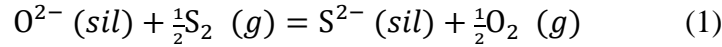


Supplementary Information: Parameterizing the metal-silicate partitioning of sulfur

Theoretical basis

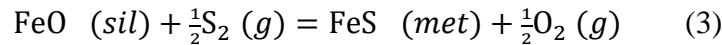
The solution of sulfur into silicate melt under reducing conditions can be described by the following reaction:



Assuming that oxygen is by far the dominant anion in silicate melt, (1) can be represented by a pseudo equilibrium constant termed the sulfide capacity (e.g., Mavrogenes & O'Neill, 1999):

$$C_S = X_S^{\text{sil}} \left(\frac{f_{\text{O}_2}}{f_{\text{S}_2}} \right)^{\frac{1}{2}} \quad (2)$$

where X_S^{sil} denotes the mole fraction of S in silicate melt and f_{O_2} , f_{S_2} are the oxygen and sulfur fugacity respectively. The equilibrium between silicate and a sulfur-bearing metallic melt can be described by the following heterogeneous reaction:



Taking the equilibrium constant (K) of (3) and given $\Delta G^0 = -RT \ln K$, where R is the universal gas constant and T is temperature, we get the relationship:

$$\frac{-\Delta G^0}{2.303RT} = \log a_{\text{FeS}}^{\text{met}} - \log a_{\text{FeO}}^{\text{met}} + \log \left(\frac{f_{\text{O}_2}}{f_{\text{S}_2}} \right)^{\frac{1}{2}} \quad (4)$$

Substituting (2) into (4) yields:

$$\frac{-\Delta G^0}{2.303RT} = \log a_{\text{FeS}}^{\text{met}} - \log a_{\text{FeO}}^{\text{met}} + \log C_S - \log X_S^{\text{sil}} \quad (5)$$

The activity of FeS in the metal phase is related to the mole fraction via $a_i = \gamma_i X_i$. Use of this relationship and a conversion factor relating $X_{\text{FeS}}^{\text{met}}$ to X_S^{met} allows $a_{\text{FeS}}^{\text{met}}$ to be recast in terms of the mole fraction of S in the metal phase:

$$\frac{-\Delta G^0}{2.303RT} = \log X_S^{\text{met}} - \log a_{\text{FeO}}^{\text{met}} + \log C_S - \log X_S^{\text{sil}} + \log \gamma_S^{\text{met}} + \log B \quad (6)$$

where the $\log B$ term includes both the conversion factor and activity coefficient terms. Rearranging in terms of the partition coefficient, expanding the ΔG^0 term, and replacing the entropy, enthalpy, and molar volume terms with fitting parameters in the usual fashion (e.g., Righter et al., 1997), we arrive at:

$$\log \left(\frac{X_S^{\text{met}}}{X_S^{\text{sil}}} \right) = a + \frac{b}{T} + \frac{cP}{T} + \log a_{\text{FeO}}^{\text{met}} - \log C_S - \log \gamma_S^{\text{met}} \quad (7)$$

note that in (7) the B term is collected into the constant a . For fitting experimental data, the γ_S^{met} and C_S terms can be replaced with fitting parameters based on the composition of the metal and silicate phases respectively. Further detail on which compositional terms were included in our regression are given below.

Choice of experimental data

The existing metal-silicate partitioning database for S covers a wide range of P , T , fO_2 and compositional space. In particular, the range of metal compositions is highly variable. Furthermore, some previous studies have included results that lie on both sides of the Fe-FeS eutectic (e.g., Boujibar et al., 2014). There is evidence that melts on the sulfur-rich side of this eutectic have behavior that is distinct from that on the Fe-rich side (e.g., Laurenz et al., 2016) and thus perhaps should not be considered suitable for regression together. For the present study we have selected only those experiments which lie to the Fe-rich side of the eutectic, i.e., where our newly derived trace element partitioning relationship is applicable. We compiled data from the following studies for inclusion in the regression: Kilburn & Wood, 1997; Jana & Walker, 1997; Chabot & Agee, 2003; Li & Agee, 2001; Asahara et al., 2004; Malavergne et al., 2007; Corgne et al., 2008; Berthet et al., 2009; Rose-Weston et al., 2009; Boujibar et al., 2014. A noteworthy omission from this database are the diamond anvil cell (DAC) experiments of Sauer et al. (2017), performed at 46-91 GPa. These authors found a significantly smaller pressure effect than is suggested by the lower pressure data. It is not immediately apparent how best to reconcile this data with that from 1 atm and large-volume press experiments, and doing so is beyond the scope of the present work. Instead, we have chosen to focus on the better constrained results from lower pressures but caution that extrapolation beyond ~25 GPa should be approached with these DAC experiments in mind.

The effects of metal composition were incorporated into the regression with terms of the following form:

$$\ln \gamma_S^{met} = \sum_i^n W_i \frac{T^0}{T} \ln(1 - X_i^{met}) \quad (8)$$

Where W_i is a fitting parameter specific to each of the elements i through n . Only elements that have a significant effect on the quality of the regression at the 95% confidence level (i.e., p -values <0.05) were included in the parameterization. The reference temperature (T^0) is set to 2073 K. No statistically significant difference was found when regressing the dataset with individual fitting coefficients for each light element in the metal versus combining the light element component (excluding S) into a single term (designated by the subscript LE in equation 9). A significant improvement was found, however, by including a distinct term for S (p -value = 0.0001); suggesting a strong self-interaction is present. This is consistent with values for the self-interaction parameter for S tabulated in the Steelmaking Data Sourcebook ($\epsilon_S^S = -5.66$ at 1873 K).

