EFFECT OF SILICON ON ACTIVITY COEFFICIENTS OF SIDEROPHILE ELEMENTS (P, Au, Pd, As, Ge, Sb, AND In) IN LIQUID Fe, WITH APPLICATION TO CORE FORMATION. K. Righter[1], K. Pando[2], L.R. Danielson[3], M. Humayun[4], M. Righter[5], T. Lapen[5], and A. Boujibar[1], [1]NASA JSC, Mailcode XI2, 2101 NASA Pkwy, Houston, TX 77058. [2]UTC– Jacobs JETS Contract, NASA JSC, Houston, TX 77058, [3]Jacobs, NASA JSC, Houston, TX 77058, [4]National High Magnetic Field Laboratory, Florida State Univ., Tallahassee, FL 32306. [5] University of Houston, Dept. of Earth and Atmospheric Sciences, Houston, TX 77002.

Introduction: Earth's core contains ~10% light elements that are likely a combination of S, C, Si, and O, with Si possibly being the most abundant [1]. Si dissolved into Fe liquids can have a large effect on the magnitude of the activity coefficient of siderophile elements (SE) in Fe liquids, and thus the partitioning behavior of those elements between core and mantle. The effect of Si can be small such as for Ni and Co [2], or large such as for Mo, Ge, Sb, As [3]. The effect of Si on many siderophile elements is unknown yet could be an important, and as yet unquantified, influence on the core-mantle partitioning of SE. Here we report new experiments designed to quantify the effect of Si on the partitioning of P, Au, Pd, and many other SE between metal and silicate melt. The results will be applied to Earth, for which we have excellent constraints on the mantle siderophile element concentrations.

Experimental: Experiments were carried out using a piston cylinder apparatus and run conditions of 1 GPa and 1600 °C. The starting materials comprised basaltic silicate (70% by mass) mixed with metallic Fe + 5% Au (series 1), or + 5% Pd (series 2), or + 2% Ge, As, In, and Sb (series 3) (30% by mass). Silicon metal was also added to the metallic mixture at 2, 4, 6, and 10 %, to alloy with the Fe liquid and create a variable amount of Si alloyed with Fe in each series. The MgO capsule reacts with the silicate melt to form more MgO-rich liquids that have 22-26 wt% MgO.

Analytical: Experimental metals and silicates were analyzed using a combination of electron microprobe analysis (EMPA) at NASA-JSC, and laser ablation ICP-MS at both University of Houston and Florida State University. EMPA analysis (using both Cameca SX100 and JEOL 8530 FEG microprobes) was used for major and minor elements and utilized a variety of mineral and glass standards with 15 kV and 20 nA conditions. Trace elements (typically those < 100 ppm) were measured with LA-ICP-MS using glass and metal standards and either spot or line analyses depending on the size of the metal or silicate regions of interest.

Results: Measured P, Au, Pd, and other siderophile elements were used to calculate metal (met) - silicate (sil) exchange Kd according to this equation:

(1) $MO_{n/2}{}^{sil} + (n/2)Fe^{met} = M^{met} + (n/2)FeO^{sil}$

Expanding equation (1) and following a similar approach to [4],

$$\ln K = \ln \frac{[a_M^{metal}][a_{FeO}^{silicate}]^{n/2}}{[a_{MO(n/2)}^{silicate}][a_{Fe}^{metal}]^{n/2}} =$$

$$\ln \frac{[X_M^{metal}][X_{FeO}^{silicate}]^{n/2}}{[X_{MO(n/2)}^{silicate}][X_{Fe}^{metal}]^{n/2}} + \ln \frac{[\gamma_M^{metal}][\gamma_{FeO}^{silicate}]^{n/2}}{[\gamma_{MO(n/2)}^{silicate}][\gamma_{Fe}^{metal}]^{n/2}} .$$

