

HIGH-TEMPERATURE PARTITIONING OF VOLATILE ELEMENTS IN THE CORES OF MOON AND MARS? E.S. Steenstra^{1,3}, W. van Westrenen¹, J. Berndt³, S. Klemme³, Y. Fei² ¹Vrije Universiteit Amsterdam, the Netherlands, ²The Geophysical Laboratory, Washington D.C., United States, ³Institute of Mineralogy, Münster University, Germany (e.s.steenstra@vu.nl)

Introduction: Core formation in planetary bodies profoundly affects planetary mantle geochemistry. Volatile elements may exhibit siderophile and/or chalcophile tendencies, depending on the redox state, pressure (P), temperature (T) and composition during core formation. Several previous studies were focused on the possibility of volatile siderophile element (VSE) storage in planetary cores, including that of the Earth [1,2], the Moon [2,3], Mars [2,4], Vesta [5], Mercury [6,7] and the aubrite parent body [8]. In case of the Earth, Moon and Mars, modeled T effects on metal-silicate partition coefficients ($D_{\text{met/sil}}$) of many volatile elements (e.g. Se, Te, Cd, Sb) are mainly based on extrapolations of the low- T dependencies. Here, we performed a systematic set of experiments to better constrain the effect of high T on the $D_{\text{met/sil}}$ of VSE.

Methods: High P - T experiments were performed in a 1500-ton multi-anvil apparatus at the Geophysical Laboratory, using 18mm edge length Cr-doped MgO or ZrO₂ octahedra. Outer ZrO₂ sleeves were used as thermal insulators in the MgO+Cr assemblies. Experiments were conducted at 3.5-5 GPa between 1973–2873 K. All experiments were conducted using C heaters, MgO spacers, and MgO capsules (1 or 1.6 mm I.D.). Temperatures were measured up to 2473 K with a type C thermocouple and higher run T were constrained by linearly extrapolating power- T curves obtained at 4 GPa. Starting compositions consisted of a synthetic equivalent of the A15 green glass [5] and Fe(S) powder doped with trace elements including volatile siderophile elements (VSE) P, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te and Pb. Run times, which varied between 15 min at 1873 K to 20 s at 2873 K, are sufficient for metal-silicate equilibrium [9]. Polished experimental run products were analysed using EPMA and LA-ICP-MS at Münster University. Matrix effects arising from the use of silicate calibrants for LA-ICP-MS metal measurements were addressed using the model of [10].

Results: Run products are characterized by S-rich metal blobs in quenched silicate melts. Both phases show various quench textures including spinifex and metallic liquid immiscibility (Fig. 1). After normalization of $D_{\text{met/sil}}$ values to a common $f\text{O}_2$ or FeO reference value (S, Se, Te [3]), results show that the siderophile behavior of S, Cu, Ge, Se, Sn, Te decreases with T (Fig. 2). The siderophile behavior of Ga, Cd, Zn, Pb increases with T , consistent with previous observations [12-14]. The metal-silicate partitioning behavior of In is unaffected by changes in T .

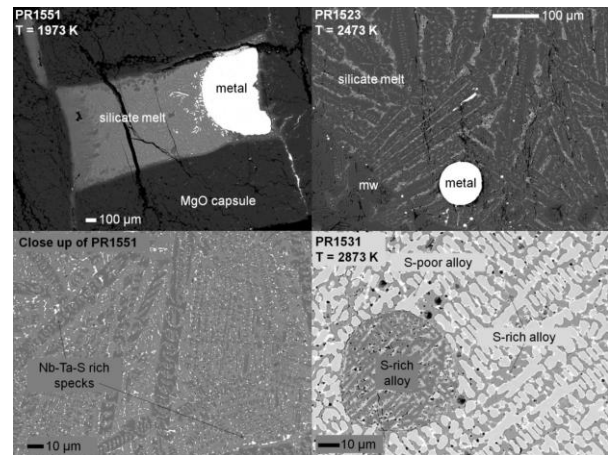


Fig. 1 Backscattered electron images of typical experimental run products.

