Activity coefficients of siderophile elements in Fe-Si liquids at high pressure

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Supplementary Information

The Supplementary Information includes:

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1) Experimental and Analytical Techniques

Starting materials were a mixture of natural Knippa basalt (Lewis et al., 1993) (70% by mass), Fe metal (25% by mass), and Au metal (5% by mass); this is the same mixture as those used in previous studies at 1 GPa (Righter et al., 2018). Gold has a very low solubility in silicate melts and if natural (ppm) levels in the metal were used, it would be undetectable in the silicate melt. Therefore, Au was added to these higher levels to make its concentrations higher and detectable in the silicate melts. We know from our previous studies that addition of ~5% Au makes the solubility levels high enough to be measured in the quenched silicate melts of the run products (e.g., Righter et al., 2015, 2018).
Finally, silicon metal was added to the silicate and metal mixtures at increments of 2 wt% (2, 4, 6, 8, and 10% by weight), to ensure a wide range of Si alloyed in the final quenched metallic liquids.

Experiments were carried out using the 880-ton multi-anvil press in the Experimental Petrology Laboratory, in the Astromaterials Research and Exploration Science Division at NASA Johnson Space Center. To attain PT conditions of 10 GPa and 2373 K, we utilised a 10/5 assembly (available through COMPRES; Leinenweber et al., 2012) in a Walker-module (Walker et al., 1990). Pressure was calibrated for this assembly using three different transitions between 9 and 20 GPa: SiO$_2$ transitions at 9.4 GPa and 1873 K), the transition in (Mg$_{82}$Fe$_{18}$)$_2$SiO$_4$ from olivine to wadsleyite at 13.4 GPa and 1673 K, and the transition in Mg$_2$SiO$_4$ from wadsleyite to ringwoodite at 20.0 GPa and 1873 K. The assembly utilises a pre-cast ceramic octahedral pressure medium, Re foil furnaces, pyrophyllite gaskets, and temperature is monitored with type C Re/W thermocouples (Righter et al., 2008). Uncertainty in temperature and pressure are ±15-20 K and ±0.5 GPa, respectively, based on temperature gradients no larger than 25 K; the emf of the thermocouple has not been pressure-corrected. Single crystal MgO capsules contained the metal and silicate mixtures, and once loaded into the assembly, were pressurised before heating to the run temperature. Thermocouple failure in some cases led to the need to heat by power curve which was established using the correlation between power and temperature from previous experiments. Experimental run durations at the desired temperature were between 1 and 5 min, required to approach equilibrium; shutting off power to the experiments ensured a rapid temperature drop and quenching of the run products.

Metals and quenched silicate glasses were analysed for major and minor elements with Electron Probe Microanalysis (EPMA) at NASA Johnson Space Center using a Cameca SX100 microprobe. Operating conditions for metals and silicates included 15 kV accelerating voltage and 30 nA sample current, and 15 kV accelerating voltage and 20 nA sample current, respectively. In addition, standardisation was done using various metal (Fe, Ni metal), glass (basalt), and mineral (diopside, rhodonite, rutile, potassium feldspar, apatite, olivine) standards. Some metals and glasses had coarse-grained quench texture, and thus a defocused electron beam of 20-30 μm diameter was used for analysis. In these cases, 30-50 analytical points were averaged to obtain a representative composition. Uncertainties in microprobe analyses are ~1% for Ti, Fe, Mn, Ca, and K, and 2% for Si, Al, Mg, Na, and P.

Some elements were present in quantities too low to be detectable using EMPA. Therefore, many trace elements (defined as being <100 ppm in concentration) were measured using a more sensitive analytical approach -
Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Each sample was analysed by an ElectroScientific Instruments (ESI) New Wave™ UP193FX excimer (193 nm) laser ablation system coupled to a Thermo Element XR™ Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Plasma Analytical Facility of the National High Magnetic Field Laboratory, Florida State University. Isotopes measured included $^{29}$Si, $^{31}$P, $^{51}$V, $^{53}$Cr, $^{55}$Mn, $^{57}$Fe, $^{65}$Zn, $^{71}$Ga, $^{93}$Nb, $^{111}$Cd, $^{120}$Sn, $^{182}$W, $^{197}$Au, $^{208}$Pb, following the analytical protocol of Yang et al. (2015). $^{57}$Fe and $^{29}$Si were used as internal standards for metal+sulfide and for silicates, respectively. Laser fluence was 2 GW/cm$^2$, and relevant isobaric interferences are discussed in Yang et al. (2015). Relative sensitivity factors were obtained using Hoba IVB (Walker et al., 2008), Filomena IIA (Wasson et al., 1989) and NIST SRM 1263a for siderophile elements (Humayun et al., 2007; Gaboardi and Humayun, 2009; Humayun, 2012) and NIST SRM 610 glass, USGS basaltic glasses BHVO-2G, BIR-1G, and BCR-2G for lithophile elements (Jochum et al., 2011). Spot sizes of 50 μm at 50 Hz for 10 seconds were used to measure both silicate and metal portions of the samples. The average of multiple analyses (2-5) was used to obtain the representative compositions for silicates and metals in each sample. In all samples, Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb were detectable in both metals and silicates and thus all 11 elements could be included in the investigation. The relative standard deviation (RSD) of ~5% is typical for elemental abundances in metal and silicate from each of the runs.

