

**Partitioning of phosphorus and molybdenum between the Earth's mantle and core and the conditions of core formation.** K.M. Acuff<sup>1</sup>, L. Danielson<sup>2</sup>, K. Richter<sup>2</sup> and C.T. Lee<sup>3</sup>, <sup>1</sup>Lunar and Planetary Institute, Houston, TX 77058; <sup>2</sup>Mailcode KT, NASA Johnson Space Center, 2101 NASA Pkwy., Houston, TX 77058; <sup>3</sup>Dept. of Earth Science, Rice University, Houston, TX 77005.

**Introduction:** There are several hypotheses on the specific processes that might have occurred during the formation of the Earth. One hypothesis that has been proposed is that early in the Earth's formation, there was a magma ocean present [1], and within this body, siderophile elements separated out of the silicate liquid to form the metal core [2]. This study addresses this hypothesis.

P and Mo are moderately siderophile elements that are present in both the mantle and the core [3]. The concentrations of P and Mo in silicate vs. metal can be measured and in turn used to determine the temperatures, pressures, oxygen fugacity and melt composition required to achieve the same concentrations as observed in the mantle.

The data here include eight experiments examining the partitioning of P and Mo between metallic liquid and silicate liquid. The purpose of the experiments has been to gain a greater understanding of core-mantle separation during the Earth formation process and examines temperature effect on P and Mo, which has not been systematically studied before.

**Procedures:** The sample used in this series of experiments was composed of 70% Knippa Basalt, the composition of which is described in [4], 29% Fe and 1% MoO<sub>3</sub>. These were ground to a powder and mixed. Two types of capsules were used: graphite and MgO. Runs were conducted at a constant pressure using a piston cylinder apparatus. Once the samples were under pressure, they were heated to silicate superliquidus temperatures and allowed to equilibrate for a set amount of time depending on the run temperature. A Type C thermocouple (W-Re) wire with an accuracy of  $\pm 2^\circ$  C was used to measure the temperature. The samples were then quenched to a silicate glass containing

large metallic liquid spheres. Quenching occurred by turning off the power. The two different temperature series consisted of eight successful runs at 10.3 kbars and at temperatures between 1500° and 1800° C (Table 1). Run durations were chosen based on equilibration times from previous experiments ([1] and [5]), and on several additional experiments of variable duration (time series).

**Analysis:** Samples were analyzed for major element composition using the electron microprobe at NASA-JSC including Mo concentrations in the metal. The operating conditions were an accelerating voltage of 20 kV and sample current of 20 nA [6]. Samples cow1, cow3, cow8 and cow20 were run using the graphite capsules, causing the metal spheres to be C saturated. Wt% C was calculated based on the melting temperature of each run using the Fe-C phase diagram showing graphite solubility in liquid phase [7]. Molybdenum (and several other elements) in the silicate glasses and metals at ppm levels were analyzed using Laser Ablation Inductively Coupled Plasma mass spectrometry (LA-ICP-MS) at Rice University [8]. This system has a NewWave 213 nm wavelength laser system coupled with a ThermoFinnegan Element 2, operating in both low and medium resolution modes [8]. The standards for this analysis were NIST610 and 612 glasses, BCR and BHVO-2G glasses, and HOBA iron meteorite. BHVO-2G basaltic glass contains 3.78 ppm Mo and 7.8% Fe. The partition coefficients (D) were calculated as ratios of wt% element in the metal to wt% element in the silicate.

**Results:** Wt% P and Mo were measured in the metal and silicate of each sample (Table 1). There were measurable variations in wt% MgO with increasing

**Table 1: Summary of experimental and analytical results; all experiments at 10.3 kb**

Sample	Temp (C)	Duration	Capsule	$\Delta$ IW	P glass (wt%)	D <sub>P</sub>	Mo glass (ppm)	D <sub>Mo</sub>
cow 1	1500	3 hrs	graphite	-1.44	0.33	0.34	2.9	9330
cow 3	1600	90 min	graphite	-1.48	0.30	0.40	4.2	5000
cow 8	1700	45 min	graphite	-1.45	0.30	0.31	4.9	5200
cow 20	1800	15 min	graphite	-1.44	0.29	0.69	6.0	3700
cow 10	1500	3 hrs	MgO	-1.60	0.51	0.07	84.5	370
cow 12	1600	90 min	MgO	-1.76	0.43	0.41	37.8	865
cow 17	1700	45 min	MgO	-1.76	0.35	1.00	25.7	1120
cow 16	1800	15 min	MgO	-1.81	0.30	1.16	19.8	1250

temperature for the four experiments that were run in MgO capsules. The sample was originally 13 wt% MgO but as the basalt reacted with the capsules, the amount of MgO within the sample increased to up to 20 wt%. The 1600° run (cow12) did not show the dramatic increase in MgO like the other three runs. During quenching of the cow10 and cow12 runs, olivine and/or magnesiowustite crystals formed within the silicate. These were analyzed and the olivine crystals showed to have an average of 49.83 to 53.20 wt% MgO and the magnesiowustite crystals had an average of 77.99 wt% MgO. This crystal formation resulted in the MgO being removed from the silicate in the cow12 run.

