NEW EXPERIMENTS AND MODELING OF SILICON PARTITIONING BETWEEN IRON-RICH METAL AND SILICATE MELT.

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Introduction: Understanding the partitioning of light elements (e.g., Si, C, H, etc.) between silicate melts and iron metal alloys as a function of pressure and temperature is critical in defining the compositional evolution of planetary interiors. Here we present new experimental data, as well as modeling of a comprehensive and internally consistent data set culled from the literature for the partitioning of silicon between iron-rich metal alloy and silicate melt, according to reaction (1):

$$Si(metal) + 2FeO(melt) = SiO_2(melt) + 2Fe(metal)$$

While there are a significant number of experimental studies in the literature [e.g., 1, 2, 3, and references therein] that examine the various influences of oxygen fugacity (fO_2), temperature (*T*), pressure (*P*), and composition (X_i) on silicon metal/melt partitioning, it is difficult to disentangle the effects of each variable due to the nominally independent parameters (e.g., pressure and temperature) being correlated (Fig 1). An important example of this difficulty is that previous studies [1] have concluded that there is not a statistically discernable effect of melt composition on silicon metal/melt partitioning. This statistical observation could be due to experimental and petrologic constraints that result in covariance between *P*, *T*, and fO_2, making it difficult for any single study to cover a broad enough range of conditions to unveil the dependencies hiding in the covariance. Cross-study comparisons are also complicated by the various methods used in the literature to estimate fO_2, making an internally consistent data set necessary for assessing and successfully modeling the data.

Modeling and Experimental approach: In an effort to achieve a robust model for silicon partitioning between metal and silicate melt, we compiled data from 52 literature studies conducted at $fO_2 \leq$ IW that reported compositions of both the silicate melt and Si-bearing metal phase. The data were filtered to remove low quality points and compositional outliers. The resulting data set contains 271 points, and ranges from 1100-5152°C and 0-75 GPa (Fig 1). fO_2's were re-calculated for all experiments based on Fe-FeO equilibrium, where the activities of FeO were calculated using the parameterization of [4], and activities of Fe followed the method of [5]. Equilibrium partition coefficients for reaction (1) were calculated for the new experiments and the literature data assuming ideal behavior and the equation:

$$K = \frac{X_{SiO2}^{melt} \cdot X_{Fe}^{mtl^{\wedge}2}}{X_{FeO}^{melt^{\wedge}2} \cdot X_{Si}^{mtl}} \qquad (2)$$

where X_i^j represents the mole fraction of component i in phase j. In an attempt to minimize the inherent covariance in chemical composition due to the closure problem (i.e., all components must add up to 100%), the optical basicity [6] of the silicate melts was calcuated to test for compositional dependence.

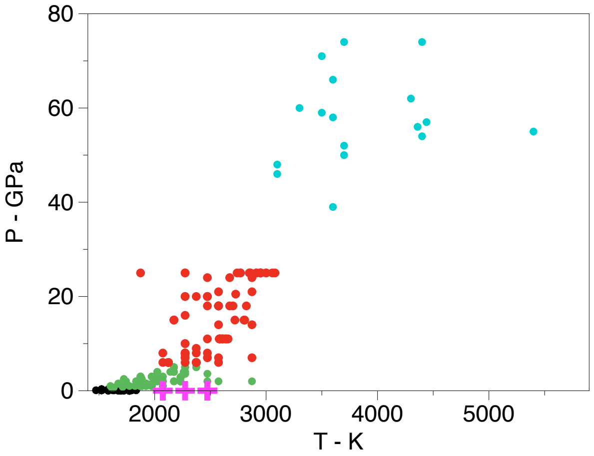

Figure 1. Pressure vs. Temperature plot of literature data used in partitioning model, color coded by pressure range (black: 0.0001-0.01 GPa; ; green: 0.01-5 GPa; red: 5-25 GPa; blue: 25-75 GPa. Note new 1 bar laser levitation data is shown as pink crosses on X-axis.

