

HIGH PRESSURE AND TEMPERATURE CORE FORMATION AS AN ALTERNATIVE TO THE “LATE VENEER” HYPOTHESIS. K. Righter¹, Pando, K.¹, Humayun, M.², and Danielson, L.¹, ¹NASA Johnson Space Center, Mailcode KT, 2101 NASA Pkwy, Houston, TX 77058 (kevin.righter-1@nasa.gov), ²Dept. of Earth, Ocean, and Atmospheric Science, and National High Magnetic Field Lab., Florida State Univ., Tallahassee, FL 32310.

Introduction: The highly siderophile elements (HSE; Re, Au and the Platinum Group Elements - Pd Pt, Rh, Ru, Ir, Os) are commonly utilized to constrain accretion processes in terrestrial differentiated bodies due to their affinity for FeNi metal [1]. These eight elements exhibit highly siderophile behavior, but nonetheless have highly diverse metal-silicate partition coefficients [2]. Therefore the near chondritic relative concentrations of HSEs in the terrestrial and lunar mantles, as well as some other bodies, are attributed to late accretion rather than core formation [1]. Evaluation of competing theories, such as high pressure metal-silicate partitioning or magma ocean hypotheses has been hindered by a lack of relevant partitioning data for this group of eight elements. In particular, systematic studies isolating the effect of one variable (e.g. temperature or melt compositions) are lacking. Here we undertake new experiments on all eight elements, using Fe metal and FeO-bearing silicate melts at fixed pressure, but variable temperatures. These experiments, as well as some additional planned experiments should allow partition coefficients to be more accurately calculated or estimated at the PT conditions and compositions at which core formation is thought to have occurred.

Methods: Experiments were conducted using a Quickpress non end-loaded piston cylinder apparatus at Johnson Space Center (JSC) with a BaCO₃ pressure medium, graphite furnaces, MgO spacers and graphite sample capsules [3]. The experiments utilized a natural basaltic melt for the silicate portion, and a mixture of Fe metal and 3 wt% each of the HSE for the metallic portion. The metal and silicate were mixed in 3:7 proportions by volume. The samples were heated to five different temperatures (1500 to 1900 °C) for between 15 and 180 minutes at 1.0 GPa, and then quenched to <100 C in 5 seconds by cutting power to the experiment. Experimental charges were analyzed by laser ablation ICP-MS at Florida State University for major elements and HSE following the approach of [4] and by electron microprobe (Cameca SX-100) at JSC for major and minor elements. Line scans were taken on glass using a 50 μm spot size scanned at 10 μm/s, and on metal using a 15 μm beam scanned at 5 μm/s. Two separate line scans were taken on different parts of the silicate glass to check for consistency.

Results: The partitioning of siderophile elements between metal and silicate melt can be examined as an exchange equilibrium such as: Fe + Au₂O = 2Au +

FeO. When such equilibria are examined for our dataset, systematic behavior is evident for Au, Pd, and Ru, but the other HSE show more dispersion suggesting that there may be disequilibrium at lower temperatures and/or there may be sub-micron-sized metal in the silicate melts. The regular behavior for Au and Pd is similar to that documented for other moderately siderophile elements such as Ni, Mo, or V [3]. The irregular behavior for Rh, Ir, Re, Pt, and Os is not unexpected, and we are pursuing additional approaches to eliminate the potential effects of sub-micron sized metal formation.

