA 7755 shown in reflected light. A Pt-rich alloy has been sampled in the top grain but not the bottom one. Scale bar corresponds to 100 μm. Py = pyrrhotite; Ilm = ilmenite; Px = pyroxene; Ol = olivine; Msk = maskelynite.

The sulfide compositions, particularly those from DaG 476, are in good agreement with those reported in [1]. The similarities in relative HSE abundances between whole-rock compositions and sulfides of our data support the major role of sulfides in controlling the HSE during the petrogenesis of shergottites. Because HSE abundances in sulfides are 100 to 200 times greater than in whole-rocks, 0.5 to 1% by mass of sulfide can reproduce the abundance and distribution

of the HSE in shergottites (Fig. 2), which is consistent with the modal abundance of sulfide assemblages in the shergottites (≤ 1 modal %, e.g. [5,6]), as described by [2]. Rhenium depletion, compared to the Pd abundance, in most of the sulfides (and thus the whole-rocks) is likely explained by redistribution of Re due to mobility during alteration [1,7].

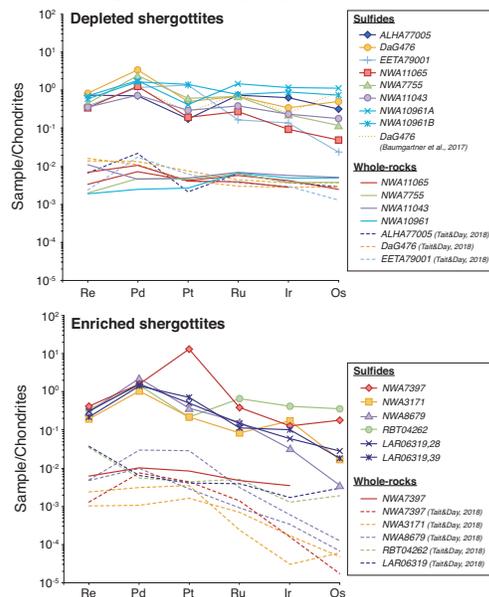


Figure 2. CI-chondrite normalized HSE patterns for whole-rock samples and average sulfide compositions. Solid lines are from this study. Dotted lines are from [1] for the median sulfide composition of DaG 476 and [2] for the whole-rock compositions. (a) Depleted shergottites. (b) Enriched shergottites. Classification from [2].

As described by [1], Pt-rich alloys were identified in some of the analyzed sulfides (up to 6 alloys in some sections) in both enriched and depleted shergottites (Fig. 1). We also observed the presence of sulfides enriched in Ir, Ru and Os in both enriched and depleted shergottites. We recorded no systematic macroscopic differences between the sulfides associated with or without HSE-rich alloys. The characterization of the sulfides in two sections of the same sample (NWA 10961) shows a good spatial homogeneity of sulfide composition at the scale of the sample. The positive anomaly in Pt for NWA 10961B is due to the presence of a highly enriched Pt-rich alloy (20 ppm Pt). The same phenomenon is observed for NWA 7397 which contains two of these Pt-rich alloys (15 and 250 ppm Pt respectively).

There is a strong positive correlation between MgO and Ru, Ir and Os in the whole-rocks and the sulfides, suggesting that these elements behave highly compatibly during martian fractional crystallization processes

(Fig. 3). Such correlation is not noticeable between MgO and Pd (or Re and Pt). These observations are also valid in the sulfides, suggesting that the sulfides are the major carrier of the HSE [e.g. 1, 2] and fractionate these elements throughout progressive fractional crystallization processes on Mars (up to 30% of fractional crystallization of an olivine-dominated cumulate; partition coefficients from [8]). Fractional crystallization modeling can reproduce the fractionation behavior of Ru, Ir and Os in the whole-rocks, but cannot reproduce the high Pd and Pt contents of some of the low-MgO enriched shergottites, as previously described in [2], suggesting that Pd and Pt appear to be even more incompatible during martian petrogenetic processes [2] than during equivalent terrestrial processes.

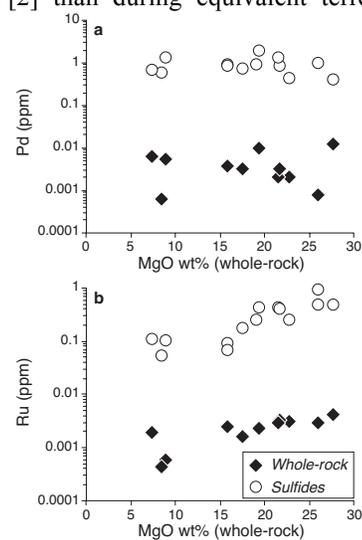


Figure 3. Concentrations in (a) Pd and (b) Ru (ppm) in the host rocks and the sulfides in function of the MgO content of the host rock. Data from this study, and Tait & Day [2].

The same characteristics (high Pt+Pd/[Os+Ir+Ru]) are also observed in the sulfides of the low-MgO enriched shergottites. The sulfides of the depleted shergottites and high-MgO enriched shergottites show relatively flat unfractionated HSE patterns. Our results demonstrate that the HSE abundances in the sulfides (and hence in the shergottites) are mostly controlled by petrogenetic processes such as fractional crystallization.

References: [1] Baumgartner R.J. et al. (2017) *GCA*, 210, 1-24. [2] Tait K.T. and Day J.M.D. (2018) *EPSL*, 494, 99-108. [3] Rahib R.R. et al. (2019) *LPSC Abstracts*. [4] Brandon A.D. et al. (2012) *GCA*, 76, 206-235. [5] Basu Sarbadhikari A. et al. (2009) *GCA*, 73, 2190-2214. [6] Riches A.J.V. et al. (2011) *Polar Sci.*, 4(4), 497-514. [7] Hyde B.C. et al. (2014) *Meteorit. Planet. Sci.*, 49, 1141-1156. [8] Day J.M.D. (2013) *Chem. Geol.*, 341, 50-74.