

**EFFECTS OF  $fO_2$  AND Si ON METAL-SILICATE PARTITIONING OF REFRACTORY AND MODERATELY VOLATILE SIDEROPHILE ELEMENTS: IMPLICATIONS FOR THE Si CONTENT OF MERCURY'S CORE** R. Putter<sup>1</sup>, E. S. Steenstra<sup>1</sup>, A. X. Seegers<sup>1</sup>, Y. H. Lin<sup>1</sup>, S. Matveev<sup>2</sup>, J. Berndt<sup>3</sup>, N. Rai<sup>4</sup>, S. Klemme<sup>3</sup>, W. van Westrenen<sup>1</sup> <sup>1</sup>Faculty of Earth & Life Sciences, Vrije Universiteit Amsterdam, NL ([e.s.steenstra@vu.nl](mailto:e.s.steenstra@vu.nl)), <sup>2</sup>Department of Petrology, Utrecht University, Utrecht, NL <sup>3</sup>Department of Mineralogy, University of Münster, Germany <sup>4</sup>Indian Institute of Technology Roorkee, India

**Introduction:** Siderophile elements provide constraints on planetary differentiation conditions, by considering the extent of their mantle depletions relative to the inferred planetary building blocks [1-4].

It is well known from various lines of evidence (including the FeO content of the mantles of the Mercury, Earth and Mars) that oxygen fugacity ( $fO_2$ ) during planetary differentiation varied significantly between terrestrial bodies. Previous studies have also shown that many siderophile elements exist in different valence states in silicate melts at different  $fO_2$ . The outcome of geochemical core formation models therefore relies in part on the assumed valence state(s) of the siderophile elements considered.

The siderophile behavior of Si is a strong function of  $fO_2$ . Some planetary cores that accreted under reducing conditions are therefore believed to contain significant amounts of Si (e.g., the Earth, Mercury) [5-7]. The effects of metallic Si on siderophile element activities are not well constrained. To address these issues, we performed high  $P$ - $T$  experiments in which metal and silicate mixtures were equilibrated at low  $fO_2$ . Related work from our group is shown in several companion abstracts [8-11].

**Approach:** Experiments were conducted in a piston cylinder press at 1-2.5 GPa and 1883 K. Synthetic equivalents of Apollo 15C green glass and Knippa basalt were loaded in Pt-C capsules and were equilibrated with Fe metal plus trace elements. EMPA and LA-ICP-MS were used to quantify major and trace elements, respectively. The  $fO_2$  is defined relative to the iron-wüstite buffer ( $\Delta IW$ ) (1):

$$\Delta IW = 2 \log \left( \frac{a_{\text{FeO}}^{\text{silicate}}}{a_{\text{Fe}}^{\text{metal}}} \right) = 2 \log \left( \frac{x_{\text{FeO}}^{\text{silicate}}}{x_{\text{Fe}}^{\text{metal}}} \right) + 2 \log \frac{\gamma_{\text{FeO}}^{\text{silicate}}}{\gamma_{\text{Fe}}^{\text{metal}}} \quad (1)$$

The activity of Fe ( $\gamma_{\text{Fe}}$ ) was calculated using [12] and we assumed  $\gamma_{\text{FeO}} = 1$ . Effects of Si were studied by considering  $K_D$  or  $\ln(D_i/D_{\text{Fe}}^{n/2})$ , where  $n$  is the valence of element  $i$  [see 11]. The slope of  $K_D$  with  $\ln(1-X_{\text{Si}})$  yields the interaction coefficient or  $\epsilon_i^{\text{Si}}$  for element  $i$  with Si. For elements with a valence different than 2+, corrections on  $\gamma_{\text{Fe}}$  were made [see 11].

**Results:** Run products consist of metallic blobs within homogeneous quenched silicate melts (Fig. 1).

**Oxygen fugacity:** Metallic Si varied between 0-6 wt%, resulting in a  $fO_2$  range of  $\Delta IW = -1$  to  $-5$ . Fig. 2 shows the effect of  $fO_2$ , where the slope corresponds to

$1/4^{\text{th}}$  of the dominant valence. Our results suggest  $\text{Cu}^{1+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ge}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Mo}^{4+}$ ,  $\text{P}^{5+}$ , and  $\text{W}^{6+}$  are the dominant species across the  $fO_2$  range studied. From  $<\Delta IW -3$ , the slopes for some elements change due to the effects of interacting with metallic Si (Fig. 2 bottom panel).

