

EFFECT OF PRESSURE ON THE ACTIVITY COEFFICIENTS OF AU AND OTHER SIDEROPHILE ELEMENTS IN LIQUID FE-SI ALLOYS. K. Righter¹, R. Rowland II², S. Yang³, and M. Humayun³, ¹NASA Johnson Space Center, Mail Code XI2, Houston, TX 77058; ²Los Alamos National Laboratory (MS C928, Los Alamos, NM 87545); ³National High Magnetic Field Laboratory, Florida State Univ., Tallahassee, FL 32310.

Introduction: Light elements can alloy into the iron cores of terrestrial planetary bodies. It is estimated that the Earth's core contains ~10% of a light element, most likely a combination of S, C, Si, and O with Si probably being the most abundant [1]. Si dissolved into Fe metal liquids can have a significant influence on the activity coefficients of siderophile elements, and thus the partitioning behavior of those elements between the core and mantle [2-5].

Many of these elements have been investigated extensively at ambient pressure, and studies up to 1 GPa are becoming more common, but few have been studied at pressures above this [6]. The formation of the Earth's core has been estimated to have formed at pressures between 40-60 GPa [7-9], so investigating the effect pressure has on Si's influence on siderophile element partitioning is important for modeling core formation in the Earth and smaller planets. Pressure is well known to influence volumetric properties of metallic and silicate liquids, and oxygen fugacity (e.g., [10,11]), but less is known about its effect on activity coefficients (e.g., [12]). Some activity coefficients depend strongly upon the Si content of Fe liquids, and the concentration of siderophile elements such as P, Sb, and As [3] in the terrestrial mantle is easily influenced by dissolved Si in the core. Thus, isolating the effect of pressure on activity coefficients in general is critical in quantitative analysis of core formation models.

In this work, we investigate the effect variable Si content has on the partitioning of Au between Fe metal and silicate melt at 10 GPa and 2373 K, with the intention of comparing the behavior to that already investigated at lower pressures [4]. In addition, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb were also measured and could thus be included in the assessment of potential pressure effects.

Experimental: Starting materials were the same as those used in previous studies at 1 GPa [4]: basalt (70% by mass) mixed with Fe metal (25% by mass), and Au metal (5% by mass). Silicon metal was then added to the silicate and metal mixture at 2, 4, 6, 8, and 10% by weight to create a variable amount of Si alloyed in the Fe metal liquid.

Experiments were conducted in an 880-ton multi-anvil press at NASA Johnson Space Center Astro-materials Research and Exploration Science division. The COMPRES 10/5 [13] assembly in a Walker-module was used to attain conditions of 10 GPa and 2100°C. The assembly was calibrated for pressure

using SiO₂ transitions (at 9.4 GPa, 1600 °C), (Mg₈₂Fe₁₈)₂SiO₄ transitions from olivine to wadsleyite (13.4 GPa, 1673 K), and Mg₂SiO₄ transitions from wadsleyite to ringwoodite (15.0 GPa, 1473 K, and 20.0 GPa, 1873 K). The assembly utilizes pre-cast octahedra, pyrophyllite gaskets, Re foil furnaces, and type C Re/W thermocouples [14]. Uncertainty in pressure and temperature are ±0.5 GPa and ±15-20 K, respectively, based on temperature gradients no larger than 25 K; thermocouple emf has not been corrected for pressure. The metal and silicate mixtures were packed into single-crystal MgO capsules. Samples were pressurized and then heated to the run temperature. In some cases thermocouple failure led to heating by power curve (established by correlation between power and temperature from previous experiments). Samples were held at run conditions for between 1 and 5 min as required to approach equilibrium, and then quenched by cutting power to the furnace assembly.

Analytical: Metals and quenched silicates were analyzed for major and minor elements with electron probe microanalysis at NASA Johnson Space Center using a Cameca SX100 microprobe. Metals and glasses were analyzed with the electron beam set to 15 kV and 30 nA, and 15 kV and 20 nA, respectively, using various metal, glass, and mineral standards. For both metal and glasses with coarse-grained quench texture, a defocused electron beam of 20-30 μm is used for analysis, with 30-50 analysis points averaged to obtain a representative composition.