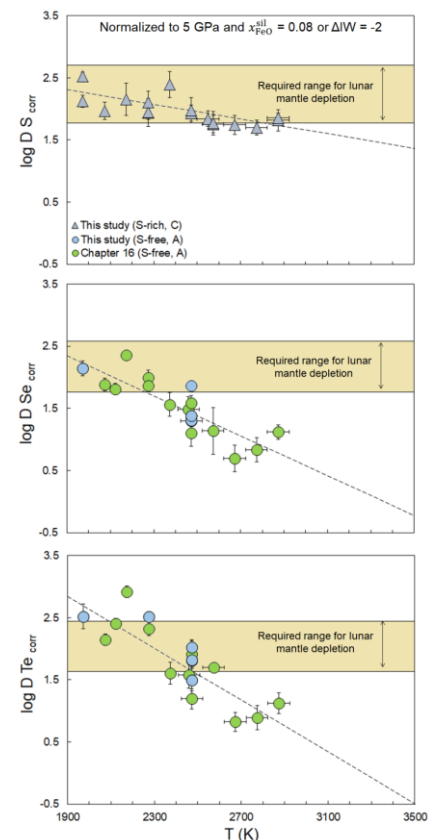


Fig. 2: $D_{\text{met/sil}}$ values for S, Se, Te corrected to lunar relevant $f\text{O}_2$ [3] and 5 GPa as a function of T . Triangles and circles represent $D_{\text{met/sil}}$ values obtained in S-rich and S-free systems, respectively. Dashed lines represent derived T dependencies of $D_{\text{met/sil}}$. Shaded bars represent required $D_{\text{met/sil}}$ range for explaining lunar mantle depletions. Letters denote different metal compositions, see [15].

Discussion: The new experimental results are applied to re-assess the nature of VSE depletions in the lunar and martian mantle. In case of the Moon, we consider three core formation scenarios: cold and shallow = 2.8 GPa, 1850 K; deep and hot = 5 GPa, 2200 K and deep and super-liquidus $T = 5$ GPa, 3100 K. To calculate lunar VSE mantle depletions, we assume a core mass of 1-2.5 %, a BSE bulk Moon composition [16,17] and mantle VSE abundances from [18]. For Mars, we use bulk Mars estimates from [19-20], mantle abundances of [21-24] and core masses of 21-28 %.

Moon: Results for the Moon confirm our earlier hypothesis that S, Se and Te lunar mantle depletions can be the result of their partitioning into the lunar core [3] (Figs. 2, 3). Results for several other elements (Zn, Ga, In, Cd, Pb) suggest that additional devolatilization is required either during or after the Moon-forming event (Fig. 3). This is consistent with measured Zn and Ga isotopic compositions of primitive lunar lithologies [25,26]. However, the extent of partitioning of these elements in the lunar core is still significant and should not be ignored in interpretations of lunar mantle volatile element depletions. It should also be noted that, although unlikely from current constraints on S abundances and chalcophile element systematics, segregation of FeS liquids during lunar differentiation would have additionally depleted most of these elements [6].

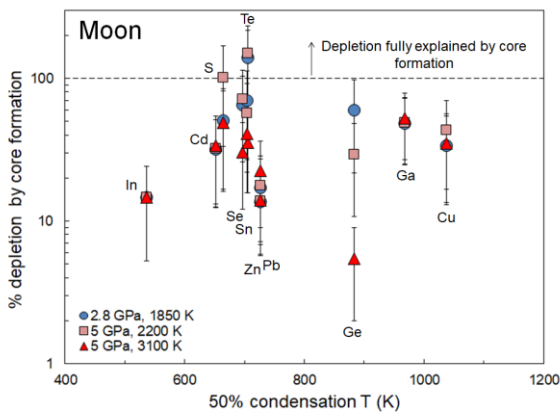


Fig. 3: Calculated percentages of lunar mantle VSE depletions due to core formation for the different P - T scenarios as a function of 50% condensation T [11]

