

EFFECT OF SILICON ON THE ACTIVITY COEFFICIENT OF RHENIUM IN FE-SI LIQUIDS: IMPLICATIONS FOR HSE AND OS ISOTOPES IN PLANETARY MANTLES. K. Righter¹, K. Pando², S. Yang³, M. Humayun³, ¹NASA-JSC, Mailcode XI2, 2101 NASA Pkwy, Houston, TX 77058. ² Jacobs JETS Contract, NASA-JSC, Houston, TX 77058, ³National High Magnetic Field Laboratory, Florida State Univ., Tallahassee, FL 32310.

Introduction: Metallic cores contain light alloying elements that can be a combination of S, C, Si, and O, all of which have important chemical and physical influences. For Earth, Si may be the most abundant light element in the core [1]. Si dissolved into Fe liquids can have a large effect on the magnitude of the activity coefficient of siderophile elements (SE), and thus the partitioning behavior of those elements between core and mantle [2,3,4]. The effect of Si on the highly siderophile elements is only beginning to be studied and the effects on Au, Pd and Pt are significant [5]. Here we report new experiments designed to quantify the effect of Si on the partitioning of Re between metal and silicate melt. A solid understanding of Re partitioning is required for a complete understanding of the Re-Os isotopic systems. The results will be applied to understanding the HSEs and Os isotopic data for planetary mantles, and especially Earth.

Experimental: Experiments were carried out using a piston cylinder apparatus and run conditions of 1 GPa and 1600 °C (Fig. 1). The starting materials comprised basaltic silicate (70% by mass) mixed with metallic Fe + 5% Re. 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. The MgO capsule reacts with the silicate melt to form more MgO-rich liquids that have 22-26 wt% MgO.

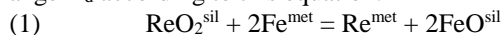


Figure 1: Reflected light photo of metal-silicate experiment Re-4B at 1600 °C and 1 GPa. Metallic sphere (bright white) contains Fe-Si-Re, and the surrounding silicate melt contains ~25 wt% MgO. Capsule material is MgO; width of field is ~ 3 mm.

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 JEOL 8530 FEG microprobe) was used for major and minor elements and utilized a variety of mineral and glass standards with 15 kV and 20 nA conditions. Rhenium and other trace siderophile 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 Re and other siderophile elements were used to calculate metal (met) - silicate (sil) exchange K_d according to this equation:



Expanding equation (1) and following a similar approach to [5], the exchange coefficient K_d can be represented as:

$$(2) \quad \ln K_d - \ln \gamma_{\text{Fe}}^{\text{metal}} = \varepsilon_{\text{Re}}^{\text{Si}} \ln(1-X_{\text{Si}}) + \text{const} - \ln \gamma_{\text{Re}}^0$$

Here γ_{Re}^0 is the activity of Re in Fe metal at infinite dilution, $\gamma_{\text{Fe}}^{\text{metal}}$ is the activity coefficient of Fe in metallic liquid, and $\varepsilon_{\text{Re}}^{\text{Si}}$ is an interaction parameter (e.g., [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 Re. The slope of $\ln K_d$ versus $\ln(1-X_{\text{Si}})$ gives $\varepsilon_{\text{Re}}^{\text{Si}}$ directly for each element.

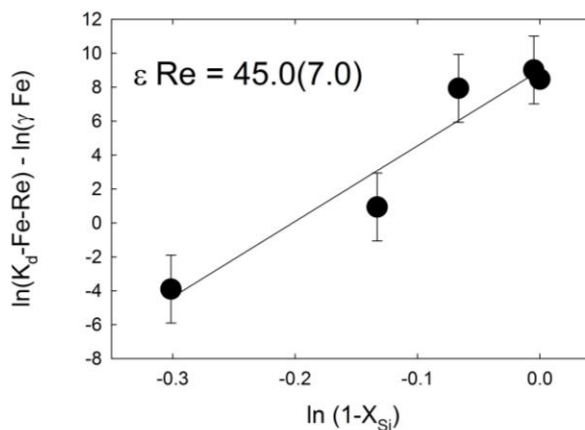


Figure 2: $\ln K_d(\text{Fe-Re}) - \ln \gamma_{\text{Fe}}$ versus $\ln(1-X_{\text{Si}})$ from 5 experiments across a wide range of Si contents in metallic Fe.

We have previously determined $\varepsilon_M^{\text{Si}}$ for a large number of siderophile elements (M) [5,6,7], and here present the results for Re which has a high value of $\varepsilon_{\text{Re}}^{\text{Si}} = 45$ at 1 GPa and 1600 °C (Fig. 2). This high value is comparable to what we've found for P, Bi, Sn,

As, and Sb [5,6,7], and much higher than some of the moderately siderophile elements such as Ni, Co, and W [2,5].

