

## CHALCOPHILE ELEMENT CONSTRAINTS ON THE SULFUR CONTENT OF THE MARTIAN MANTLE.

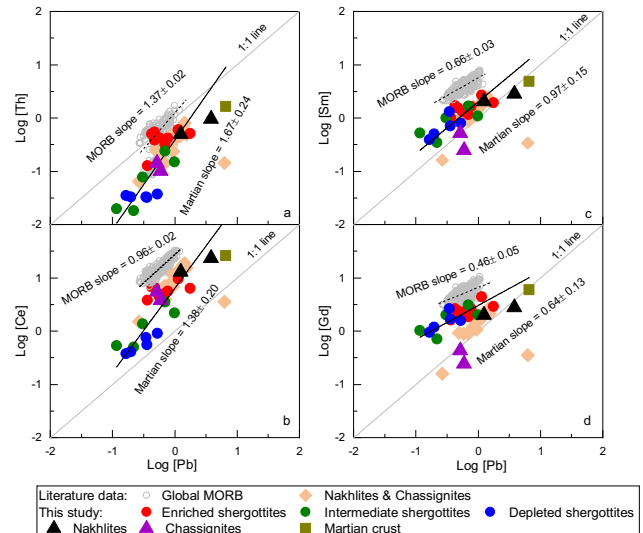
S. Yang<sup>1</sup>, M. Humayun<sup>1</sup>, K. Righter<sup>2</sup>, A. J. Irving<sup>3</sup>, R. H. Hewins<sup>4,5</sup> and B. Zanda<sup>4,6</sup>. <sup>1</sup>Florida State University, Tallahassee, FL 32310, USA ([syang@magnet.fsu.edu](mailto:syang@magnet.fsu.edu)); <sup>2</sup>NASA Johnson Space Center, Mail code XI2, Houston, TX 77058, USA; <sup>3</sup>Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA; <sup>4</sup>IMPMC, Sorbonne Université, MNHN-UPMC, 75005 Paris, France; <sup>5</sup>Rutgers University, Piscataway, NJ 08854, USA; <sup>6</sup>IMCCE, Observatoire de Paris - CNRS UMR 8028, 75014 Paris, France.

**Introduction:** The sulfur content of the Martian mantle is critical to understanding volcanic volatiles supplied to the surface of Mars and possibly climate [1-5]. In the absence of Martian mantle rocks, sulfur content of the mantle has been inferred from S contents of Martian meteorites [1, 3, 4] or from sedimentary sulfate abundances [5]. Estimates of the sulfur content of the Martian mantle vary from 390-2,000 ppm, all of which are higher than that of the terrestrial mantle (~250 ppm; [6]). Residual sulfide in the Martian mantle controls the distribution of chalcophile elements during partial melting. In this study, we report new analyses of Martian meteorites, and use the incompatible behavior of As, Tl and Pb to infer the sulfide mode of the Martian mantle using a different set of assumptions than those of prior studies.

**Analytical Methodology:** The abundances of 69 elements in eleven shergottites (ALHA 77005, DaG 670, Lar 12011, NWA 2975, NWA 7397, NWA 7635, NWA 8159, NWA 8657, QUE 94201, RBT 04261 and SaU 005), two nakhlites (NWA 10159 and NWA 6148), two chassignites (NWA 2737 and NWA 8694) and the Martian breccia (NWA 7533) were analyzed with an Elemental Scientific Lasers New Wave™ UP193FX excimer (193 nm) laser ablation system coupled to a Thermo Element XR™ ICP-MS at the Plasma Analytical Facility, FSU [7-8]. All sample sections were rastered using a 75 μm beam spot, at 15 μm s<sup>-1</sup>, 50 Hz repetition rate, over about 4 mm<sup>2</sup> surface area. USGS glasses (BCR-2g, BHVO-2g and BIR-1g) were used as the external standards for major elements, and most of the lithophile elements. Two synthetic glass standards (GSD-1g and NIST SRM 610) were used as the external standards for elements that were poorly constrained in USGS glasses, e.g., As, Mo, Sn, W, Tl and Pb. The reproducibility of this technique is better than 5% for major elements, REEs and most of the lithophile elements and is better than 10% for As, Sn, Tl and Pb if their abundances are above 10<sup>-1</sup> ng/g in samples [8].

