

COMPOSITIONAL EFFECTS ON MOLYBDENUM METAL-SILICATE PARTITION COEFFICIENTS AT HIGH PRESSURE. L. K. Burkemper¹, C. B. Agee¹, and K. A. Garcia¹; ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, 1 University of New Mexico, MSC03 2050, Albuquerque, NM 87131; BURKEML@unm.edu.

Introduction: For over 20 years, experimental studies on siderophile (iron-loving) element partitioning have been used to investigate core formation. Core formation depleted the mantle in these elements relative to the bulk Earth, leaving a chemical signature that can be measured. Partitioning studies attempt to find pressure, temperature, composition, and oxygen fugacity conditions that reproduce the observed upper mantle depletions. Results from nickel and cobalt suggest that Earth's core formed out of a silicate magma ocean at depth [1]. This theory is supported by geophysical arguments that large impacts early in Earth's history would release enough heat to melt a large portion of the planet [2]. However, a consensus on the conditions of the magma ocean has not been reached, and more data is needed.

Molybdenum is a moderately siderophile element, it favorably enters the core, yet enough Mo stays behind in the mantle to measure with some accuracy. Mo is a refractory element; therefore, its abundance in the bulk Earth is assumed to be chondritic. Unlike Ni and Co, Mo is a high valence cation that also has multiple oxidation states, with Mo⁴⁺ and Mo⁶⁺ being the most prominent at terrestrial oxygen fugacities [3].

As a result of molybdenum's multivalence nature, oxygen fugacity will have a large effect on Mo partition coefficients ($D_{\text{Mo}} = c_{\text{metal}}/c_{\text{silicate}}$) and this effect has been examined previously [3, 4]. However, there is a paucity of data on the effect of pressure, temperature, and silicate and metal composition. Furthermore, the work that has been done on Mo partitioning is almost exclusively at pressures below 1.5 GPa, which are then extrapolated to the suggested pressures of ~20-60 GPa. The present study focuses on the effect of composition on D_{Mo} and all of the experiments were performed at pressures of 2.5 GPa and greater.

Experimental: Starting materials consisted of a synthetic Apollo-14 black glass (high-TiO₂ high-FeO basalt), a natural basalt from southeastern Oregon, two synthetic peridotites (with varying Mg#), a natural andesite (AGV-2), and two other high-Ti synthetic compositions used to investigate the effect of TiO₂. 50+ near-liquidus and super-liquidus experiments were conducted, consisting of two different types. First, solubility experiments that used a Mo⁰ capsule which also served as the pure metal phase. Powdered starting materials for the desired experiment were loaded into the capsule and capped with a friction fit lid. Second, partitioning experiments that used an MgO capsule and

an FeNiMo metal phase. The metal phase was mixed with the desired silicate material and then loaded into the capsule. BSE images of run products from both experiment types can be seen in the Figure. All experiments were conducted in a Walker-type multi-anvil press in the High Pressure Laboratory at the Institute of Meteoritics. The experiment was brought up to pressure (2.5-9.7 GPa) and temperature (1585-2200 °C) and held from 2-120 minutes. The experiment was quenched by cutting power to the system, causing the temperature to drop below 200 °C in less than 25s.

Run products were analyzed for major, minor, and trace elements on a JEOL 8200 electron microprobe (Institute of Meteoritics). During quench, the silicate phase formed a glass that was interspersed with quench crystals, therefore a 20 μm broad beam was employed. Molybdenum is reported as MoO₂ in the silicate because it is in equilibrium with Mo metal so minimal MoO₃ is expected [3]. Element totals were 100 +/-1 %. Silicate MoO₂ values in the solubility experiments ranged from 0.4-7 wt.%. For these run products, probe conditions of 15 kV, 20 nA, and 30s-15s peak-background count times were used, which resulted in a limit of detection (LOD) of 100 ppm. The MoO₂ concentrations in the partitioning experiments were much lower so the conditions were changed to 20 kV, 60 nA, and 60s-30s peak-background count times, which brought the LOD down to 32 ppm. The metal phase was analyzed using the first set of conditions and a 10 μm beam.

