EFFECT OF SILICON ON ACTIVITY COEFFICIENTS OF PLATINUM IN LIQUID Fe-Si, WITH APPLICATION TO CORE FORMATION.

K. Righter[1], K. Pando[2], L.R. Danielson[3], and M. Humayun[4], [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 32310.

Introduction: Earth's core contains ~10% of a light element that is likely a combination of S, C, Si, and O, with Si possibly being the most abundant light element [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 Pt (with Re and Ru in progress or planned) between metal and silicate melt. The results will be applied to Earth, for which we have excellent constraints on the mantle Pt 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% Pt (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 Florida State University. EMPA analysis (using Cameca SX100 microprobe) 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 depend-ing on the size of the metal or silicate regions of interest. Pt contents of the silicates ranged from 6 to 46 ppb.

Results: Measured Pt and Fe were used to calculate metal (met) - silicate (sil) exchange Kd according to this equation: $PtO^{sil} + Fe^{met} = Pt^{met} + FeO^{sil}$. Expanding and following a similar approach to [4],

$$\ln K = \ln \frac{[a_{Pt}^{metal}][a_{FeO}^{silicate}]}{[a_{PtO}^{silicate}][a_{Fe}^{metal}]} =$$

$$\ln \frac{[X_{Pt}^{metal}][X_{FeO}^{silicate}]}{[X_{PtO}^{silicate}][X_{Fe}^{metal}]} + \ln \frac{[\gamma_{Pt}^{metal}][\gamma_{FeO}^{silicate}]}{[\gamma_{PtO}^{silicate}][\gamma_{Fe}^{metal}]}$$

We set $K_d = \dfrac{[X_{Pt}^{metal}][X_{FeO}^{silicate}]}{[X_{PtO}^{silicate}][X_{Fe}^{metal}]}$ 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, $[\gamma_{Pt}^{metal}]/[\gamma_{Fe}^{metal}]$, is dependent upon variation in metal composition. The above equations can be re-arranged to yield:

$\ln K_D = \text{constant} + 2\ln \gamma_{Fe}^{metal} - \ln \gamma_{Pt}^{metal}$. Combination with $\ln \gamma_{Pt}^{metal} = \ln \gamma_{Fe}^{metal} + \ln \gamma_{Pt}^{0} - \varepsilon_{Pt}^{Si} \ln(1-X_{Si})$ yields $\ln K_d - \ln \gamma_{Fe}^{metal} = \text{const} - \ln \gamma_{Pt}^{0} + \varepsilon_{Pt}^{Si} \ln(1-X_{Si})$. Here ε_{Pt}^{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 Pt. The slope of $\ln K_d$ vs. $\ln(1-X_{Si})$ gives ε_{Pt}^{Si} directly at 1600 °C (Fig. 1).

Application to Earth: Combination of our results for Pt with previous Pt studies constraining its valence, the effect of S and C, melt composition, temperature and pressure (see compilation in [8]) allows us to examine the effect of Si and other light elements on D(Pt) metal/silicate, and examine the resulting mantle Pt concentrations during Earth accretion, following the approach of [3] and [10].
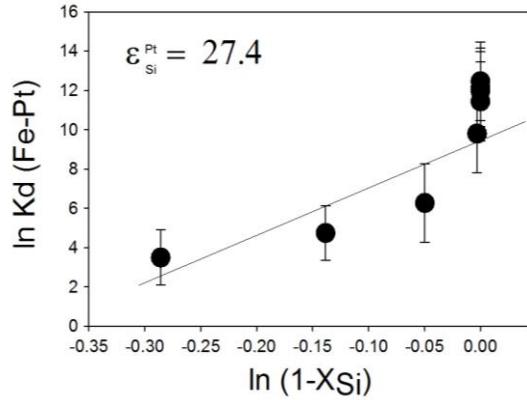
Figure 1: lnK$_d$(Fe-Pt) versus ln (1-X$_{Si}$) from our 10 experiments across a wide range of Si contents in metallic Fe. Slope indicates an epsilon value of 27.4 for Pt in FeSi alloys.