2) Phase Equilibria and Equilibrium

In all experiments, metallic liquid equilibrated with silicate melt, and the MgO capsule reacted with the silicate melt to form more MgO-rich liquids. The run products contain a mixture of glass and coarse-grained, skeletal-shaped, quench silicate crystals (Figure 1), because most of our liquids contain > 20% MgO, and MgO-rich silicate melts are generally difficult to quench to a glass even at high quench rates. Similarly, metallic liquids also quench to a matte of quench crystals, rather than a single phase. For analyses of our run products, metallic regions were selected from the largest metallic spheres, and closest to the silicate melt regions. Typically several large (50 μm) spots were measured on any given metallic sphere and then averaged to obtain a representative analysis. For silicate melts analyses, multiple 50 μm spots were identified and selected that were representative of the melt, and avoiding capsule MgO, small metallic blebs, or equilibrium growth oxides or silicates that might interfere with determination of a liquid composition. This approach has been discussed and reported in detail by (Righter et al., 2017).
Some studies of HSEs report the stability and existence of micronuggets of HSE-rich metal (e.g., Ertel et al., 2008; Malavergne et al., 2016), and because Au is an HSE, and we have added a small amount of Au (5%) to the metallic portion of the experiment, this effect must be considered. However, we observed no HSE or Au micronuggets in our experiments (Fig. 1). Furthermore, if any HSE particles appeared as “spikes” in the analysis of the glasses, they could be filtered out during the data reduction, as also explained by (Righter et al., 2015).

In order to promote more reduced conditions in the experiments, elemental Si was added to the metal phase. Oxygen fugacity can be calculated relative to the iron-wüstite (IW) oxygen buffer, and we used the expression \( \Delta IW = -2\log [X_{Fe}/X_{FeO}] \), or otherwise referred to as “\( \Delta IW \)”. The \( \Delta IW \) values for our experiments ranged from ~ -3.3 for low Si runs to ~ -6.4 for Si bearing runs (Table 1). \( \Delta IW \) can also be calculated using activities of Fe and FeO instead of mole fractions, and thus the equation becomes \( \Delta IW = -2\log [a_{Fe}/a_{FeO}] \). For this calculation \( a_{Fe} \) in metal was calculated using the epsilon interaction parameter model for metallic liquids (e.g., Righter et al., 2018), and \( a_{FeO} \) in silicate melt was calculated using the results of Holzheid et al. (1997). \( \Delta IW \) values calculated using activities are slightly higher than those using mole fractions, from IW-2.9 to -6.11 (Table 1). Most studies utilise the mole fraction approach, and therefore we include those in the tables and figures. However, it is important to understand the difference in these two approaches that is caused by the non-idealitity in the Fe-Si system. Activities are used in all the calculations of accretion and core-mantle equilibrium. The range of \( \Delta IW \) values typically considered relevant to Earth’s accretion and core formation is IW-4 to IW-2, and falling right in the middle of the range of relative \( fO_2 \) for these experiments. This relative \( fO_2 \) bracket also produces a wide range of Si concentrations in the metal (and thus of \( \ln (1-X_{Si}) \)) that minimises error on the epsilon value.

3) Determination of Epsilon Interaction Parameters

Concentrations of Au, P, and other siderophile elements in metal and silicate (see Supplementary Information sections 1 and 2) were used to calculate Fe-M exchange \( K_d \) according to this equation (where M is the trace element of interest):

\[
MO_{(n/2)}^{sil} + (n/2)Fe^{net} = M^{net} + (n/2)FeO^{sil}
\]

(Eq. S-1)
Equation S-1 can be expanded to,
\[ \ln K = \ln \left( \frac{a_{\text{metal}}^{\text{silicate}}}{a_{\text{MO(n/2)}}^{\text{silicate}}} \right)^{n/2} = \ln \left( \frac{X_{\text{metal}}^{\text{silicate}}}{X_{\text{FeO}}^{\text{silicate}}} \right)^{n/2} + \ln \left( \frac{X_{\text{metal}}^{\text{metal}}}{X_{\text{Fe}}^{\text{metal}}} \right)^{n/2} \]  \tag{Eq. S-2}

Then, setting \( K_d = \frac{X_{\text{metal}}^{\text{MO(n/2)}}}{X_{\text{FeO}}^{\text{MO(n/2)}}} \) and using the approach detailed by Wood et al., (2014), the ratio of oxide activity coefficients in the silicate, \( \frac{\gamma_{\text{metal}}^{\text{silicate}}}{\gamma_{\text{FeO}}^{\text{silicate}}} \), is assumed to be constant because the silicate melt compositions in this study are all similar. The metal composition, however, varies significantly in Si content and the ratio of activity coefficients in the metal, \( \frac{\gamma_{\text{metal}}^{\text{metal}}}{\gamma_{\text{Fe}}^{\text{metal}}} \), is dependent upon variation in metal composition. The above equations are re-arranged yielding:

\[ \ln K_d = \text{constant} + \frac{n}{2} \ln \gamma_{\text{Fe}}^{\text{metal}} - \ln \gamma_{M}^{\text{metal}} \]  \tag{Eq. S-3}