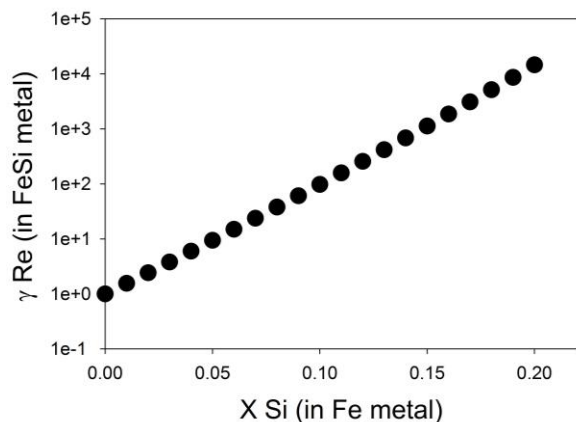


Figure 3: Variation of activity coefficient for Re in Fe-Si alloys at 1600 °C.

Activity model: The activity model presented by [5] (based on [8,9]) has been updated to include a total 34 trace siderophile elements. The newly acquired epsilon interaction parameters obtained here for Re, as well as previously determined [4,8] epsilon parameters in Fe-S and Fe-C liquids were combined into one model which allows us to calculate activities in Fe-Ni-Si-S-C metallic liquids.

As an example of how large the effect of Si can be, these epsilon values correspond to activity coefficients (γ) for Re of ~ 1 when $X_{Si} = 0$, and up to $\gamma \sim 10,000$ when $X_{Si} = 0.2$ in Fe-Si alloys at 1600 °C (Fig. 3).

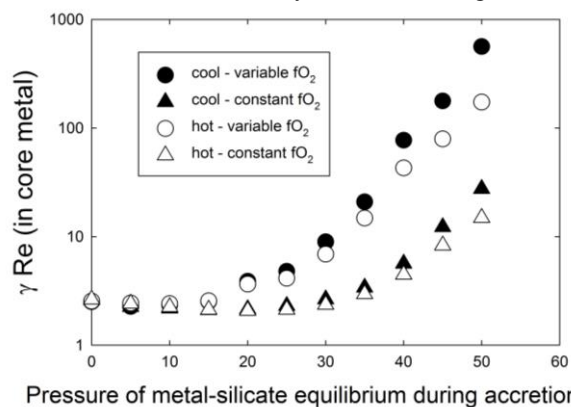


Figure 4: Variation of activity coefficient for Re as accretion proceeds (and pressure in magma ocean increases) for two different fO_2 paths – one which is constant (triangles) and one which starts reduced (IW-4) and ends more oxidized (IW-2) (circles). Cooler magma ocean gradient [12] indicated by solid symbols and hotter gradient of [13] indicated by open symbols.

Application: We apply this model to Earth (with a likely Si-rich core), and examine the variation of activity coefficient for Re in core-forming metal during accretion. 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. Models with variable 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. 4). These large activity coefficients under conditions of a deep magma ocean will lower $D(Re)$ metal/silicate by several orders of magnitude, which would result in higher Re concentrations in the early mantle.

When these activity variations are combined with pressure and temperature effects, the mantle abundances of these elements can be calculated for a deep magma ocean. For example, the combination of the temperature and pressure effects measured by [14] and the Si effects measured here may lead to mantle Re contents much closer to those measured in the primitive upper mantle (PUM). We will consider models of variable depth magma ocean to test whether: 1) Re concentration of the PUM can be explained by metal-silicate equilibrium, or 2) Re also becomes “overabundant” in the mantle requiring a removal mechanism such as segregation of a late sulfide matte [8], and 3) an additional source of Re is required, such as from a late veneer [15].

The model derived here can also be used to evaluate models for core formation in bodies of variable size and cores of variable compositions such as the reduced aubrites and acapulcoite-lodranite parent bodies, or applied to Mars (S-rich core), Moon (S-, C-, and Si-poor core), and Vesta.

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] Nickodem, K. et al. 2012. 43rd LPSC, Abstract # 2295. [4] Wood, B.J. et al. 2014. *GCA* 145, 248-267; [5] Righter, K. et al. (2017) *GCA* 198, 1-16; [6] Righter, K. et al. (2018) *GCA*, in review; [7] Righter, K. et al. (2018) this meeting. [8] Wade, J. and Wood, B.J. (2005) *EPSL* 236, 78-95. [9] Ma, Z. et al. (2001) *Metallurg. Mat. Trans. B* 32, 87-103. [10] Lupis, C. (1983) *Chemical Thermodynamics of Materials*. Elsevier, 581 pp; [11] Sourcebook, *Steelmaking Data* (1988) Japan Soc. Prom. Sci. Gordon and Breach, Tokyo. [12] Andrault, D. et al. (2011) *EPSL* 304, 251-259; [13] Fiquet, G. et al. (2010) *Science* 329, 1516-1518. [14] Mann, U. et al. (2012) *GCA* 84, 593-613; [15] Day, J.M., Brandon, A.D., & Walker, R.J. (2016) *In Rev Mineral. Geochem.* 81, 161-238.