

SULFIDE-SILICATE AND METAL-SILICATE PARTITIONING SYSTEMATICS AT HIGHLY REDUCED CONDITIONS: IMPLICATIONS FOR DISTRIBUTION OF VOLATILE ELEMENTS IN MERCURY AND THE AUBRITE PARENT BODY. V. Trautner¹, E.S. Steenstra^{1,3}, J. Berndt³, S. Klemme³, W. van Westrenen¹ 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: Assessment of the magnitude of volatile loss through evaporative events relies heavily on the extent to which these volatile elements partition into minerals, metals and sulfides during planetary differentiation. Here, we focus on the potential volatile element storage capabilities of sulfides. Several studies focused on quantification of the sulfide-silicate partitioning behavior of trace elements at moderately reduced conditions [e.g. 1-3]. However, their sulfide-silicate partitioning behavior at highly reduced conditions remains not well constrained. Wood and Kiseeva [4] found that chalcophile elements prefer the silicate melt at highly reduced conditions, whereas lithophile elements show increasingly chalcophile behavior. Steenstra et al. [5] recently assessed to which extent volatile elements in aubrites can be reconciled with their preferential partitioning into Fe-Si metals during core formation in the aubrite parent body (AuPB). Their results showed that most volatile elements will partition into Fe-Si metal, but not sufficient to explain their depletions in aubrites, i.e. requiring other mechanisms to explain their depletions. The latter experiments were conducted in the absence of sulfide phase. Given the abundance of various types of sulfides in aubrites, these phases may also be important carriers of volatile elements. To assess the geochemical behavior of major and trace elements in sulfide-metal-silicate systems at highly reduced conditions, we present a systematic study of their partitioning behavior as a function of fO_2 ($\Delta IW = -9$ to -1) and T (1673–1873 K) at 1 GPa. In companion abstracts we also present sulfide-silicate partitioning data for actinides and alkalis [6], halogens [7] and S solubilities for more oxidized lunar and asteroidal melts [8,9].

Methods: High P - T experiments were performed in Bristol-type piston cylinder end-loaded presses at VU and Münster University. Experiments were performed using a primitive basaltic silicate composition used in previous studies [3,6,7], Fe(-Si) and FeS powder doped with 0.1 wt.% of trace elements P, V, Co, Ni, Cu, Zn, Ga, Ge, Se, Nb, Mo, Cd, Sn, Sb, Te, Ta, W, Pb, Bi. Powders were loaded in C capsules that were placed within talc-pyrex assemblies. After the experiments, samples were polished and analysed for using EPMA and LA-ICP-MS at Münster University [see 10]. The LA-ICP-MS derived trace element corrections for metals and sulfides were corrected for matrix effects using a recently derived model [10,11].

Results: Fig. 1 shows a typical experimental run product which was performed at highly reduced conditions. Phase assemblages include FeS and/or (Fe,Mg,Ca)S, Fe-Si metal, glass and occasionally quartz crystals. In one highly reduced experiment a P-rich metal phase was found as well as a Ti-rich sulfide.

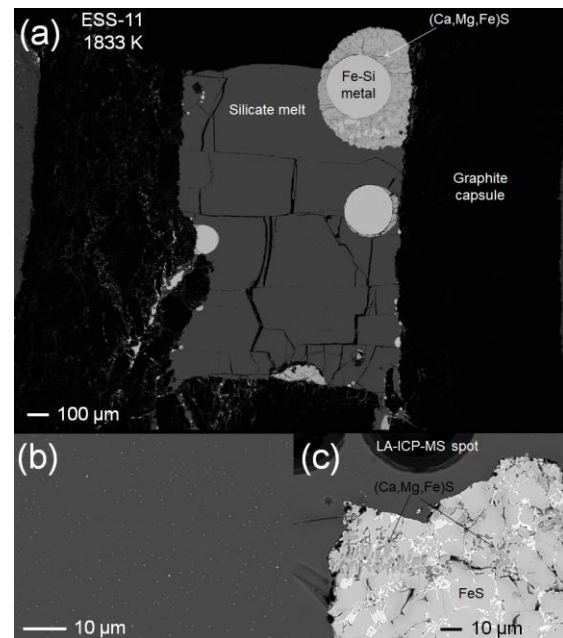


Fig. 1: Backscattered electron image of run ESS-11.

SCSS: Given the importance of S in the silicate melt for the sulfide-silicate partitioning systematics [4,6,12,13], we also studied the sulfur concentration at sulfide saturation (SCSS) as a function of fO_2 . Our results reproduce the initial decrease of the SCSS with decreasing FeO contents, followed a substantial increase of the SCSS (up to 20 wt%) at highly reduced conditions (Fig. 2a). The addition of S affects the activity coefficient of FeO (γ_{FeO}). This results in higher FeO concentrations than that would be expected at the extremely reduced conditions of the experiments. Similar but less pronounced variations of γ_{FeO} were also observed for S-free systems (Fig. 2b).

Sulfide-silicate partitioning: The high S concentrations at reduced conditions results in significantly more chalcophile behavior of nominally lithophile elements, including Ca and Mg and U and Th as previously proposed [4,6,12,13]. Nominal chalcophile elements such as Cu and Ni behave less chalcophile than that would be predicted from thermodynamic considerations.