**Results:** In a log-log plot, a pair of elements with identical partition yields a correlation with a slope of unity [9]. In Fig.1(a-d), Log[Pb] of Martian meteorites analyzed in this study and [7] were plotted against Log[Th], Log[Ce], Log[Sm] and Log[Gd] with compatibilities changing from highly incompatible (Th) to moderately incompatible (Gd). The following samples

were excluded because of surficial Pb-contamination (Shergotty, Los Angeles and Zagami [7]), sulfide assimilation (NWA 7635 and NWA 8159) and extreme fractionation (QUE 94201). The data from a recent study of nakhlites and chassignites [10] were also plotted for comparison. Terrestrial MORB data analyzed by the same methods [8] are shown in Fig. 1 for comparison with Martian igneous rocks. The slopes of the correlations were calculated from York regression [11] of Martian data (n=24) and MORB data (n=234) separately where errors in contents of both elements were taken into account.



**Fig. 1(a-d):** Correlations of Pb vs. Th, Ce, Sm and Gd for Martian meteorites analyzed in this study and [7, 11]. Terrestrial MORB glasses from [8] are shown for comparison.

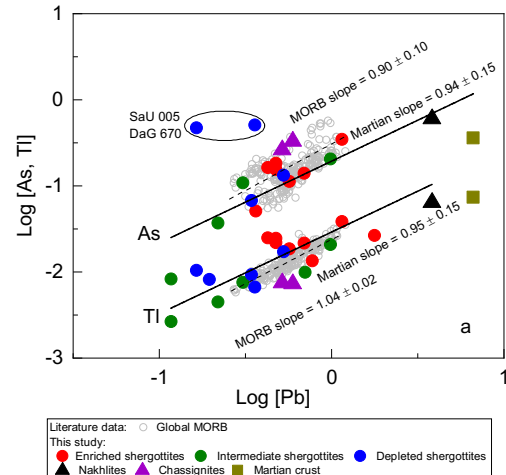
Fig. 2 compares the mutual compatibilities of As, Tl and Pb. Fig. 2(a) shows that the slopes of the correlations between Log[Pb] and Log[As] or Log[Tl] are close to unity for both MORB and Martian trends, indicating the partitioning of As and Tl are the same as that of Pb during the partial melting of both Martian mantle and MORB mantle. Two depleted shergottites (SaU 005 and DaG 670) plot off the Log[Pb]-Log[As] trend with both being higher in As. This observation is not an artifact of our analytical method, since the As contents of SaU 005 and DaG 670 obtained in this study agree well with literature values [12, 13].

**Discussion:** The compatibilities of a series of lithophile trace elements (Rb, Th, U, Nb, Ta, K, Sn, Zr, Hf, Ti, Na and REE) were tested to ascertain if the relative compatibilities of these elements are consistent between Martian and terrestrial igneous processes. The higher relative uncertainties on the correlations for Martian rocks relative to terrestrial MORB glasses [8] is likely due to the coarse-grained nature of Martian igneous rocks. The REE and Y are principally in phosphates, and the correlations between two adjacent REE (e.g., La and Ce) are better than 5%. The relative uncertainties on the correlations of Nb vs. Ta and Zr vs. Hf are also similar to those observed for MORB glasses, but inter-group correlations, e.g. La vs. Nb, are less precise due to the distinct hosts for each of these elements not being representatively sampled.

