CORE-MANTLE PARTITIONING OF VOLATILE SIDEROPHILE ELEMENTS AND THE ORIGIN OF VOLATILE ELEMENTS IN THE EARTH. K. Nickodem[1], K. Righter[2], L. Danielson[3], K. Pando[3], C. Lee[4] [1]Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556 (knickod1@nd.edu) [2]Johnson Space Center, Houston, TX 77058 [3]ESCG, Houston, TX 77058 [4]Department of Earth Science, Rice University, Houston, TX 77005

Introduction: There are currently several hypotheses on the origin of volatile siderophile elements in the Earth. One hypothesis is that they were added during Earth's accretion and core formation and mobilized into the metallic core [1], others claim multiple stage origin [2], while some hypothesize that volatiles were added after the core already formed [3].

Several volatile siderophile elements are depleted in Earth's mantle relative to the chondrites, something which continues to puzzle many scientists. This depletion is likely due to a combination of volatility and core formation. The Earth's core is composed of Fe and some lighter constituents, although the abundances of these lighter elements are unknown [4]. Si is one of these potential light elements [5] although few studies have analyzed the effect of Si on metal-silicate partitioning, in particular the volatile elements.

As, In, Ge, and Sb are trace volatile siderophile elements which are depleted in the mantle but have yet to be extensively studied. The metal-silicate partition coefficients of these elements will be measured to determine the effect of Si. Partition coefficients depend on temperature, pressure, oxygen fugacity, and metal and silicate composition and can constrain the concentrations of volatile, siderophile elements found in the mantle.

Reported here are the results from 13 experiments examining the partitioning of As, In, Ge, and Sb between metallic and silicate liquid. These experiments will examine the effect of temperature, and metal-composition (i.e., Si content) on these elements in order to gain a greater understanding of the core-mantle separation which occurred during the Earth's early stages. The data can then be applied to the origin of volatile elements in the Earth.

Procedures: The samples used for the series of experiments were powders composed of 70 wt.% Knippa Basalt, composition described in Lewis et al. [6], 30 wt.% metal mixture, and varying amounts of Si ranging from 0 to 10 wt.% Si. The metal mixture contained 80.9 wt.% Fe, 8.2 wt.% FeS, 2.4 wt.% Ge, 3.2 wt.% As_2O_3, 2.9 wt.% Sb_2O_3, and 2.4 wt.% In. These were ground into a powder and mechanically mixed. All experiments were run using graphite capsules. The runs were conducted using a piston cylinder apparatus at constant pressure of 1.0 GPa with various times and temperatures. Once at constant pressure, samples were heated to high enough temperatures to melt and attain equilibrium for durations based on diffusion time across the capsule [7]. The temperature was measured using a type C thermocouple (W-Re) wires with an accuracy of ±2° C. Samples were then quenched to a silicate glass with large metallic spheres by turning off the power and keeping constant pressure until the temperatures reached 100° C.

Three series were performed (Table 1): two metal-silicate composition series with varying amounts of silicon performed at 1600°C and 1800°C, and an Si free temperature series ranging between 1500°C and 1800°C.

Analysis: Samples were analyzed for major element composition using a Cameca SX100 for electron microprobe analysis at NASA-JSC. A 1 µm beam was used at 20kV and 10nA. A variety of natural and synthetic standards were used. All samples used graphite capsules and were carbon saturated, but carbon was not analyzed yet. However, based on previous studies, the carbon solubility within the metal can be up to 5.5 wt.% C between 1300°C and 1800°C [8].

For all samples the In, As, Sb, and Ge content of the glass was lower than the detection limit of the EMPA; therefore, the samples were analyzed for trace element composition using Laser Ablation Inductively Coupled Mass Spectrometer (LA-ICP-MS) at Rice University. Analysis was performed at Low Resolution (LR) and normalized to ^{43}Ca isotope. Isotopes ^{75}As, ^{115}In, ^{73}Ge, ^{74}Ge, and ^{121}Sb were the only trace elements specifically studied for this research.

Results: Oxygen fugacity was calculated relative to the Iron-Wüstite (IW) buffer using ΔIW= -2log[X_{Fe}/X_{FeO}]. The ΔIW values ranged from ~-1.3 to -1.37 for Si free runs, compared to Si bearing runs which produced ΔIW values from -4.9 to -7.5. The partition coefficient is strongly dependent on oxygen fugacity (fO_2). An increase in Si content will cause a decrease in fO_2. The range of ΔIW values for these experiments falls in the range considered during Earth's core formation (-1 to -5) [1,2].