Equation S-3 is then combined with \( \ln \gamma_{M}^{\text{metal}} = \ln \gamma_{\text{Fe}}^{\text{metal}} + \ln \gamma_{0}^{\text{M}} + e_{M}^{\text{Si}} \ln (1-X_{\text{Si}}) \) to become:

\[ \ln K_d - (n/2 - 1) \ln \gamma_{\text{Fe}}^{\text{metal}} = \text{const} - \ln \gamma_{0}^{\text{M}} + e_{M}^{\text{Si}} \ln (1-X_{\text{Si}}) \]  \tag{Eq. S-4}

In Equation S-4, \( \gamma_{0}^{\text{M}} \) is defined as the activity coefficient of M at infinite dilution, \( \gamma_{\text{Fe}}^{\text{metal}} \) is defined as the activity coefficient of Fe in Fe metal (e.g., as in Righter et al., 2017, 2018), and \( e_{M}^{\text{Si}} \) is an interaction parameter (e.g., Lupis, 1983) that is a measure of the effect of a solute such as Si (in Fe metallic liquid) on the activity of a trace element that liquid (e.g., As, Sb, Ge, or In; Righter et al., 2017). The slope of \( \ln K_d \) versus \( \ln (1-X_{\text{Si}}) \) in Equation S-4 provides \( e_{M}^{\text{Si}} \) directly for each element at 2373 K and 10 GPa.

The interaction parameter \( e_{M}^{\text{Si}} \) can be used to calculate activity coefficients (\( \gamma \)) for a trace metal (i) in a multi-component (N) system according to:

\[ \ln \gamma_i = \ln \gamma_{Fe} + \ln \gamma_{0}^{i} - \sum_{j=1,j\neq i}^{N} e_{j}^{i} X_{j} \left( 1 + \frac{\ln (1-X_{j})}{X_{j}} - \frac{1}{1-X} \right) \]

\[ + \sum_{j=1,j\neq i}^{N} e_{j}^{i} X_{j}^2 \left( \frac{1}{1-X_{i}} + \frac{1}{1-X_{j}} + \frac{X_{j}}{2(1-X_{i})^2 - 1} \right) \]
Where $X_i$, $X_j$ and $\gamma_i$, $\gamma_j$ are mole fractions and activity coefficients of components i and j, respectively, and $\gamma_i^0$ is the activity of i in Fe at infinite dilution (from Ma, 2001; Righter et al., 2017). We calculated interaction parameter $\varepsilon_{Si}^{M}$ for Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb, by using a linear fit to the data, with the standard error (1 sigma) and the fits passing variance tests in SigmaPlot 12.0.

4) Stability of Phosphides in Early Earth Mantle

Phosphorus can be stable in phosphates and phosphides, with the latter being more soluble than the former. Some have argued that phosphates are stable to secondary alteration processes in the crust, thus locking up P and requiring an extraterrestrial late accreted source (Pasek, 2008). However, P prefers more soluble phosphides at early terrestrial mantle oxygen fugacities of IW-2, based on the equilibrium:

$$2P + 3CaSiO_3 + 5/2O_2 = Ca_3(PO_4)_2 + 3SiO_2$$  \hspace{1cm} (Eq. S-5)

and thermodynamic data from Robie et al. (1978) (Fig. S-3). Phosphides may thus facilitate transfer of P to the crust by secondary alteration processes in the early Earth.
Supplementary Figures

Figure S-1 BSE images of Experiments 2, 3, 5, 6, and 7. For each experiment, images show the bright white metallic liquid, and lighter gray silicate melts which mostly quenched to a matte of quench crystals. All experiments were carried out in MgO capsules, which reacted slightly with the silicate melt. All scale bars are 200 μm.
Figure S-2  ln K_d versus ln (1-Xsi) for all elements measured in this study. lnK_d(Fe-X^{5+})–1.5ln(\gamma_{Fe}), ln K_d(Fe-X^{4+})–ln(\gamma_{Fe}), ln K_d(Fe-X^{3+})–0.5ln(\gamma_{Fe}), ln K_d(Fe-X^{2+}), and ln K_d(Fe-X^{1+})+0.5ln(\gamma_{Fe}) versus ln(1-X_{Si}) from experiments across a wide range of Si contents in metallic Fe. The slope of the lines yields the interaction parameter for each – \epsilon_{X} – in Fe-Si liquids.
Figure S-3 Oxygen fugacity relative to the iron-wüstite buffer (IW) calculated from thermodynamic data from Robie et al. (1978) for equilibrium (Eq. S-5). IW reference buffer is calculated using the expression of Campbell et al. (2009). Note that phosphide is stable at high temperatures and fO₂ of the early Earth. Calculations assume $a\text{SiO}_2 = a\text{CaSiO}_3 = a\text{Ca}_3(\text{PO}_4)_2 = 1$, and $aP = 0.01$. 
Supplementary Information References