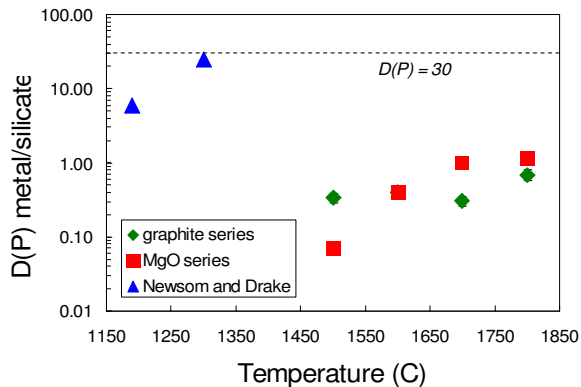


Figure 1: Results for  $D(P)$  metal/silicate compared to the results of Newsom and Drake (1982) [9], run at 1 bar, lower temperatures, and with different melt compositions. Horizontal line at  $D(P) = 30$  indicates the value necessary to explain the P depletion in the terrestrial primitive mantle.

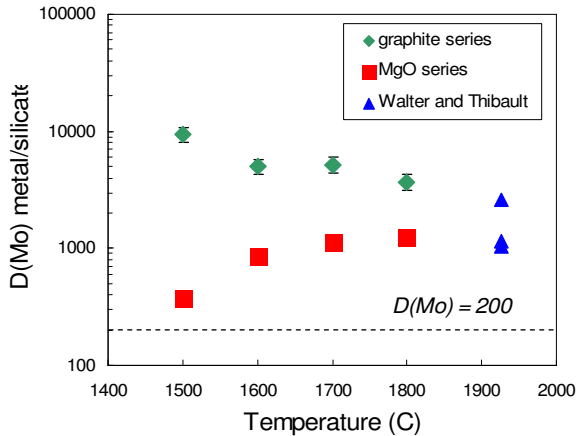


Figure 2: Results for  $D(Mo)$  metal/silicate compared to the results of Walter and Thibault (1995) [10], also run at similar pressures (10 kb) in graphite capsules at temperatures overlapping with this study. Horizontal line at  $D(Mo) = 200$  indicates the value necessary to

explain the Mo depletion in the terrestrial primitive mantle.

Figures 1 and 2 show the results from the eight experimental runs that were analyzed for this project along with added data from [9] and [10]. The two data sets from this study and [9] for  $D_P$  are compared in Figure 1. Each set of data showed a similar trend that agrees with the idea that increasing temperature will in fact increase D values for P. The four experiments that were run with graphite capsules did not seem to show as much of a change in D values from 1500° to 1800° C as the experiments that were run in the MgO capsules. The data from this study and [10] for  $D_{Mo}$  are compared in Figure 2. The data points from both studies do fall into a similar trend however the MgO capsules caused the D values for Mo to increase rather than decrease.

**Discussion:** The information in this study can be applied to the current understanding about the conditions necessary to achieve the current concentrations of P and Mo in the mantle. A  $D_P$  value of 30 [5] and  $D_{Mo}$  value of ~200 [10] are required to explain these conditions and these values were not achieved with the experiments in this study. Based on the data here, and in other studies predicting an increasing D value for P with increasing temperature (e.g., [11]), it is assumed that these D values might be reached at ~2100° C, however this temperature would change at higher pressures. Further research that will include high pressure and temperature experiments using the 880-ton multi anvil press might be able to achieve these conditions.

**References:** [1] Li J. and Agee C.B. (1996) *Nature* 381, 686-689; [2] Righter K. (2003) *Annu. Rev. Earth Planet Sci.* 31, 135-74; [3] Agee et al. (2007) *LPS XXXVII*, abstract # 2170; [4] Lewis et al. (1993) *Meteoritics* 28, 622-628; [5] Righter, K. et al. (1997) *Physics of the Earth and Planetary Interiors* 100, 115-134; [6] Righter, K. et al. (2006) *American Mineralogist* 91, 1643-1656; [7] Sundman, B. et al. (1985) *Calphad* 9, 153-190; [8] Agranier, A. and Lee, C.-T.A. (2007) *Earth and Planetary Science Letters* 257, 290-298; [9] Newsom H.E. and Drake M.J. (1982) *Geochimica et Cosmochimica Acta* 47, 93-100; [10] Walter, M.J. and Thibault, Y. (1995) *Science* 270, 1186-1189; [11] Righter K. and Drake M. (1999) *Earth and Planetary Science Letters* 171, 383-399.