Partitioning behavior of As, Sb, Ge, and In can be calculated in a differnent way using an exchange reaction of element i with valence n:

$$iO_{n/2}^{\mathrm{silicate}} + (n/2)\mathrm{Fe}^{\mathrm{metal}} = i^{\mathrm{metal}} + (n/2)\mathrm{FeO}^{\mathrm{silicate}}$$

The K_D was calculated for each sample using the equation:

$$K_D=[XFeO]^{n/2}[Xi]/[XFe]^{n/2}[XiO]$$

Where K_D= exchange coefficient, Xi and XiO= molar concentration of element i in the metal and metal oxide of *i* in the silicate respectively. The advantage of K_D is that it is independent of fO_2.

The results show a general decrease in the K_D with increasing temperature and Si content for all elements (Fig. 1, 2), and log K_D values for As and Ge from [9] also fall along this trend. The 1600°C and 1800°C Si-bearing series show decreasing log K_D values for each element, but there is more scatter in the 1800°C series.

Discussion: To test whether these four elements can be explained by an equilibrium core-mantle partitioning scenario, one must know the values of logK_D that would be required for such a scenario. To calculate the K_D or D required for equilibrium in the early Earth, it is necessary to determine the approximate abundance of the metals in the core. The bulk composition of early Earth will be assumed to be the same as CI chondrites. The target log K_D was calculated using the abundances in the primitive upper mantle [10], CI chondrites adjusted for volatility factors [11], a 32 mass% core and 68 mass% mantle.

The new experimental data are compared to the equilibrium log K_D values in Figure 2. The necessary log K_D value for the elements based on chondritic ratios can be attained when additional Si is added to the metal composition. The combined effect of temperature and metallic Si content shows that even at 1600°C the necessary concentration of these metals found in the primitive upper mantle can be met. However, specific P-T-fO_2 conditions for equilibrium await additional experimental data constraining the role of pressure and silicate melt composition.

The large effect of silicon on the magnitude of the K_D values is expected based on the work of Chabot et al. [12] who demonstrated that As, Sb, and Ge all prefer Si-free metal to Si-bearing metal. However, another factor contributing to the low K_Ds is the sulphur present in the silicate melt. With increasing Si in the metal (and lower fO_2), more S dissolves into the silicate melt [13]. Some of the trace elements may then have a stronger affinity for S (As and Sb), increasing their concentrations in the silicate melt. The large effect on the partition coefficient seen in these results may be a combination of increased Si content in the metal and as S content in silicate melt. Further calculations and data will be needed to understand the interaction between these elements and to know the individual effect of Si

Evidence here suggests that Si has a large effect on the partitioning of As, Sb, Ge, and In. Based on the data, if Si is present in the core then the concentrations of these elements found in the mantle can be explained by early stage equilibrium between the core and the silicate melt, supporting the hypothesis that volatiles were added during Earth's accretion and core formation.

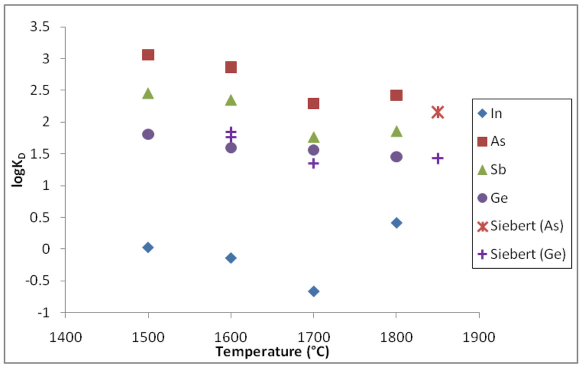

Fig. 1. Log K_D (exchange coefficient) with respect to temperature for the Si-free metal series. Data shows a general decreasing trend with increasing T, with several additional literature data ([9] at 3 GPa) also supporting the trends for As and Ge.

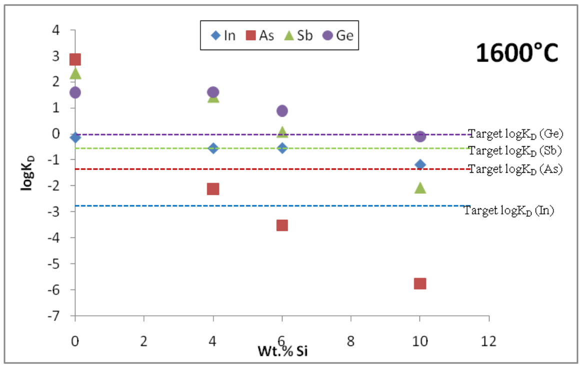

Fig. 2. Log K_D values plotted against wt.% Si (in metal) for the 1600°C series. General trends show a decrease in log K_D with increasing Si content. Target log K_D drawn for each element indicating values necessary to explain metal content in mantle.

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