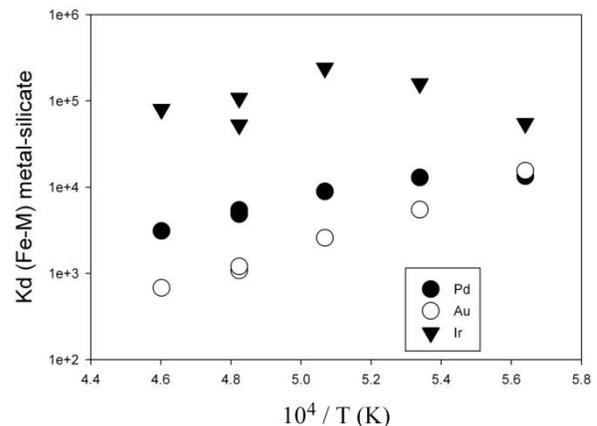


Figure 1: $K_{d_{M-Fe}}$ versus $10^4 / T(K)$ for Au, Pd and Ir, illustrating clear temperature dependence for Au and Pd, but more irregular behavior for Ir.

Discussion: Our results for Ru are the first high pressure and temperature partitioning data available for silicate melts containing FeO. A previous study [5] at higher fO₂ and lower temperatures yielded much lower Ru solubilities in silicate melt, but that study utilized FeO-free melt and was carried out at one bar, so a direct comparison is difficult. However, our results suggest $D(Ru)$ metal-silicate is reduced substantially at high pressures and temperatures with FeO-bearing melts. This is primarily due to the increase in solubility of Ru in silicate melts at these conditions.

The results for Pd and Au can be added to previous work for these two elements. Palladium was previously examined by [4] who concluded that Pd could be consistent with an equilibrium metal-silicate scenario in a magma ocean on the early Earth. Previous work on Au resulted in a similar conclusion [6], but there were limited data available for Au which hindered a

systematic look at its behavior. Combining our new results for Pd with those of previous studies (summarized in [4]) and the new results for Au with the results of [6-10], we can derive predictive equations as a function of the controlling parameters temperature, pressure, oxygen fugacity, melt composition, and metallic liquid composition. Such expressions have the form: $\ln D(\text{Au}) = a \ln f\text{O}_2 + b/T + cP/T + d \ln(1-X_s) + e \ln(1-X_c) + f(\text{NBO}/T) + g$ (where X_s and X_c are mole fraction of sulfur and carbon in metallic liquid and NBO/T is a measure of melt polymerization). For gold, there are systematic studies with temperature (this dataset and [10]), pressure [6], oxygen fugacity [11], S-bearing metals [7-9], and C-bearing metals (this study). The regression analysis indicates that $D(\text{Au})$ increases with increasing melt depolymerization, similar to other elements such as Mo, Sn, P, Mn, and V [3].

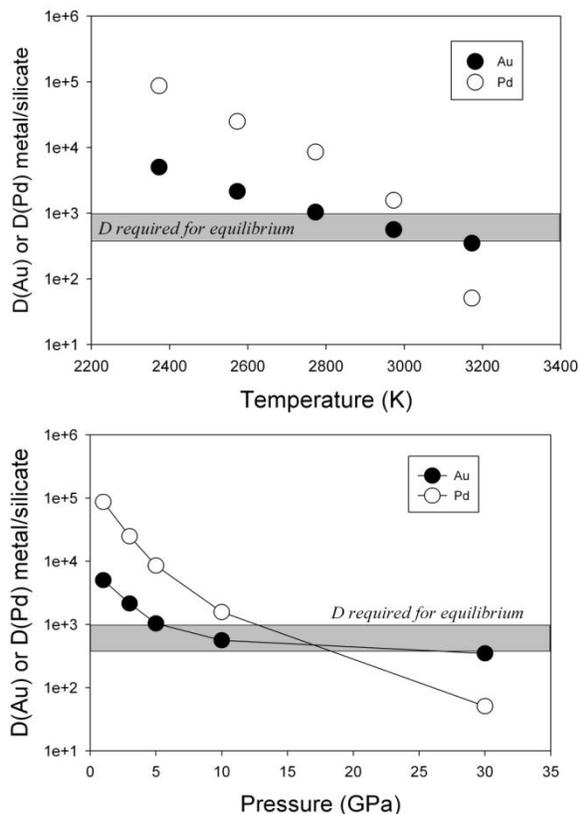


Figure 2 (top): Calculated $D(\text{Au})$ and $D(\text{Pd})$ vs. Temperature (K), and Figure 3 (bottom): vs. pressure (GPa) showing the clear decrease in the values to the range that would be required for an explanation by metal-silicate equilibrium. For the calculations, metal composition is fixed with $X_s = X_c = 0.05$, $\text{NBO}/T = 2.7$ and $\Delta \text{IW} = -2$. Pressure and temperature vary along an adiabat.