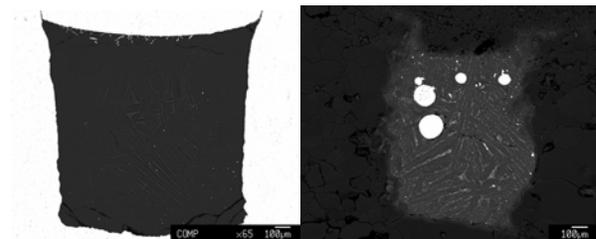


Figure. BSE images. Left: Run product from a solubility experiment. The gray is the peridotite silicate phase with noticeable quench texture. The bright white around the silicate is the Mo capsule. Right: Run product from a partitioning experiment. The light gray is the peridotite silicate phase with noticeable quench texture. The dark gray surrounding the silicate is the MgO capsule. The bright white blebs are the FeNiMo metal phase.

Results and Discussion: For the FeNiMo metal phase experiments, partition coefficients were calculated by taking the weight percent Mo in the metal divided by the weight percent Mo in the silicate. Oxygen fugacity was calculated relative to the iron-wustite buffer according to $\Delta IW = -2\log(X_{FeO}/X_{Fe})$. For the solubility experiments, partition coefficients were calculated using the approach of [5], which takes into account activity coefficients at the temperature of interest. Oxygen fugacity was estimated relative to the Mo-MoO₂ buffer using the approach of [6] for their pure tungsten metal phase experiments.

Unlike in the partitioning experiments, the metal phase in the solubility experiments remains solid, requiring potentially longer times to reach equilibrium. Therefore, a suite of time-series experiments were conducted to ensure a steady state. The results show that experiments at 1585 °C (our lowest temperature) take 90 minutes to reach a steady state. Whereas, it took 60 minutes at 1650 °C and only two minutes at 2000 °C.

The wide range of conditions used for our solubility experiments allowed us to investigate trends in pressure and temperature as well as composition. Our data supports the results of [7] that temperature has only a slight effect on Mo solubility and pressure has a negligible effect over the pressure range examined here.

The main goal of this study was to determine the effect of silicate composition on D_{Mo} . This was done by performing multiple suites of solubility experiments that were at constant pressure and temperature, consisting of over 20 experiments. The compositions used spanned an NBO/T (non-bridging oxygens to tetrahedrally coordinated oxygens ratio) range from peridotite to andesite (2.20-0.12). Our results indicate that there is not a linear relationship between D_{Mo} and NBO/T. As seen in the Table, the andesite composition has a lower NBO/T than the basalt composition, but higher than the peridotite. When we examined our data in more detail, trends due to individual oxides were observed. First, changing SiO₂ content appears to have no effect on D_{Mo} over the range investigated. Therefore, the difference between the basalt and andesite compositions must be due to CaO, Na₂O, and K₂O since the compositions are otherwise similar. Addition of Al₂O₃ to the basaltic composition caused an increase in Mo solubility. A composition with 17.51 wt.% Al₂O₃ had a D_{Mo} of 418; Al₂O₃ was increased to 25.04 wt.% causing a decrease in D_{Mo} to 175. The black glass compositions had lower D_{Mo} values, similar to the peridotite compositions. This is most likely due to the high FeO contents (~22 wt.%) of the black glass because experiments performed on a peridotite composition showed no change when ~12 wt.% TiO₂ was

added. Finally, increasing MgO appears to cause D_{Mo} to decrease slightly.

Previous studies on the effect of silicate composition on D_{Mo} showed D_{Mo} to decrease with increasing NBO/T [8]. However, [8] only examined compositions from peridotite to basalt. They did note that D_{Mo} decreases with increasing MgO, as shown here and in [4]. [4] also showed an increase in Mo solubility with increasing CaO, the opposite of our results; however, the compositions used in [4] were CaO-rich and FeO-free which may be the cause of the disagreement.

We also performed partitioning experiments where the metal composition was changed from pure Mo to a more Earth relevant FeNi-rich phase. This change greatly increased the value of D_{Mo} compared to a solubility experiment at the same pressure, temperature, and silicate composition, due to the differing metal compositions and a significant decrease in oxygen fugacity.

Table. Partition coefficients of three experiments with different starting silicate compositions (NBO/T). All three experiments were run at 2100 °C and 2.5 GPa.

Sample	NBO/T	D_{Mo}
Peridotite	2.20	56
Basalt	0.72	235
Andesite	0.12	83

Future Work: Continuation of this study will be to perform more high pressure partitioning experiments in order to quantitate their difference between the solubility experiments. This work will focus on peridotite silicate compositions since compositions that greatly differ from peridotite can produce alternate results. Our future work along with the present study will allow us to determine specific magma ocean conditions that reproduce the observed molybdenum mantle depletion.

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