Trace elements (<100 ppm) were measured using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at Florida State University using glass and metal standards and either spot or line analyses depending on the size of the metal or silicate regions of interest. Each sample was analyzed by an ElectroScientific Instruments (ESI) New Wave UP193FX excimer (193 nm) laser ablation system coupled to a Thermo Element XR™ Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Plasma Analytical Facility of the National High Magnetic Field Laboratory, Florida State University, for: ²⁹Si, ³¹P, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁶⁶Zn, ⁷¹Ga, ⁹³Nb, ¹¹¹Cd, ¹²⁰Sn, ¹⁸²W, ¹⁹⁷Au, ²⁰⁸Pb, and other elements as described by [15]. Internal standards were ²⁹Si for silicates and ⁵⁷Fe for metal+sulfide. The relevant isobaric interferences and relative sensitivity factors are discussed in [15]. Laser fluence was 2 GW/cm². Both the silicate portions and the metal portions of the samples

were measured using a 50 μm spot at 50 Hz for 10 seconds. Three USGS glasses (BHVO-2g, BCR-2g and BIR-1g) and a synthetic glass (GSD-1g) were used as the external standards for analyzing silicate portions and for metal portions, Hoba IVB iron meteorite, Filomena IIA iron meteorite and NIST SRM 1263 were used as the external standards. Multiple analyses (2-5) were done on silicate and metal portions in each sample and the average of these analyses were used as the representative compositions. Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb were all detectable in metal and silicate and thus could be included in the investigation of the effect of pressure.

Results: The equation $\ln K_D - (n/2 - 1) \ln \gamma_{Fe}^{metal} = \text{const} - \ln \gamma_M^0 + \varepsilon_M^{Si} \ln(1-X_{Si})$ can be used to derive interaction parameters (e.g., [3]). Here γ_M^0 is the activity coefficient of M at infinite dilution, γ_{Fe}^{metal} is the activity coefficient of Fe in Fe metal, and ε_M^{Si} is an interaction parameter (e.g., [16]) 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 ([3]. The slope of $\ln K_D$ versus $\ln(1-X_{Si})$ gives ε_M^{Si} directly for each element at 2373 K and 10 GPa.

Using this approach, we have determined ε_M^{Si} for a large number of siderophile elements, including Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb, by a linear fit to the data, with the standard error (in parentheses below) and the fits passing variance tests in SigmaPlot 12.0. Phosphorus experimental data yielded the highest epsilon interaction parameter of 55.0(11.4), with the positive values indicating that dissolved Si causes a decrease in their partition coefficients. Gold, Ga, and Sn have positive epsilon parameters of moderate magnitude, 16.9(3.7), 17.1(3.8), and 23.1(3.5), respectively. Cd, Pb, Nb, and W all have positive but slightly lower epsilon values of 8.1(1.3), 6.4(1.8), 7.0(8.3) and 14.3(6.7), respectively, at 10 GPa and 2373 K. Zn and V have small and positive epsilon values of 6.2(3.3) and 3.5(6.6), respectively, whereas Mn has a negative epsilon parameters of -1.1(5.0), indicating that Si will cause a very slight increase in D(Mn) metal/silicate with Si present in the metallic liquid.

Comparison to low pressure epsilon parameters

The 10 GPa data can be compared to measured 1 GPa data determined using the same approach, but the latter must be re-calculated to 2373 K using the following equation: $\varepsilon_i^{2373} = \varepsilon_i^{1873} \frac{1873}{2373}$. Comparison of our newly determined 10 GPa epsilon parameters to

values at 1 GPa (recalculated to 2373 K) from previous studies shows very similar values (Figure 1) indicating that pressure does not cause a discernable change in the epsilon.

Discussion: Many key siderophile elements show no discernable difference between 1 GPa and 10 GPa values. Our new epsilon values for Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb, demonstrate that the 1 GPa epsilon values determined in previous studies are applicable to higher pressure equilibria and modelling applications. D(metal/silicate) will be reduced for all elements with the addition of Si to the metallic liquid.

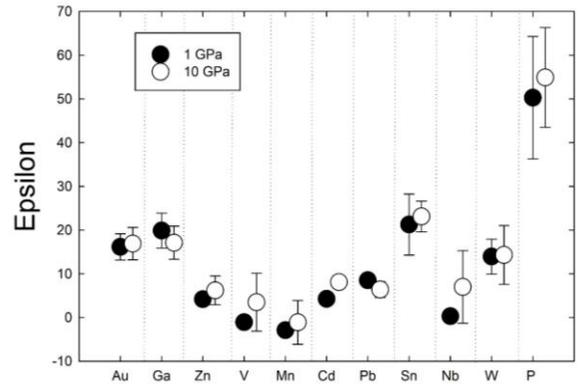


Figure 1: Comparison of epsilon interaction parameters determined at 1 GPa [4,5,6] to the 10 GPa results from this study. 1 GPa results re-calculated to 2373 (K) using the expression $\varepsilon_i^{2373} = \varepsilon_i^{1873} \frac{1873}{2373}$, so that the comparison is made at the same T (K).

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