Early assessment of the dataset led to the realization that low *P*-high *T* experiments would be extremely useful in addressing experimental covariance issues (Fig 1). Therefore, a series of 1 bar, high temperature (1800°-2200°C) aerodynamic levitation laser-heating experiments (pink crosses in Fig 1) on a powdered mixture of pure enstatite, fayalite, silicon, and iron metal (En_{65}-Fa_5-Si_3-Fe_{27})

were conducted at Indiana University-Purdue University Indianapolis. An experiment was deemed successful if the sample was levitated, laser-heated for 30-60 seconds, and quenched without interference by the gas nozzle. These successful run products were initially imaged using X-ray Computed Tomography to assess the position of the metal and silicate phases within each run product before sectioning. Once the run products were sectioned, back-scattered electron imaging (Fig 2), and the compositions of the metal and silicate material were measured using EPMA to obtain silicon metal/silicate partitioning data.

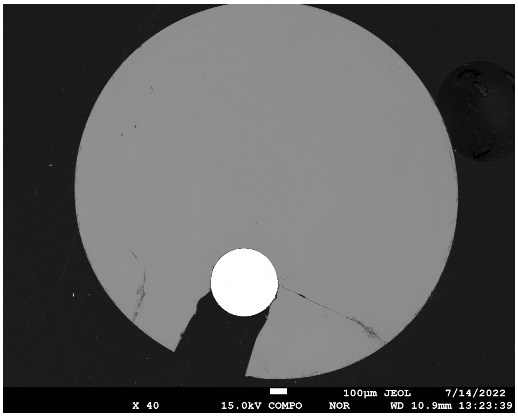

Figure 2. Back-scattered electron image of laser levitation experiment at 1 bar and 2200°C. The bright white sphere is Fe-rich metal alloy, while the homogeneous light grey is Mg-rich silicate glass.

Results: Step-wise multiple linear regression was conducted on the dataset that included the new experimental data, resulting in a model of the form :

$$\ln K = a\ln 1/T(K) + bP(GPa) + c\lambda(X_i) + d \qquad (3)$$

where T is temperature, P is pressure, λ is the optical basicity of the melt [6], and a, b, c, and d are fit parameters. The resulting model fit has an R^2 value of 0.93, and a root mean square error of 0.67. Predicted versus model values are shown in Figure 3, and the value of the fit parameters are given in Table 1.

Table 1.

Model fit parameters	***Value (s.e)***
a (1/K)	10.17 (0.42)
b (GPa)	-0.058 (0.006)
c (Xi)	25.2 (2.0)
d	75.4 (2.6)

The model was regressed both with and without the new high T laser levitation results in the dataset, with no change in the fit parameters within fit error, or in the goodness of fit, indicating the robustness of the model. The statistical significance of the pressure dependence coefficient did increase with the addition of the new low P, high T results, however. Variance impact factors (VIF) for each fit parameter were calculated to test the potential impact of collinearity between the independent variables. All VIF values were less than five, indicating that the covariance between the model parameters used in Equation 3 does not affect the parameter values or their statistical significance. Importantly, there is high collinearity between temperature and oxygen fugacity however (R=0.85), precluding any model that contains both as nominally independent variables.

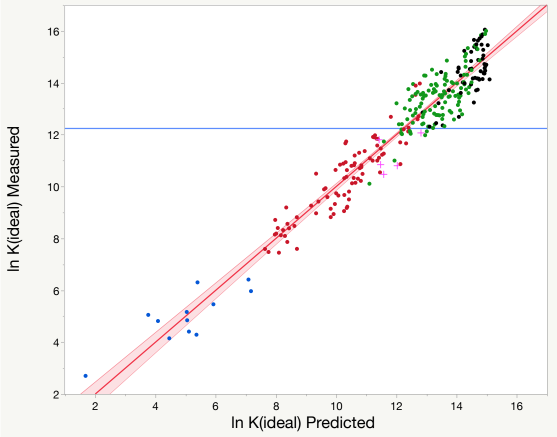

Figure 3. Measured versus predicted values for the equilibrium partitioning constant calculated using fit parameters in Table 1. Symbols color coded as in Figure 1.

Implications: The results of this experimental and modeling effort show that the partitioning of Si between a metal and silicate melt phase is indeed dependent on T, P, and the bulk X_i of the melt. This has important implications for planetary core formation in rocky planets, and places constraints on bulk core composition. More experimental work is planned to further increase the diversity of pressure-temperature and oxygen fugacity conditions and reduce the collinearity present in the overall data set.

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