

LOW SULFUR ABUNDANCES IN THE MARTIAN INTERIOR? H. Becker¹ and Z. Wang^{1,2}, ¹Freie Universität Berlin, Institut für Geologische Wissenschaften, Malteserstr. 74-100, 12249 Berlin, Germany (hbecker@zedat.fu-berlin.de). ²State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, 388 Lumo Road, Hongshan District, Wuhan, 430074, China (wzc231@163.com)

Introduction: Previous accretion and core-mantle differentiation models for Mars have assumed high S contents in the interior of Mars [1-3]. The relatively high S contents of some SNC meteorites (up to a few thousand $\mu\text{g/g}$) and the abundance of sulfate on the Martian surface also may indicate that Mars is relatively rich in sulfur [2,4]. High S abundances in the Martian interior would also satisfy the requirement that Mars' core likely contains a larger fraction of light elements than Earth's core [5]. However, recent estimates of the sulfur content at sulfide saturation for parent magmas of SNC meteorites hint that the maximum sulfur content of the Martian mantle may be only 700-1000 $\mu\text{g/g}$ [6]. Because these are maximum estimates, sulfur contents in Martian mantle sources may be even lower. The concentration of sulfur in the Martian core and mantle are critical to understand the state of Mars' core and the origin of Mars' early magnetic field and the accretion and differentiation history of the planet. We have addressed this issue by using abundances and ratios of chalcophile elements (Cu, S, Se, Te, Ag, PGE) with different $D^{\text{sulfide/silicate}}$ in SNC meteorites.

Analytical methods: 0.2 gram-size fragments of lherzolitic, olivine-phyric and basaltic shergottites, nakhrites and ALH 84001 (mostly falls and Antarctic finds) were digested in Parr bombs in conc. HF-HNO₃ and were analyzed for Cu, Ag, S, Se and Te abundances in the same digestion aliquots by isotope dilution-SF-ICP-MS. The methods are the same as reported in [7] with precisions on concentrations better than 5%. Procedural blank corrections were always applied and, except for ALH84001, negligible (<1%) for S, Se and Cu or up to a few % for Te and Ag.

Results: In shergottites, Cu, Ag, Se, S and Te display broadly negative correlations with MgO contents (e.g., Fig. 1). Nakhrites tend to have lower S, Se and Te contents relative to shergottites. A few samples have high S (up to 4000 $\mu\text{g/g}$) due to crustal contamination.

Although shergottites and nakhrites have variable contents of Cu, S, Se and Te, their ratios display less variation over the large range of MgO contents than terrestrial basalts and cumulate rocks (Variations in SNC meteorites are: < factor 2 for Cu/Se and factor 2-5 for Se/Te and Cu/Pd, the mean ratios are Cu/Se = 20±4, Cu/Te = 4400±2000, Se/Te = 200±80 and Cu/Pd = 2650±950, uncertainties 1s.d.). The relatively constant ratios (compared to terrestrial basic magmatic rocks) do not show systematic variation with indicators

of magmatic fractionation (e.g., Fig. 2), radiogenic isotope compositions or incompatible lithophile element characteristics of Martian mantle sources.

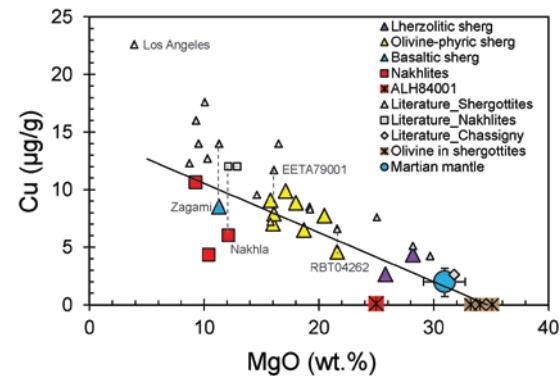


Fig. 1. Variation of Cu contents in Martian meteorites with MgO contents.

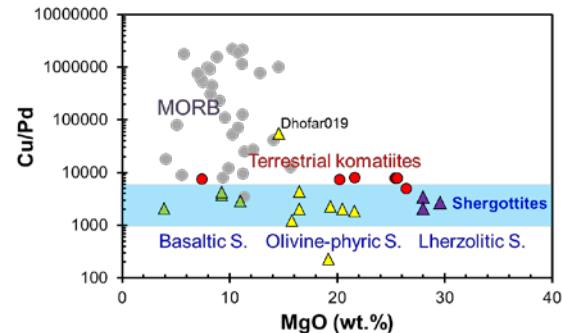


Fig. 2. Limited variation of Cu/Pd with MgO contents in different types of shergottites and in sulfide-undersaturated terrestrial komatiites. The large variations in MORBs reflect sulfide-saturated conditions and the large difference in $D^{\text{sulfide/silicate}}$ of Cu and Pd [8].

Discussion: Combining new and published data on the chalcophile elements S, Se, Te, Cu, Ag and the PGE in shergottites, ALH84001 and some nakhrites shows that the parent magmas of most of these SNC meteorites formed and evolved at sulfide-undersaturated conditions. This is most clearly indicated by the limited variation of Cu/Pd (also Cu/Te, S/Pd etc.) with MgO contents in different types of shergottites (Fig. 2) and also by the negative correlations of chalcophile elements with MgO (Fig. 1). The behavior is similar to sulfide-undersaturated terrestrial komatiites (in which chalcophile elements

also correlate negatively with MgO) and suggests sulfide-undersaturation during the formation and fractional crystallization of the SNC parent magmas. This conclusion is further supported by approximately chondritic Pt/Pd ratios but fractionation of incompatible PGE (Pt, Pd) from the compatible PGE in shergottites [9].