We set $K_D = \dfrac{[X_M^{metal}][X_{FeO}^{silicate}]^{n/2}}{[X_{MO(n/2)}^{silicate}][X_{Fe}^{metal}]^{n/2}}$ and assume the ratio

of oxide activity coefficients in the silicate is fixed, since the silicate melt compositions are nearly constant in this study. On the other hand, the metal composition varies significantly in Si content and the ratio of activity coefficients in the metal, $[\gamma_M^{metal}]/[\gamma_{Fe}^{metal}]^{n/2}$, is dependent upon variation in metal composition. The above equations can be re-arranged to yield:

$\ln K_D = $ constant $+ n/2 \ln \gamma_{Fe}^{metal} - \ln \gamma_M^{metal}$. Combination with $\ln \gamma_M^{metal} = \ln \gamma_{Fe}^{metal} + \ln \gamma_M^0 - \varepsilon_M^{Si} \ln(1-X_{Si})$ yields $\ln K_D - (n/2-1)\ln \gamma_{Fe}^{metal} = $ const $- \ln \gamma_M^0 + \varepsilon_M^{Si} \ln(1-X_{Si})$. Here ε_M^{Si} is an interaction parameter [5,6,7] that can be used to isolate the effect of a solute such as Si (in Fe metallic liquid) on the activity of a trace element such as As, Sb, Ge, and In. The slope of $\ln K_D$ versus $\ln(1-X_{Si})$ gives ε_M^{Si} directly for each element at 1600 °C.

We have determined ε_M^{Si} for a large number of siderophile elements, and here present the results for P, As, Sb, Ge, and In. Phosphorus data combined from two series of experiments all at 1600 C and in MgO capsules yield an epsilon interaction parameter of near 66 (Fig. 1). In, Ge, As, and Sb all have positive epsilon values, indicating that dissolved Si causes a decrease in the partition coefficients; values are 15.0, 18.5, 35.9 and 60.9, respectively, at 1 GPa and 1600 °C (Fig. 2). As an example of how large the effect of Si can be, these epsilon values correspond to activity coefficients (γ) for As of ~0.01 when $X_{Si} = 0$, and up to $\gamma = >2$ when $X_{Si} = 0.2$ (Fig. 3). ε_M^{Si} will also be presented for Au, Pd, Cd, Sn, Ga, Zn, Cu, Ag and W.

Application to Earth: The activity model of [6] and [7] was coded and expanded to include the newly acquired epsilon interaction parameters for P, As, Sb, Ge, and In obtained here, as well as previously determined [4,8] epsilon parameters for S and C for these elements. This updated model allows us calculate activity of Ge, In, As, and Sb in Fe-Ni-Si-S-C-O metallic liquids. We then apply this model to Earth (with a likely Si-rich

core), and examine the resulting mantle concentrations of these elements during accretion.
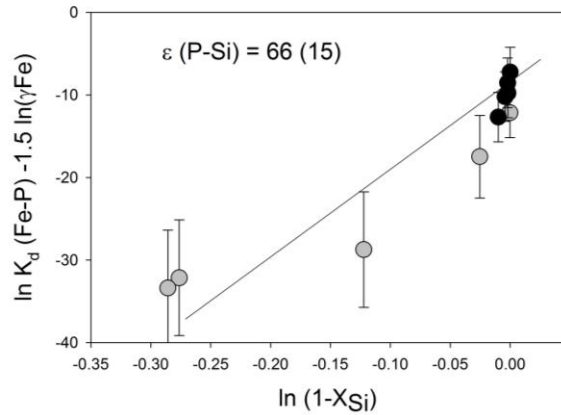