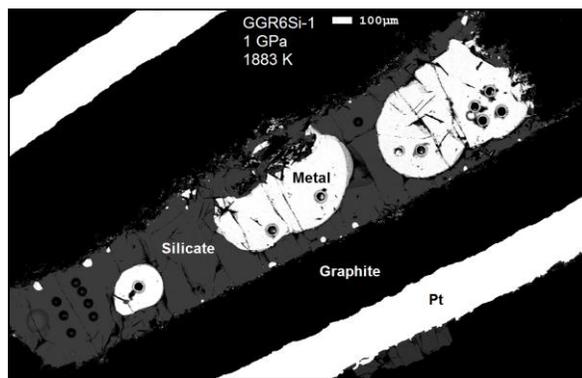


Fig. 1: BSE image of GGR6Si-1. Pits are from LA-ICP-MS.

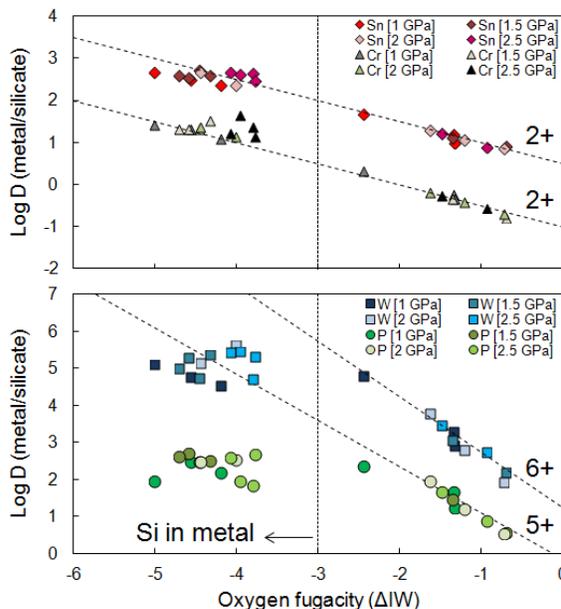


Fig. 2:  $\text{Log } D$  versus  $fO_2$  and derived valences. Vertical line indicates where Si is partitioned into metal.

**Si in metal:** The slopes of Mn and Cu with  $\ln(1-X_{\text{Si}})$  are negative and they behave more siderophile with increasing  $X_{\text{Si}}$ . The slopes are ambiguous for Cr and V and future work should try to constrain this in more detail. The siderophile behavior of most elements (P, Mo, Ni, Ge, Sn, W) is significantly decreased with  $X_{\text{Si}}$ ,

resulting in a positive slope (Fig. 3). This effect is most significant for P, Mo and W. The magnitude of the effect of  $X_{Si}$  on their  $K_D$ 's is consistent with previous work derived at the same pressures [14,15]. It is also clear from the plots that the slopes of  $K_D$  versus  $\ln(1-X_{Si})$  change with pressure for some elements. These pressure changes and their implications are discussed in more detail in [11].  $K_D(Si)$  increases significantly with pressure, which is evident from both C-free and MgO capsule experiments using near identical compositions [9]. This dependency is consistent with previous work [12,15], but not with [13,16].

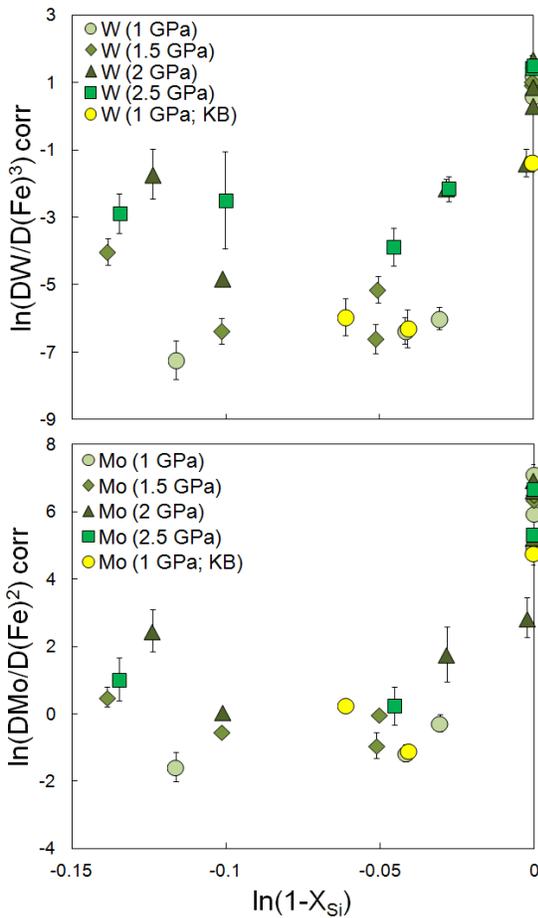


Fig. 3: Corrected  $\ln(D/D_{Fe}^{n/2})$  versus Si in metal.