The a_{FeO} term in (7) was replaced with X_{FeO} and a fitting coefficient, e , which incorporates the activity coefficient for FeO in the silicate melt, and to some degree serves to incorporate melt composition effects arising from C_S . Although a significant dependence on silicate melt composition is expected on the basis of C_S appearing in (7), the inclusion of additional silicate melt compositional terms was not found to increase the quality of the regression at the 95% confidence level, nor have any significant effect on the values found for a , b , c and W . Similarly, and surprisingly, the b term was not found to be significant at the 95% confidence level. Regression of the experimental data from individual studies suggests that b is positive (with the exception of the study by Jana & Walker, 1997, which yields a negative value for b). It is thus likely that interlaboratory offsets play a role in masking the true effects of temperature when regressing the entire dataset. This yields the following expression for the metal-silicate partitioning of S:

$$\log D_S^{met/sil} = 2.08 \pm 0.15 + \frac{193.5 \pm 17.1P \text{ (GPa)}}{T \text{ (K)}} + 0.86 \pm 0.07 \log X_{FeO}^{met} + 5.29 \pm 0.76 \frac{T^0}{T} \log(1 - X_{LE}^{met}) - 3.93 \pm 0.99 \frac{T^0}{T} \log(1 - X_S^{met}) \quad (9)$$

Experimentally measured values of $D_S^{met/sil}$ versus those predicted by (9) are displayed in Fig. S1 and reveal that this expression is satisfactory in reproducing the measured partition coefficients ($R^2 = 0.94$). This fit is comparable in quality to that found by Boujibar et al., (2014) ($R^2 = 0.93$), despite employing only 5 fit parameters, rather than 10. This result would suggest that separating sulfide-silicate from metal-silicate partitioning results for regression is warranted.

Despite the adequate fit to the data provided by (9), we expect that future work will improve significantly upon this result, particularly with regard to the effects of temperature, and also pressure above ~25 GPa. We also note that the main points of this manuscript are not materially affected by employing the either the Rose-Weston et al. (2009) or Boujibar et al. (2014) parameterizations for S partitioning, rather than that presented in this supplement, both of which contain a temperature term (b).

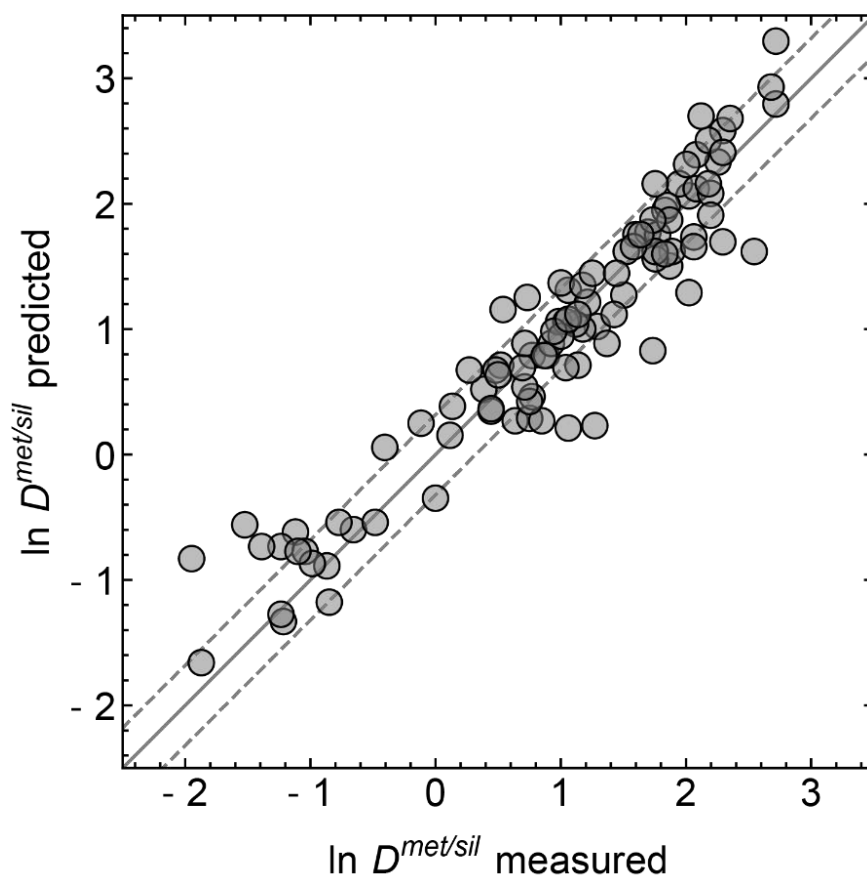


Fig S1: Experimentally determined values for the metal-silicate partitioning of sulfur versus those predicted using equation 9 of this supplementary text. Dashed and solid lines indicate the 1 sigma errors and 1:1 line respectively.

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