Mars: In case of Mars core formation is also important for establishing mantle depletions of several volatile elements (Fig. 4). Although the effects of P at >5 GPa on their $D_{\text{met/sil}}$ are not well constrained yet, preliminary results show that their depletions can be largely if not completely reconciled with formation of a S-bearing Martian core (Fig. 4). Similar results were found for S, Se and Te in an earlier study [4], suggesting that core formation in Mars has a profound effect on mantle abundances of many volatile elements. As in case of the Moon, segregation of sulfide liquids during

Martian would likely also additionally deplete many of the elements considered, especially Cu, In, Cd and Sn [6].

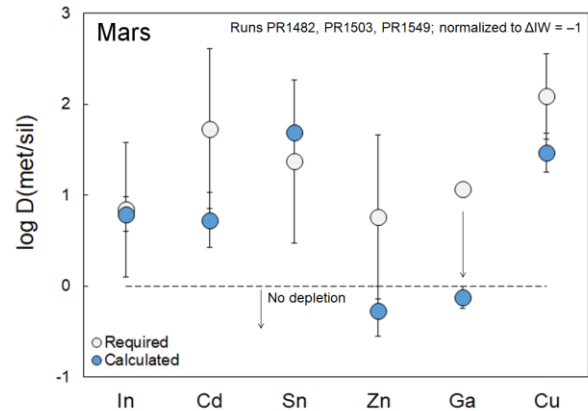


Fig. 4: Comparison between experimental $D_{\text{met/sil}}$ for S-rich alloys (13 ± 1 wt% S) at 2550 K - 4 GPa and calculated $D_{\text{met/sil}}$ values required for explaining Martian mantle depletions by core formation. $D_{\text{met/sil}}$ values were normalized to $\Delta IW = -1$ [4] assuming Cu^{1+} , Cd^{2+} , Sn^{2+} , Zn^{2+} , In^{3+} , Ga^{3+} .

Outlook: To definitely constrain the effects of Martian core formation and sulfide segregation on mantle VSE abundances, more experiments at higher pressures (>5 GPa) are required given the inferred Martian core-mantle equilibrium P of ~ 15 GPa.

References: [1] Wood & Halliday (2010) *Nature* 465, 767 [2] Righter et al (2018) *MAPS* 53, 284 [3] Steenstra et al (2017) *SR* 7, 14552 [4] Steenstra & van Westrenen (2018) *Icarus* 315, 69 [5] Steenstra et al (2018) *Icarus* 317, 669 [6] Kelderman et al (2019) *LPSC* [7] Boujibar et al (2018) *LPSC* 49 #2309 [8] Trautner et al (2019) *LPSC* [9] Tuff et al (2011) *GCA* 75, 673 [10] Steenstra et al (2019) *JAAS* 34, 222 [11] Lodders (2003) *AJ* 591, 1220 [12] Siebert et al (2011) *GCA* 75, 1451 [13] Rose-Weston et al (2009) *GCA* 73, 4598 [14] Boujibar et al (2014) *EPSL* 391, 42 [15] Steenstra (2019) *PhD thesis* [16] Wang et al (2018) *Icarus* 299, 460 [17] Wang & Becker (2013) *Nature* 499, 328 [18] Hauri et al (2015) *EPSL* 409, 252 [19] Sanloup et al (1999) *PEPI* 112, 43 [20] Lodders & Fegley (1997) *Icarus* 126, 373 [21] Taylor (2013) *Chem Erde* 73, 401 [22] Yang et al (2015) *MAPS* 50, 691 [23] Wang & Becker (2017) *EPSL* 463, 56 [24] Righter et al (2011) *EPSL* 304, 379 [25] Kato & Moynier (2017) *Sci Adv* 7, e1700571 [26] Paniello et al (2012) *Nature* 490, 376