

MOLYBDENUM METAL-SILICATE PARTITIONING BEHAVIOR: CONSTRAINING THE MAGMA OCEAN HYPOTHESIS FOR CORE FORMATION.

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Introduction: The magma ocean hypothesis, as outlined by [1], states that terrestrial core formation occurred through metal droplets separating out of a layer of liquid silicate. These droplets equilibrate with the surrounding silicate and sink to the silicate liquidus, where equilibration would stop and the metal would pond, forming a layer at the base of the magma ocean. Due to density instabilities, the metal would then sink through the solid silicate to the core in the form of large diapirs. This hypothesis is supported by the suggestion that large impacts were likely during the late stages of planetary accretion [2]. The energy released from these impacts would produce enough heat to partially, or completely, melt a growing planet, thus causing one or more magma oceans [3].

The siderophile (iron-loving) elements in the mantle are depleted relative to bulk Earth (chondritic) values due to their preference for the metal phase during separation of the core, and can therefore be used to investigate core formation [4]. By conducting equilibrium metal-silicate partitioning experiments, [5] determined that at ~28 GPa and 2000 °C, the partition coefficients [$D_i = c_i(\text{metal})/c_i(\text{silicate})$] for Ni and Co equal the values required to explain their mantle depletions. They suggest that these conditions correspond to the base of the magma ocean and provide strong evidence for equilibrium core formation on Earth. Further studies have determined that the mantle abundances of other siderophile elements (i.e. V, Cr, Mn, W, Mo) can also be explained by high P-T core formation with a wide range of suggested conditions: 10-60 GPa and 2000-3700 K.

The literature contains an extensive experimental database for Ni and Co, over 300 each; whereas, the data for Mo is not as abundant, less than 200, the majority of which are at low pressures (< 2 GPa). This study expands the high pressure Mo database by presenting results from 20 new metal-silicate partitioning experiments covering a pressure range of 3-20 GPa, a temperature range of 1900-2400 °C, with variable silicate and metal compositions. Our results help constrain the suggested magma ocean conditions.

Methods: Starting silicate materials included a natural andesite and basalt, and a synthetic peridotite and high FeO, high TiO₂ composition. Magnesia capsules were employed which caused all the final silicate compositions to be ultramafic due to MgO infiltration. The pure metals consisted of metal shavings obtained

by filing >99.5% pure Fe, Ni and Mo rods. The pure metals were used to make two metal mixtures, one with 50 wt.% Fe, 40% Mo, and 10% Ni and the other with 60 wt.% Fe and 40% Mo. These metal mixtures were then mixed with the silicate compositions in a 3:1 silicate to metal ratio so that the final Mo concentration in all cases was 10 wt.%. The 3-8 GPa experiments were performed on a Walker-type multi-anvil press (IOM) using ceramic octahedra surrounded by eight tungsten-carbide cubes with 8 mm truncated edges. The 15-20 GPa experiments were performed on a 1500T multi-anvil press at the Geophysical Laboratory (CIW) using the COMPRES sponsored 8/3 assembly. Run times were kept short (1-5 min) to minimize MgO infiltration and the experiments were quenched by cutting power to the system. All run products were analyzed with a JEOL 8200 electron microprobe using a broad beam. Mo was analyzed on two spectrometers and the peak counts were combined to get a LOD of ~15 ppm.

Results: A picture of a typical run product can be seen in Figure 1. Oxygen fugacity was calculated relative to the iron-wüstite buffer according to $\Delta IW = 2\log(X_{FeO}/a_{Fe})$ where X_{FeO} is the mole fraction of FeO in the silicate and a_{Fe} is the activity of Fe in the metal. The activity is equal to $X_{Fe}\gamma_{Fe}$, where X_{Fe} is the mole fraction of Fe in the metal and γ_{Fe} is the activity coefficient of Fe in the metal, which was determined using the Metal Activity Calculator [6].

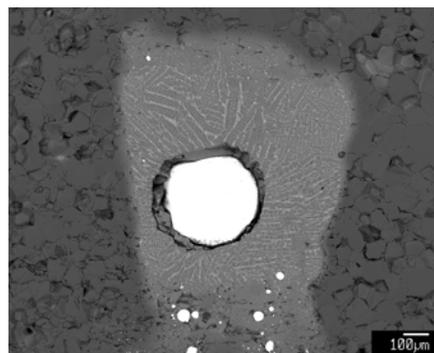


Figure 1. Back scattered electron image of a typical run product showing quench texture in the silicate phase and distinct separation between the metal (bright white) and silicate (light gray) phases. Dark gray is the magnesia capsule.

