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Constraints on core formation from molybdenum solubility in silicate melts at high pressure

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ABSTRACT

We report results from 43 new molybdenum solubility experiments performed in order to test molybdenum's compatibility with the magma ocean hypothesis for core formation. A Walker-type multi-anvil press was used for all experiments and we investigated the pressure range of 2.5–12 GPa and temperature range of 1585–2200 °C. Eight different silicate compositions were also employed. Our data show that increasing temperature causes solubility to increase, whereas pressure has a negligible effect over the range investigated here. In general, increasing silicate melt polymerization causes solubility to decrease; however, the effect of silicate composition is best addressed by looking at the effects of individual oxides versus a universal melt parameter such as NBO/T (ratio of non-bridging oxygens to tetrahedrally coordinated oxygens). From our solubility data, we calculated metal–silicate partition coefficients at infinite iron dilution. Parameterization of our data plus data from the literature shows that there is no discrepancy between partition coefficients determined directly from experiments and those calculated from solubility data, so long as all variables are taken into account, i.e. changes in metal phase composition. Additionally, most of the experiments in the literature were conducted at pressures below 2 GPa, therefore the addition of our high pressure data set makes extrapolations to deep magma ocean conditions more accurate. We determined that the observed mantle abundance of Mo can be explained by both single-stage and multi-stage magma ocean models. Previous siderophile element studies have suggested a wide range of possible single-stage core formation conditions, from 10 to 60 GPa along the peridotite liquidus. Our results narrowed this range by constraining the *P*–*T* conditions to 40–54 GPa and 3050–3400 K. Our results also further constrained the multi-stage core formation models by limiting the depth of metal–silicate equilibration during the final impacts of accretion to 31–42% of the core–mantle boundary depth.

1. Introduction

Earth's mantle depletion of the siderophile elements, relative to chondritic abundances, was first noticed in the 1960s and confidently attributed to the separation of the core from the mantle (Ringwood, 1966). Since that time, scientists have been formulating core formation hypotheses that attempt to explain these observed mantle depletions, and even after four decades, no one theory is agreed upon. In order to explain the various depletions, Wänke (1981) suggested a heterogeneous accretion hypothesis in which early accreting materials were more reduced than later accreting materials, therefore changing an element's tendency to enter the metallic phase. Revised versions of this hypothesis are still strongly supported, most recently by Rubie et al. (2011). Equilibrium metal–silicate partitioning experiments at 1 bar produced partition coefficients [$D_i = c_i(\text{metal})/c_i(\text{silicate})$] that were too large to explain the observed mantle depletions, leading to the inefficient core formation hypothesis (Jones and Drake, 1986), which states that some metal was left behind in the mantle and later oxidized and homogenized. However, over the last 15 yr, partitioning experiments conducted at pressures above 1 bar suggest that the required *D* values of certain siderophile elements may be attainable at higher pressures, leading to the promotion of the magma ocean hypothesis (e.g. Li and Agee, 1996; Righter et al., 1997; Gessmann and Rubie, 2000; Chabot and Agee, 2003; Chabot et al., 2005; Righter et al., 2008; Cottrell et al., 2009; Righter, 2011).

The magma ocean hypothesis gained popularity in the 1980s due to strong geophysical evidence. Numerical simulations of planetary accretion showed that large impacts were common during the later stages of accretion (Wetherill, 1985; Canup and Agnor, 2000). The energy released from these impacts would have produced enough heat to partially or even completely melt Earth, causing localized or global magma ocean(s) (Melosh, 1990; Tonks and Melosh, 1993). The magma ocean scenario outlined by Stevenson (1990) states that liquid metal droplets would separate

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out of the liquid silicate and sink to the peridotite liquidus/solidus region, where final equilibration would occur. The metal would eventually sink through the solid silicate as large diapirs. In this scenario, the last point of metal–silicate equilibration would be at the bottom of the magma ocean, creating considerable need for partitioning experiments at high pressure. The first and most substantial geochemical support for this theory came from experiments on Ni and Co. Li and Agee (1996) determined that D_{Ni} and D_{Co} become less siderophile with increasing pressure and converge to give the required D values at temperatures above 2000 °C and a pressure of $\sim$28 GPa, suggesting a magma ocean of depth 750–1100 km. Other studies have corroborated this result and with the expanded experimental database, concluded that the Ni and Co abundance in the mantle can be explained by equilibrium core formation out of a magma ocean of sufficient depth (e.g. Righter et al., 1997; Li and Agee, 2001; Chabot et al., 2005; Bouhifd and Jephcoat, 2011).