The terrestrial mantle HSE content is well defined by studies of mantle xenoliths [12]. Recent work has

focused on the late veneer hypothesis to explain the terrestrial HSE contents. These studies have included experimental work [10] as well as planetary dynamic modeling [13,14]. It is clear from our results that at conditions of ~ 3000 K, 30 GPa, $\Delta \text{IW} = -2$, for peridotite silicate melt, and core forming metal with $X_s = X_c = 0.05$, $D(\text{Pd})$ and $D(\text{Au})$ metal/silicate both decrease to values close to those required for metal-silicate equilibrium (i.e. between 500 and 1000; Figures 2 and 3). An admittedly more cavalier, but nonetheless compelling regression analysis of available data for Ir [7, 10, 15] shows that $D(\text{Ir})$ metal/silicate can decrease to values between 200 and 1000 at these same conditions (except at 1 bar pressure because there are too few high pressure data (all < 2 GPa) yet for Ir). These arguments for Au, Pd, and Ir are consistent with the results of [15] and [16] for Pt, and indicate that the Au, Pd, Pt and perhaps even Ir contents of the primitive upper mantle can be explained by metal-silicate equilibrium at high temperature and pressure conditions such as those suggested for many other siderophile elements [18].

Late veneer scenarios are not required to explain the Au or Pd content (and possibly Ir or Pt) of Earth's primitive upper mantle. Therefore late veneer models are based on an increasingly smaller group of the HSE, and as few as four elements. These four HSE (Rh, Re, Os, Ru) have the most poorly known behavior at high PT conditions, with major gaps in understanding the effect of pressure, temperature, and composition. Further studies to include the rest of the HSE are underway, and in addition will allow the isotopic couples Re-Os and Pt-Os to be assessed as well.

References: [1] Walker, R.J. (2009) *Chemie der Erde* 69, 101-125; [2] Righter, K. (2005) AGU Geophys. Monogr. Ser. 160, 201-218; [3] Righter, K. et al. (2010) *EPSL* 291, 1-9; [4] Righter, K. et al., (2008) *Nature Geosc.* 1, 321-323; [5] Borisov, A. and Nachtweyh, K. (1998) LPSC XXIX, 1320; [6] Danielson, L.R. et al. (2005) LPSC XXXVI, 1955; [7] Crocket, J. et al. (1992) *Austr. J. Earth Sci.* 39, 427-432; [8] Stone, W.E. et al. (1990) *GCA* 54, 2341-2344; [9] Jones, J.H. and Drake, M.J. (1986) *Nature* 322, 221 - 228; [10] Brenan, J. and McDonough, W.F. (2009) *Nature Geosc.* 2, 798-801; [11] Borisov, A. and Palme, H. (1996) *Mineral. Petrol.* 56, 297-312; [12] Becker, H. et al. (2006) *GCA* 70, 4528-4550; [13] Bottke, W. et al. (2010) *Science* 330, 1527-1530; [14] O'Brien, D.P. et al. (2006) *Icarus* 184, 39-58; [15] Lindstrom, D.J. and Jones, J.H. (1996) *GCA* 60, 1195-1203; [16] Cottrell, E. and Walker, D. (2006) *GCA* 70, 1565-1580; [17] Ertel, W. et al. (2006) *GCA* 70, 2591-2602; [18] Righter, K. (2010) LPSC XLI, 2301.