Increasing pressure caused $D(\text{Mo})$ to decrease, Figure 2. The two experiments performed at the highest P-

T conditions have the lowest D values, indicating that temperature also has a decreasing effect. As shown in Figure 2, the D values for our highest P-T experiments are still too large to explain the Mo depletion, indicating a shallow magma ocean (< 600 km) cannot explain the observed mantle abundance of molybdenum. In general, D(Mo) decreased with increasing NBO/T but there is scatter in the trend; therefore, in the parameterization below we used mole fractions of individual oxides to account for changes in silicate composition.

Discussion: 138 experiments from the literature and the 20 new experiments presented here were parameterized using the approach of [7] and the equation

$$\log D_{Mo} = a\Delta IW + b \frac{1}{T} + c \frac{P}{T} + \sum d_i X_i + e[\log(1 - X_C)] + f[\log(1 - X_S)] + g[\log(1 - X_{Si})] + h$$

where D_{Mo} is the metal-silicate partition coefficient, ΔIW is the oxygen fugacity relative to the iron-wüstite buffer, T is temperature in Kelvin, P is pressure in GPa, X_i is the mole fraction of oxide i in the silicate phase, X_C , X_S , and X_{Si} are the mole fraction of carbon, sulfur, and silicon in the metal phase, respectively, and $a-h$ are linear regression coefficients, Table. The R^2 value is 0.95, and the expression predicts both solubility and partitioning data well. Additionally, the parameterization does not include a term for Ni in the metal phase, yet predicts data with up to 99 wt.% Ni in the metal very well, suggesting Ni does not have an effect on Mo partitioning other than changing the fO_2 .

The a coefficient indicates mainly Mo^{4+} in the silicate. The positive b and negative c coefficients indicate a moderate decrease in D(Mo) with increasing pressure and temperature, consistent with our experiments. The large coefficients for SiO_2 and TiO_2 indicate that increasing these oxides relative to the other oxides will cause an increase in D(Mo). Additionally, the large $e-f$ coefficients indicate that light elements have large effects on D(Mo).

The equation can then be used to solve for a set of P-T conditions that result in $D(Mo) = 40-100$, the range required to explain the Mo depletion. An additional constraint is the P-T conditions must lie on the peridotite liquidus. Without considering light elements, at $-2.2\Delta IW$ and using KLB-1 as the silicate composition, the P-T range that fits these criteria is 42-57 GPa and 3200-3600 K. Addition of C would cause the P-T conditions to increase, whereas S and Si would cause them to decrease.

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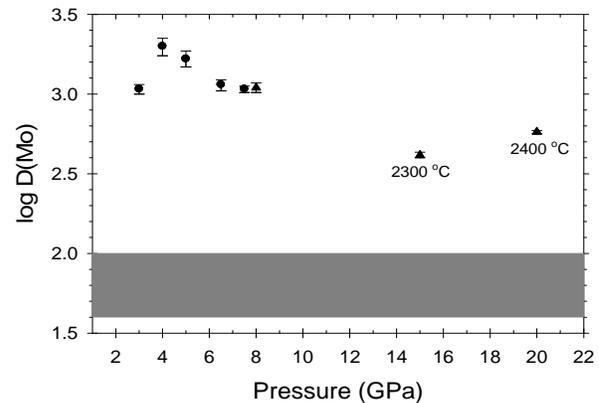


Figure 2. All the data have been adjusted to $-2.2\Delta IW$. All the experiments in this plot were performed at 2100 °C unless otherwise noted. Circular symbols indicate the starting composition was peridotite and triangles indicate a basaltic starting composition. Error bars are the standard error from the probe measurements. The gray band indicates the D values required to explain the Mo depletion.

Table. Multiple linear regression coefficients

Parameter	Value	St. Error
ΔIW	-1.11	0.03
1/T	7145	548
P/T	-47.98	17.44
SiO_2	12.88	1.83
Al_2O_3	9.24	2.26
FeO	9.83	1.88
MgO	10.17	1.80
CaO	9.33	1.83
TiO_2	11.09	2.45
$\log(1-X_C)$	-6.06	0.66
$\log(1-X_S)$	4.66	1.26
$\log(1-X_{Si})$	16.27	2.10
Intercept	-13.20	1.75

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