

## MOLYBDENUM SOLUBILITY IN SILICATE MELT AT HIGH PRESSURES AND TEMPERATURES: EXPERIMENTAL CONSTRAINTS ON PLANETARY CORE FORMATION

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**Introduction:** We present here data from more than sixty experiments on molybdenum (Mo) solubility in a wide range of silicate melt compositions at pressures from 0.5 to 11.5 GPa and temperatures from 1360 to 2080°C. The purpose of this study is to determine if there are conditions during core formation that can explain the Mo abundance in the Earth's upper mantle and the mantles of the Moon and Mars.

Mo is a refractory, moderately siderophile element that should be present in terrestrial planets with little or no depletion due to accretionary volatility effects. Hence planetary bulk Mo is expected to be "chondritic" and partitioned solely between silicate crust+mante and metallic core during differentiation. Based on estimates of the Mo content in the silicate Earth [1,2] a partition coefficient for  $D_{\text{Mo}}$  (metal/silicate) = 50-80 would be consistent with equilibrium core-mantle segregation. Interestingly, earlier experimental work done at 1-atm or modest pressures and temperatures report  $D_{\text{Mo}}$  in the range  $10^3$ - $10^5$ , depending on oxygen fugacity, valence state, and silicate melt structure expressed as non-bridging oxygens divided by tetrahedrally coordinated cations (NBO/T) (see [3] for overview of Mo partitioning behavior). Hence there is an apparent excess of Mo in the mantle based on the low pressure data, and this is similar to that observed for other moderately siderophile elements such as W, Ni, and Co. Experimental studies [4-6] have shown that the "excess" Ni and Co in the mantle can be explained by high pressure and high temperature conditions in a core-forming magma ocean and a negative temperature and pressure dependence on  $D_{\text{Ni}}$  and  $D_{\text{Co}}$ . Therefore we seek to uncover which factors during the core-forming magma ocean stage of Earth evolution could have contributed to the distribution of Mo. Elucidating the effects of P, T, X,  $f\text{O}_2$  etc. on Mo partitioning and combining them with existing high P-T data on Ni, Co, V, and Cr can further constrain the depths and temperatures of core formation in terrestrial planets.

**Experimental:** The data presented here on Mo solubility in silicate melt are from piston-cylinder and multi-anvil experiments run in the Agee High-Pressure Laboratory over the course of the last fifteen years. The melt compositions include komatiite, peridotite, komatiite-fayalite mixtures, hydrous komatiite-fayalite mixtures, lunar green glass, and lunar black glass. All experiments were saturated in molybdenum (Mo-Fe

capsules) and  $f\text{O}_2$  was fixed by the exchange of  $\text{MoO}_3$  and Fe-FeO between metal capsule and silicate melt. Liquidus or super-liquidus conditions existed in all experiments. Concentration levels of  $\text{MoO}_3$  in the silicate melt was determined by electron microprobe analyses and ranged from a minimum of 0.07 wt% in lunar green glass at 1360°C and 0.5 GPa to a maximum of 6.97 wt% in hydrous komatiite-fayalite mixture at 8 GPa and 1750°C.

**Effects of T, P, and Melt Composition:** There appears to be very strong negative effect on  $D_{\text{Mo}}$  with increasing P and T along the Apollo 14 Black Glass liquidus (figure 1). This is in agreement with previous work [7] although the D-values are much lower in the Black Glass composition and under experimental conditions which ranged from 1415-2080°C and 1.0-11.5 GPa.

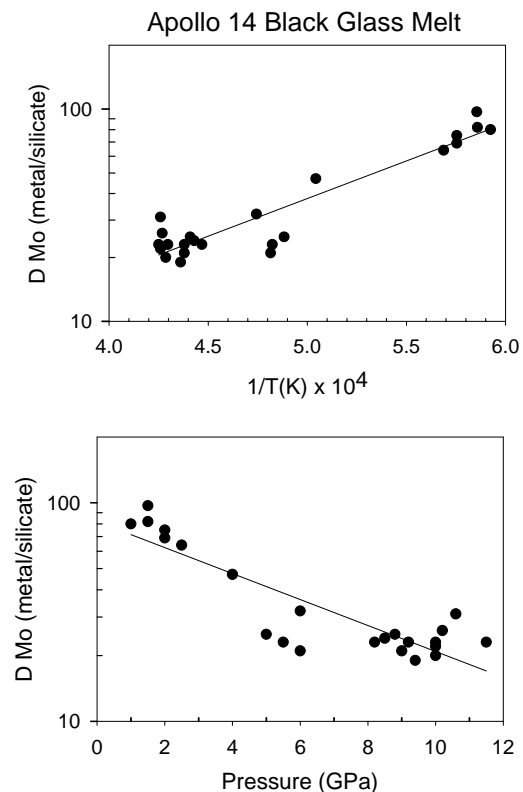


Figure 1. Plots of  $D_{\text{Mo}}$  versus inverse temperature ( $1/T$ ) and pressure showing a negative effect of T and P on the partitioning of Mo between metal and molten Black Glass. In this data set P and T are

positively correlated thus more work is required to determine the separate effects of these two variables.