With few exceptions, which were caused by shallow crustal contamination of some SNC meteorites or their parent magmas, most studied shergottites display chondritic $\delta^{34}\text{S}$ [10]. Also, there is no isotopic evidence for extensive degassing of S in most shergottites, consistent with the slightly suprachondritic S/Se ratios (Fig. 3, a likely outcome of core formation, [11]) and the pressures of crystallization of most SNC meteorites within the crust [12].

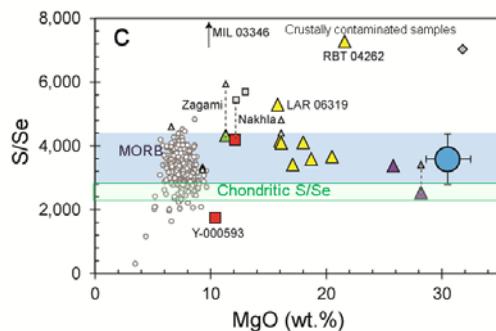


Fig. 3. SNC meteorites that were not contaminated with sulfates from Martian surface environments display slightly suprachondritic S/Se as expected from the slightly less siderophile nature of S compared to Se [10]. MORBs are shown for comparison.

The sulfur content in the Martian mantle deduced from element correlations (e. g., Cu, Se vs. MgO) and element ratios such as Cu/S or S/Se is only 360 ± 120 or $340 \pm 140 \mu\text{g/g}$ (1s), respectively. At such a low concentration, all sulfide in the Martian mantle should dissolve in the melt at a few percent partial melting [6]. Thus, if the SNC meteorite-based mantle composition of Mars is valid, most mantle-derived Martian magmas should be sulfide-undersaturated. The differences in concentrations of S at sulfide saturation in Martian and terrestrial magmas at comparable pressure-temperature conditions is caused by the very different FeO contents of the mantle-derived magmas on these planets [6].

Because chondrite-normalized S/HSE ratios of shergottites are suprachondritic, it is likely that Martian mantle inventories of S (also Se, Cu, Ag) were mostly controlled by core formation. The S content in the Martian core may be determined via S contents of the mantle and metal-silicate partition coefficients [13, 14] at the conditions of Martian core formation (14 GPa, 2100 K [15]). These data suggest that the Martian core

likely contains ≤ 9.6 wt.% S (assuming $D_{\text{metal-silicate}}^{\text{S}} \leq 200$) and that bulk Mars should have ≤ 2 wt.% S. Independent evidence for a low S concentration in Mars is the relatively low Zn concentration of 60-70 ug/g in the Martian mantle [3, 16]. Because Zn is lithophile at the relevant range of P-T conditions [15, 17], its planetary budget is mostly controlled by the mantle. Both S and Zn show similar volatility [18]. Thus, CI chondrite- and Mg-normalized abundances of both elements in bulk Mars should be very similar (0.11), implying about 1 wt.% S in bulk Mars and 4.5 wt. % S in the core (at a core mass fraction of 20 %).

Conclusions: Independent lines of geochemical evidence from the chalcophile element composition and Zn abundances of SNC meteorites suggest relatively low S concentrations in bulk Mars and possibly only 5 wt. % S in the Martian core. These results and their interpretation pose a problem as the low density of the Martian core determined from geophysical data may require a large fraction of light elements in the Martian core [5]. Some of the alternatives (Si, O and C) are no less problematic because they either require very reducing conditions or high temperatures during core formation [19-21]. Alternatively, the parent magmas of SNC meteorites may not sample reservoirs representative of the Martian mantle.

References: [1] Gaillard, F. et al. 2013. *Space Science Reviews* 174, 251-300. [2] Wänke, H. and Dreibus, G. 1988. *Phil. Trans. R. Soc. A* 325, 545-557. [3] Lodders, K. and Fegley, B. 1997. *Icarus* 126, 373-394. [4] Dreibus, G. and Wänke, H. 1985. *Meteoritics* 20, 367-381. [5] Kavner, A. et al. 2001. *EPSL* 185, 25-33. [6] Ding, S. et al. 2015. *EPSL* 409, 157-167. [7] Wang, Z. et al. 2016. *Geostand. Geoanal. Res.* 39, 185-208. [8] Mungall, J. and Brenan, J. 2014. *GCA* 125, 265-289. [9] Brandon et al. 2012. *GCA* 76, 206-235. [10] Franz, H. B. et al. 2014. *Nature* 508, 364-368. [11] Rose-Weston et al. 2009, *GCA*, 73, 4598-4615. [12] Gaillard et al. 2013, *Space Sci. Rev.* 174, 251-300. [13] Righter, K. et al. 2009. *EPSL* 288, 235-243. [14] Boujibar, A. et al. 2014. *EPSL* 391, 42-54. [15] Righter, K. and Chabot, N. L. 2011. *MAPS* 46, 157-176 [16] Yang, S. et al. 2015. *MAPS* 50, 691-714. [17] Wang, Z. et al. 2016. *EPSL* 435, 136-146. [18] Dreibus, G. and Palme, H. 1996. *GCA* 60, 1125-1130. [19] Li, Y. et al. 2015. *EPSL* 415, 54-66. [20] Fischer, R. A. et al. 2015. *GCA* 167, 177-194. [21] Rubie, D. C. et al. 2004. *Nature* 429, 58-61.

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