Two accretion models are considered for Earth – relatively constant fO$_2$ and variable fO$_2$ - and include the evolving S, C, Si content of the core as accretion proceeds. Both models include large compositional changes in the metallic liquid which also cause orders of magnitude change in the activity coefficient of Pt (and other elements). When these activity variations are combined with pressure and temperature effects, the mantle abundances of Pt can be calculated during accretion. Mantle Pt concentrations can be explained by metal-silicate equilibrium in a deep molten early Earth (35 to 45 GPa and 3200-3400 K; Fig. 2), where the core-forming metal ultimately contains significant Si, and smaller amounts of S and C. Such a scenario is also consistent with moderately siderophile refractory elements Ni, Co, Mo, and W (e.g., [3]). If metal-silicate equilibrium took place at higher PT conditions (50-60 GPa and 3600-4000 K), Pt contents in the mantle would exceed those measured in primitive mantle peridotite, and thus require a subsequent removal mechanism for Pt. Late sulfide stability in a magma ocean may be a viable mechanism, as has been proposed for Pd, Au and other elements [10,11], or Pt speciation may change at low fO$_2$ [12], causing an increase in the partition coefficient that lowers the calculated Pt mantle values.

Finally, we observe siderophile behavior for Ti in our experiments. At fO$_2$ lower than IW-7, Ti becomes siderophile; however, even at IW-6, with D(Ti) ~ 0.08, only ~100 ppm Ti would parti-

tion into the core thus not affecting the mantle Ti concentration significantly.

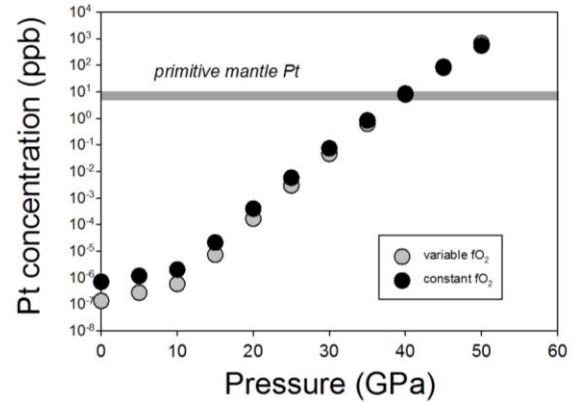*Figure 2: Variation of Pt in silicate portion of mantle as accretion proceeds, for constant fO$_2$ (solid) and increasing fO$_2$ (open), compared to primitive mantle Pt estimates. PUM Pt from [9].*

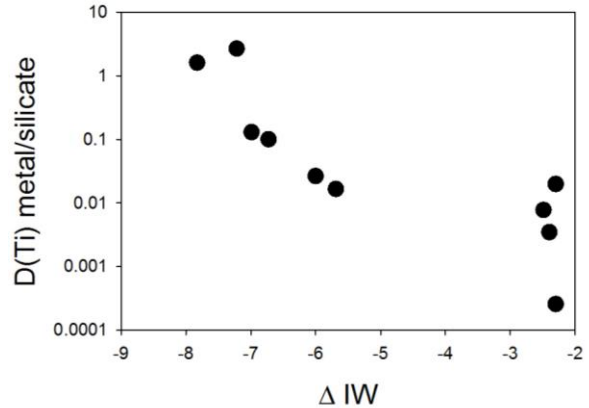*Figure 3: Variation of D(Ti) metal/silicate with fO$_2$, from our experiments with Au and Pd [10], showing Ti become siderophile below IW-6.*

References: [1] Hirose, K. et al. (2013) Ann. Rev. Earth Planet. Sci. 41, 657-691. [2] Tuff, J. et al. (2011) GCA 75, 673-690. [3] Righter, K. et al. (2017) GCA 198, 1-16. [4] Wood, B.J. et al. (2014) GCA 145, 248-267; [5] Lupis, C. (1983) Chemical Thermod. Of Materials. Elsevier, 581 pp; [6] Wade, J. and Wood, B.J. (2005) EPSL 236, 78-95. [7] Ma, Z. et al. (2001) Metallurg. Mat. Trans. B32, 87-103. [8] Yang, S. et al. (2015) MaPS 50, 691-714; [9] Becker, H. et al. (2006) GCA 70, 4528-4550; [10] Righter et al. (2016) 47th LPSC, abstr. 2116; [11] Rubie, D.C. et al. (2016) Science 353, 1141-1144; [12] Medard, E. et al. (2017) this meeting.