Figure 1: $lnK_d(Fe\text{-}P)–1.5ln(\gamma Fe)$ versus $ln(1\text{-}X_{Si})$ from 10 experiments (low Si series experiments = black circles and high Si series = grey circles) across a wide range of Si contents in metallic Fe.
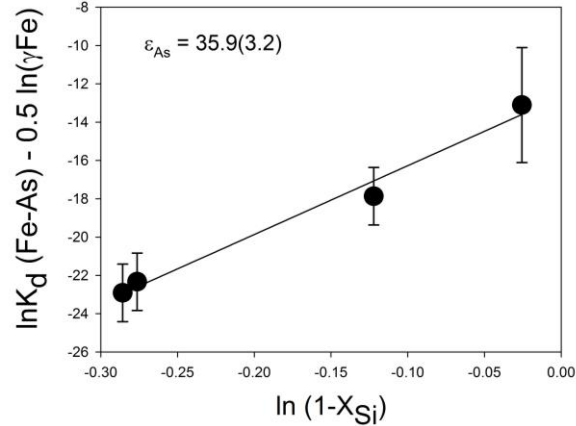

Figure 2: Effect of $lnK_d(Fe\text{-}As)\text{-}0.5ln(\gamma Fe)$ versus $ln(1\text{-}X_{Si})$ from 4 experiments across a wide range of Si contents in metallic Fe.

Two accretion models are considered for Earth – relatively constant fO_2 and increasing fO_2 - and include the evolving S, C, Si content of the core as accretion proceeds. Models with increasing fO_2 have large compositional changes in the metallic liquid which also cause orders of magnitude change in the activity coefficient of the trace SE (Fig. 3). When these activity variations are combined with pressure and temperature effects, the mantle abundances of these elements can be explained by metal-silicate equilibrium in a deep molten early Earth (35 to 50 GPa and 3400-3800 K; Fig. 4), where the core-forming metal ultimately contains significant Si, and smaller amounts of S and C. The effect of Si is important, and such models do not successfully match the mantle concentrations if the core does not contain Si. Such a scenario is consistent with moderately siderophile refractory elements Ni, Co, Mo, and W (e.g., [9]), that also suggest a core-mantle differentiation

at high pressure with Si as a dominant light element [2]. Given the flexibility of the thermodynamic models, this approach and model can also be applied to Mars (S-rich core), Moon (S-, C-, and Si-poor core), and Vesta.
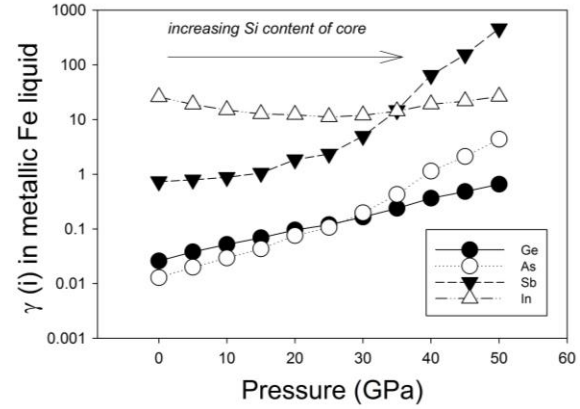

Figure 3: Variation of activity coefficients for As, Sb, Ge, and In as accretion proceeds for an fO_2 path which starts reduced (IW-4) and ends more oxidized (IW-2), and Fe metallic liquid becomes more Si-rich.
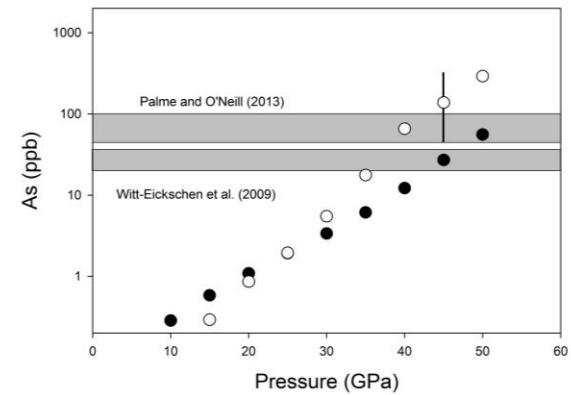

Figure 4: Variation of As in Earth's silicate mantle as accretion proceeds, for constant fO_2 (solid circles) and increasing fO_2 (open circles), compared to two primitive mantle As estimates [10].

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