Mo is an ideal element for studying core formation. It is refractory, so there is no need for a volatility correction to determine its abundance in the bulk Earth (assumed to be chondritic). Mo is also moderately siderophile, as opposed to highly siderophile, thus it is present in the mantle in great enough abundance to measure with some accuracy. Yet, compared to Ni and Co, experimental data on Mo is sparse, and parameterizations of the existing data may bias the effects of certain parameters (i.e. pressure, P, and temperature, T) because of the wide range of experimental conditions from various studies in which multiple variables are changed simultaneously. Experiments that employ the typical alumina, magnesia, or graphite capsules are at a disadvantage in this respect because these materials drastically change the silicate (alumina and magnesia) and metal (graphite) compositions during the experiment. Furthermore, MgO contamination from a magnesia capsule has been shown to increase as temperature increases (Righter et al., 2010), making it difficult to distinguish between the two effects; and C addition to the metal phase has been shown to have a large effect on element partitioning (Jana and Walker, 1997b). In this study, we avoided unwanted silicate and metal phase contamination by performing Mo solubility experiments (solubility experiments = pure metal phase), in which the desired metal phase, in this case Mo, was the capsule material. This makes it easy to hold composition constant as changes in P and T are made, in order to elucidate the effects of each variable. In addition, O'Neill et al. (2008) noted that partition coefficients determined directly from partitioning experiments, when extrapolated to the same conditions, do not agree with those calculated from solubility experiments. Our solubility experiments will allow us to address this discrepancy.

In the current study, we present results from the first Mo solubility experiments conducted at pressure. Previous solubility studies, investigating the effect of oxygen fugacity, determined that the valence state of Mo changes from $4+$ to $6+$ at approximately 1 log unit below the iron-wüstite buffer (-1ΔIW) using an anorthite–diopside eutectic composition at 1 bar (Holzheid et al., 1994; O'Neill and Eggins, 2002). Additionally, O'Neill and Eggins (2002) looked at the effect of silicate melt composition in FeO-free systems, and Holzheid et al. (1994) looked at the effect of temperature over the range of 1349–1438 °C. The present study has filled in gaps in the data set by examining the effect of silicate melt composition in systems that contain FeO, and expanding the P–T space covered to 12 GPa and 2200 °C. This was done in order to identify pressure, temperature, and compositional trends, to further constrain the conditions of core formation, and to determine if the observed mantle Mo depletion is compatible with the magma ocean hypothesis. This work is the first part of a comprehensive study that involves both solubility and partitioning experiments in order to fully understand the behavior of Mo in silicate melts.

2. Methods

2.1. Strategy

We conducted a systematic study of Mo solubility in which 43 new experiments were performed. Pressure, temperature, and silicate composition were examined by holding all parameters constant, except the one in question, in order to elucidate the specific effects of each. This was done over a wide range of pressure, temperature, and compositional space: 2.5–12 GPa, 1585–2200 °C, and with silicate compositions that varied in degree of polymerization from peridotite–andesite. The Mo source for all of our experiments was the Mo capsule, and we ran all of our experiments using a multi-anvil press, in contrast to the traditional metal loop technique used in most solubility experiments. This is similar to the approach of Ertel et al. (2006), who used a piston cylinder and multi-anvil to investigate Pt solubility. One advantage of this method is the ability to do experiments at pressure, but the tradeoff with using the multi-anvil is that oxygen fugacity cannot be independently controlled (see Section 3.3 for full discussion).

2.2. Starting materials

Eight different starting silicate compositions were employed in this study, including both natural and synthetic materials (Table 1). The natural compositions included a powdered basalt, NB219, from

Table 1
Compositions of the eight different starting materials and their calculated NBO/T values. Compositions were determined from averaging the probe measurements of each experiment done on the same composition after correcting for the Mo content.

	Peridotite 1	Peridotite 2	Black glass 1	Black glass 2	Ti-rich 1	Ti-rich 2	Basalt	Andesite
SiO_2	45.7	47.2	35.0	35.3	30.8	35.1	48.9	58.5
TiO_2	–	–	13.4	15.5	10.4	14.0	0.6	1.0
Al_2O_3	6.1	7.9	5.2	4.8	4.2	17.1	17.9	19.2
FeO	8.3	12.1	23.4	23.5	9.6	8.7	8.5	5.7
MgO	36.9	28.9	13.9	13.5	41.9	14.2	10.5	2.6
CaO	2.8	4.5	5.1	6.7	2.5	5.3	11.4	5.0
K_2O	–	–	–	–	–	–	–	2.9
MnO	–	–	0.4	0.3	–	0.3	–	0.1
Na_2O	–	–	–	0.2	–	–	2.2	4.0
SrO	–	–	0.2	–	–	0.3	–	–
ZrO_2	–	–	3.0	–	–	3.3	–	–
P_2O_5	–	–	–	–	–	–	–	0.4
Cr_2O_3	–	–	–	0.9	–	–	–	–
TOTAL	99.8	100.7	99.7	100.7	99.3	98.3	99.9	99.4
NBO/T	2.3	1.9	1.7	1.7	3.2	0.7	0.8	0.2