The comparatively low  $D$ -values in Black Glass can be understood if one considers the effect of melt composition, in particular FeO content. Figure 2 shows that FeO content of the silicate melt is negatively correlated with  $D_{\text{Mo}}$  for three different compositions at approximately isothermal and isobaric conditions.

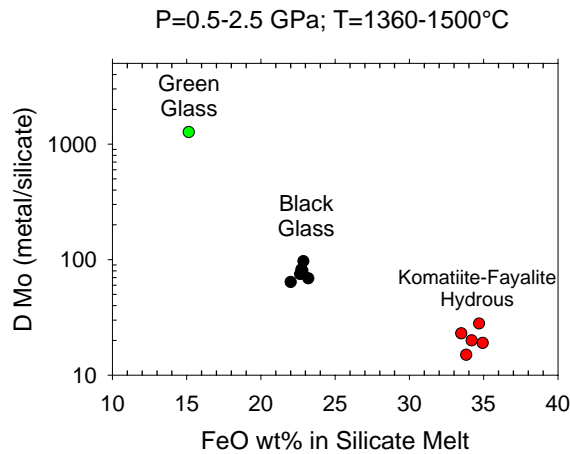


Figure 2. Plot of  $D_{\text{Mo}}$  versus FeO content of the silicate melt for three different compositions. The data subsets are not strictly isothermal and isobaric, though they do minimize possible effects by covering only modest T-P ranges.

Accordingly, Black Glass melt and hydrous komatiite-fayalite liquid mixture with very high FeO-contents have much lower  $D$ s that that observed in by [7] who studied basalt and peridotite melts.

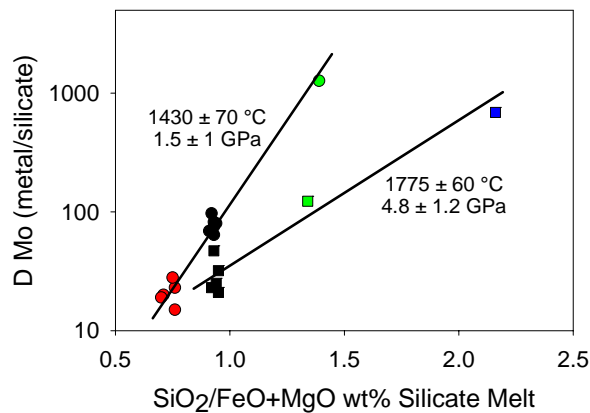


Figure 3. Plot of  $D_{\text{Mo}}$  versus  $\text{SiO}_2/\text{FeO}+\text{MgO}$  in silicate melt showing that decreasing silica content and increasing MgO and FeO decreases  $D_{\text{Mo}}$ . Symbol colors are the same as in figure 2, with the addition of the blue square which is a melt with 66 wt%  $\text{SiO}_2$ , 24 wt% FeO, 7 wt% MgO, 3 wt%  $\text{H}_2\text{O}$ . The shallower sloping line for the high temperature – high pressure data illustrates the negative T-P effect on  $D_{\text{Mo}}$ .

The compositional effect on  $D_{\text{Mo}}$  is also revealed in figure 3 and indicates a strong dependence on melt structure. The data show that  $D_{\text{Mo}}$  decreases dramatically with melt depolymerization. In other words, the lower the  $\text{SiO}_2$  and the higher the FeO+MgO of the melt, the lower  $D_{\text{Mo}}$  becomes. This is in good agreement with [7] who showed that increasing NBO/T decreases  $D_{\text{Mo}}$ .

**Discussion:** It is noteworthy that many of the experiments presented here have  $D_{\text{Mo}}$  that are in the range required to explain Mo mantle abundances through equilibrium core formation. On the other hand, many of the melt compositions are much more FeO-rich or water-rich than is likely for the Earth's magma ocean. Thus a correction or normalization of the trends reported here should be applied in order to solve for the depth and temperature of Mo partitioning in a core-forming terrestrial magma ocean. We have nine experiments on komatiite and peridotite melts with a P-T span of 7.2-10.1 GPa and 1900-2000°C that are realistic for a magma ocean composition and here the values for  $D_{\text{Mo}}$  range from 40-70, supporting equilibrium partitioning in a deep magma ocean.

**References:** [1] McDonough. (2003) in *Treatise on Geochemistry: Mantle and Core*, 547-566. [2] Palme H. and O'Neill H. (2003) in *Treatise on Geochemistry: Mantle and Core* 1-35. [3] Walter M.J. et al. (2000) in *Origin of the Earth and Moon*, 265-289. [4] Thibault Y. and Walter M.J. (1995) *GCA*, 59, 991-1002. [5] Li and Agee (1996) *Nature* 381, 686-689. [6] Chabot et al. (2005) *GCA* 69, 2141-2151. [7] Walter M.J. and Thibault Y. (1995) *Science*, 270, 1186-1189.