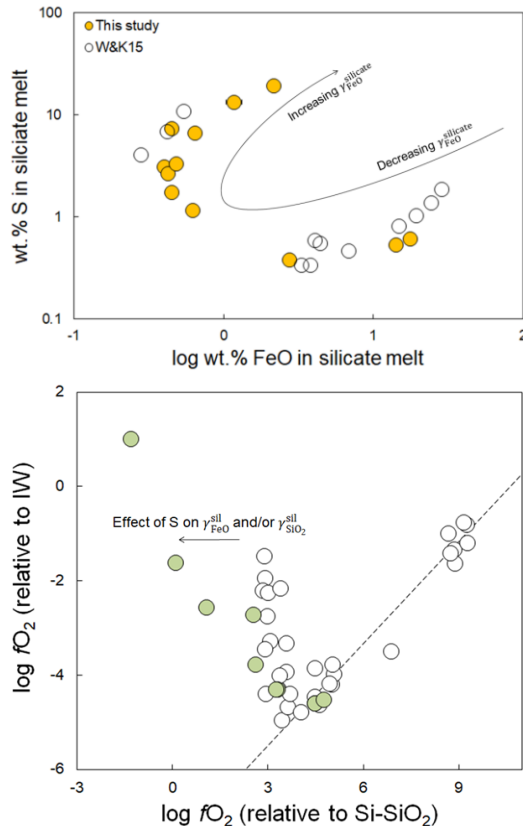


Fig. 2: (a) The SCSS as a function of log FeO (wt%) (b) Comparison between fO_2 values calculated using the iron-wustite buffer (dIW) and the Si-SiO₂ buffer. Open symbols are S-free data from [14].

Discussion: Volatile element distribution in Mercury and aubrites: To qualitatively assess the potential of volatile element depletion by preferential partitioning into Fe-Si metal and/or sulfide liquids during differentiation of the AuPB and Mercury, we summarize in Fig. 3 calculated D values as a function of condensation T . Fig. 3 shows that all the volatile elements considered here behave slightly to strongly chalcophile. Some of these elements are also additionally depleted by segregation of Fe-Si metal such as Sn, Bi, Ge, Sb, Ga and Cu. Fig. 3 also shows the high compatibility of Zn and Cd in (Fe,Mg,Ca)S liquids and to a lesser extent FeS. Given that CaS, MnS, FeS and other sulfides are important minor phase in aubrites [15] our results suggest that sulfide melts likely play a key role in establishing the Zn, Cd and other volatile element abundances in differentiated reduced achondrites. This suggestion is supported by the high Zn concentrations (~0.05–0.3 wt%) measured in daubreelite in various aubrites [16] and high abundances of for example Zn (>120 ppm), Cu (>150 ppm), Se (>195 ppm) and Te (>8 ppm) in FeS phases in the Shallowater aubrite [17] as well as in alabandite and oldhamite minerals in the Peña Blanca Spring aubrite [18].

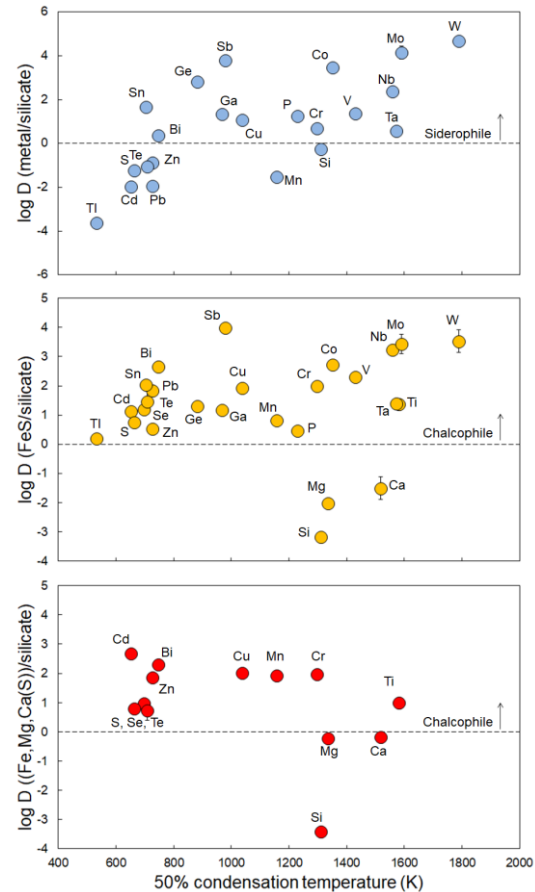


Fig. 3: D values of run VT-6 obtained at the highly reduced conditions as inferred for aubrites [18].

Conclusions and outlook: It is clear that many aspects of trace element partitioning at highly reduced conditions remain not well constrained and that more experimental studies are required. However, a robust finding is that segregation of sulfides at highly reduced conditions will significantly deplete all of the volatile elements considered here.

References: [1] Kiseeva & Wood (2013) *EPSL* 383, 68 [2] Kiseeva & Wood (2015) *EPSL* 424, 280 [3] Steenstra et al (2018) *GCA* 231, 130 [4] Wood & Kiseeva (2015) *AM* 100, 2371 [5] Steenstra & van Westrenen, *submitted* [6] Kelderman et al (2019) *This meeting* [7] van Haaster et al (2019) *This meeting* [8] Steenstra et al (2019) *This meeting* [9] Westrenen et al (2019) *This meeting* [10] Berndt et al (2019) *This meeting* [11] Steenstra et al (2019) *JAAS*, in press [12] Wohlers & Wood (2015) *Nature* 520, 337 [13] Wohlers and Wood (2017) *GCA* 205, 226 [14] Steenstra et al, *submitted* [15] Keil (2010) *Chem Erde* 70, 295 [16] Kimura et al (1993) *PNSA* 6, 186 [17] van Acken et al (2012) *GCA* 83, 272 [18] Lodders et al (1993) *MAPS* 28, 538 [19] Fogel (2005) *GCA* 69, 1633