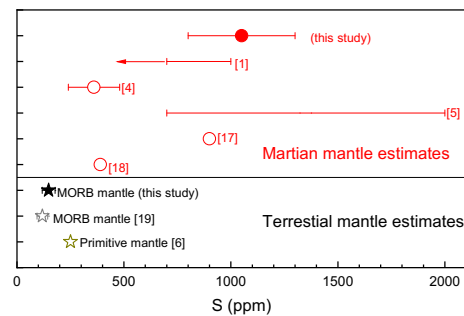
Fig. 1 shows that Pb is about as compatible as Sm in Martian igneous rocks, with a slope of  $0.97 \pm 0.15$  (Fig. 1c). For MORBs, Pb is best correlated with Ce with a slope of  $0.96 \pm 0.15$  (Fig. 1b), consistent with other studies [8, 14], and the correlation for Pb with Sm in terrestrial rocks is distinctly poorer (slope: 0.66). Thus, Pb, As and Tl are all more compatible during melt extraction from the Martian mantle than from the terrestrial mantle.

It has been shown for terrestrial rocks, that Pb behaves more compatibly (like Ce rather than Th) than cpx-silicate melt partitioning would indicate due to the presence of sulfide in the source [14]. Similarly, Tl has been shown to be more compatible for the same reason [9]. Experimental partitioning of various chalcophile elements between liquid sulfide and silicate melts [14-16] shows that As and Pb are both compatible in sulfide melt, and the presence of small quantities of sulfide (~0.1 %) in the terrestrial source accounts for the higher compatibilities of both elements. The only available partitioning of Tl between liquid sulfide and liquid silicate [15] indicates that Tl is not sufficiently compatible in sulfide liquid to fully explain the compatibility of Tl in terrestrial rocks [9]. Thus, it is interesting that Tl follows Pb on Mars like Earth (Fig. 2), even though the reasons for this are not fully understood.

Knowing that the partition coefficient for Pb is comparable to that of Sm, and assuming that Sm partitioning between basaltic melts and silicate mantles is the same for Earth and Mars, we calculated the abundance of sulfide needed to make Pb (and As) as compatible as Sm. This calculation yielded a Martian mantle sulfur content of  $1,050 \pm 250$  ppm. This sulfur content is applicable to sources of shergottites, nakhlites-chassignites and of the breccias precursors, i.e. generally applicable to the entire Martian mantle.



**Fig. 2:** Correlations of Pb vs. As and Tl in Martian meteorites analyzed in this study and [7, 11]. Terrestrial MORB glasses from [8] are shown for comparison.



**Fig. 3:** Sulfur contents estimated in this study compared with literature estimates for Martian and terrestrial mantles.

**References:** [1] Ding S. et al. (2015) *EPSL* 409, 157-167. [2] Righter K. et al. (2009) *EPSL* 288, 235-243. [3] Halevy I. et al. (2007) *Science* 318, 1903-1907. [4] Wang Z. and Becker H. (2017) *EPSL* 463, 56-68. [5] Gaillard F. et al. (2013) *Space Sci. Rev.* 174, 251-300. [6] McDonough W. F. and Sun S.-s. (1995) *Chem. Geol.* 120, 233-253. [7] Yang S. et al. (2015) *MaPS* 50, 694-714 [8] Yang S. et al. (2018) *G<sup>3</sup>* 19, 4236-4259. [9] Nielsen S. et al. (2014) *G<sup>3</sup>* 15, 4905-4919. [10] Udry A. and Day J. M. D. (2018) *GCA* 238, 292-315. [11] York D. et al. (2004) *Am. J. Phys.* 72, 367-375. [12] Zipfel J., et al. (2000) *MaPS* 35, A178. [13] Dreibus G., et al. (2000) *MaPS* 35, A49. [14] Hart S. and Gaetani G. (2016) *GCA* 185, 9-20. [15] Kiseeva E. and Wood B. J. (2015) *EPSL* 383, 68-81. [16] Li Y. and Audetat A. (2015) *EPSL* 355-356, 327-340. [17] Lodders J. and Fegley B. (1997) *Icarus* 126, 373-394. [18] Sanloup C. et al. (1999) *PEPI* 112, 43-54. [19] Salters V. J. M and Stracke A. (2004) *G<sup>3</sup>* 5, doi:10.1029/2003GC000597.