**Discussion:** We use our new results [this study and 9] to provide constraints on the Si content of Mercury's core. Metal-silicate partitioning data of Si of this study and [9] was parameterized to Eq. (2):

$$\log D = a + b*(\Delta IW) + c*(P/T) + d*\ln(1-X_C) \quad (2)$$

where  $D$  is the metal-silicate partition coefficient,  $P$  is pressure,  $T$  is temperature and  $X_C$  is the molar fraction of carbon in the metal. All data were obtained at 1883 K, and we assume that  $T$  does not greatly affect  $D(Si)$  within the range relevant for Mercury [7]. As the sili-

cate compositions used in this study are similar, we do not include a silicate compositional term. We also do not take the activity of Si into account explicitly [11]. Using Eqn. (2), we modeled the Si content of Mercury's core and mantle for different bulk compositions [18,19]. Fig. 4 shows the results for a core-mantle equilibration pressure of 5.5 GPa [19] and a core mass of 65 mass% [17], as a function of  $fO_2$  during core formation. Assuming the 25 wt% Si content of the mantle of Mercury is an upper limit, we find that the core abundance of Si must be >12 wt%. This lower limit is obtained using an EH bulk composition, whereas consideration of a chondritic CB or a non-chondritic CB bulk composition would result in >21 wt% Si and >31 wt% Si in Mercury's core. All together, this corresponds with an upper  $fO_2$  limit of  $\Delta IW = -3.9$  at which the core of Mercury must have formed (Fig. 4). At  $fO_2 < \Delta IW - 5$  the Si contents of Mercury's mantle become unrealistically low [19] and that of the core unrealistically high given Mercury's moment of inertia [20].

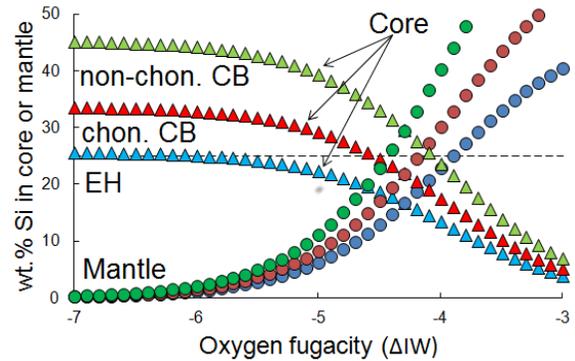


Fig. 4: Calculated wt% Si in Mercury's mantle and core versus  $fO_2$  for EH (blue) and CB (red and green) bulk compositions. Horizontal line is the estimated Si content of 25 wt%.

**References:** [1] Righter & Drake (1996) *Icarus* 124, 513 [2] Rai & van Westrenen (2014) *EPSL* 388, 343 [3] Steenstra et al (2016) *EPSL* 441, 1 [4] Wood et al. (2014) *GCA* 145, 248 [5] Fitoussi et al (2009) *EPSL* 287, 77 [6] Chabot et al (2014) 390, 199 [7] Knibbe & van Westrenen (2017) *LPSC (this meeting)* [8] Crockett et al (2017) *LPSC (this meeting)* [9] Seegers et al (2017) *LPSC (this meeting)* [10] Agmon et al (2017) *LPSC (this meeting)* [11] Steenstra et al (2017) *LPSC (this meeting)* [12] Wade & Wood (2005) *EPSL* 236, 78 [13] Tuff et al (2011) *GCA* 75, 673 [14] Righter et al (2016) *LPSC #2116* [15] Ricolleau et al (2011) *EPSL* 310, 409 [16] Corgne et al (2008) *GCA* 72, 574 [17] Hauck et al (2013) *JRG* 118, 1204 [18] Brown & Elkins-Tanton (2009) *EPSL* 286, 446 [19] Namur et al (2016) *EPSL* 448, 102 [20] Knibbe & van Westrenen (2015) *JGR* 120, 1904