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Valence and metal/silicate partitioning of Mo: Implications for conditions of Earth accretion and core formation

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ABSTRACT

To better understand and predict the partition coefficient of Mo at the conditions of the deep interior of Earth and other terrestrial planets or bodies, we have undertaken new measurements of the valence and partitioning of Mo. X-ray absorption near edge structure (XANES) K-edge spectra for Mo have been measured in a series of Fe-bearing glasses produced at 1 bar and higher PT conditions. High pressure experiments have been carried out up to 19 GPa in order to better understand the effect of pressure on Mo partitioning. And, finally, a series of experiments at very low fO_2 conditions and high Si content metallic liquids has been carried out to constrain the effect of Si on the partitioning of Mo between metallic liquids and silicate melt. The valence measurements demonstrate that Mo undergoes a transition from 4+ to 6+ near IW−1, in general agreement with previous 1 bar studies on FeO-free silicate melts. High pressure experiments demonstrate a modest pressure dependence of D(Mo) metal/silicate and, combined with previous results, show a significant decrease with pressure that must be quantified in any predictive expression. Finally, the effect of dissolved Si in Fe-rich metallic liquid is to decrease D(Mo) significantly, as suggested by previous work in metallurgical systems. The effect of pressure, temperature, oxygen fugacity, metallic liquid composition, and silicate melt composition can be quantified by using multiple linear regression of available experimental data for Mo. Our XANES results show that Mo will be 4+ at conditions of core formation, so only experiments carried out at fO_2 of IW−1 and lower were used in the regressions. Application of predictive expressions to Earth accretion shows that D(Mo) decreases to values consistent with an equilibrium scenario for early Earth core–mantle. The Mo content of the primitive upper mantle (PUM) can be attained by metal–silicate equilibrium involving S-, C-, and Si-bearing metallic liquid, and peridotite silicate melt along the peridotite liquidus near 45 GPa and 3600 °C, late in the accretion process. This conclusion is insensitive to late giant impacts unless the degree of equilibration is very low (<5%).

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1. Introduction

Siderophile elements have an affinity for Fe-rich metallic liquids and thus offer information about the conditions of core formation in terrestrial planets. The distribution of siderophile elements (e.g., Fe, Ni, Co, Mo, W) between metal and silicate melt depends upon the variables of pressure, temperature, silicate melt and metal composition, and oxygen fugacity. As such, an understanding of their partitioning behavior can lead to a better understanding of the conditions surrounding the formation of the metallic core of the Earth and other differentiated planetary bodies for which we have samples of their mantles or basaltic crusts.

Molybdenum is an important siderophile element for several reasons: a) it is refractory which means its abundances in the Earth's mantle and building blocks are better known than most elements -23 ± 7 ppb (Greber et al., 2015), b) it is a moderately siderophile element which means its partition coefficient between the core and mantle is a large number, possibly between 10 and 1000, nonetheless leaving a significant concentration in the man-

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tle, c) it has a well-defined depletion in the Earth's primitive upper mantle compared to chondrites, and d) it carries important isotopic anomalies that may result from metal–silicate partitioning and/or nebular heterogeneity and thus understanding the partitioning behavior can help constrain when Mo isotopic signature was established. Despite these attractions, molybdenum partitioning between metal and silicate melt is more difficult to quantify in natural systems due to uncertainties in (1) its valence at high temperature and pressure, (2) the effect of high pressures, and (3) the effect of dissolved light elements (S, C, and Si) in the metallic liquid.

First, Mo can be stable in two oxidation states (4+ and 6+) in silicate melts and the transition between 4+ and 6+ takes place under oxygen fugacity conditions near the IW buffer at 1 bar (e.g., Holzheid et al., 1994; Farges et al., 2006a, 2006b). Although various studies have tried to constrain the valence (Holzheid et al., 1994; Farges et al., 2006a, 2006b; Wade et al., 2012), the approaches are either indirect with large uncertainties based on solubility or D(Mo) metal/silicate (wt% Mo in metal/wt% Mo in silicate) variation with fO_2, or they are based on measurements on FeO-free and/or SiO_2–Na_2O–Al_2O_3 melts at temperatures of 1100 to 1400 °C. Because 4+ or 6+ cation solubility in a silicate melt will be strongly fO_2 dependent, and solubility is linked to the value of D(Mo) metal/silicate, it is very important to know under what conditions Mo is 4+ and/or 6+ and whether that transition occurs at fO_2s that are within the range of core formation especially at the high temperature and pressure conditions at which the core may have formed.

Second, current models predict high PT metal–silicate equilibrium conditions (30 to 70 GPa; 3000–4000 K) to explain Mo content of the mantle, but most experimental data are acquired from experiments at relatively low PT conditions (<10 GPa, <2300 K), especially relative to moderately siderophile elements such as Ni, Co, or W (Cottrell et al., 2009; Kegler et al., 2008). Mo solubility in silicate melts is strongly dependent upon silicate melt structure and composition (e.g., O'Neill and Eggins, 2002). Melt structure can change significantly at higher pressures (e.g., Poe et al., 2001; Sanloup et al., 2013). Therefore, more partitioning data at the high pressures of a deep magma ocean are needed, and a solid understanding of these effects is needed before quantitative and high precision modeling can be undertaken.

Third, Earth's core contains 10 wt% of a light element that might include all or some of C, S, Si, H, O or N (e.g., Hillgren et al., 2000). The effects of C and S are well understood through various previous studies (Siebert et al., 2011; Wade et al., 2012; Jana and Walker, 1997a, 1997b). Because Si has been proposed as a major component of the Earth's core (Armytage et al., 2011; Shahar et al., 2009; Georg et al., 2007; Ziegler et al., 2010; Savage and Moynier, 2013; Fitoussi et al., 2009; Chakrabarti and Jacobsen, 2010; Dauphas et al., 2015), understanding the magnitude of its effect is important. There is an indication that D(Mo) metal/silicate may be strongly dependent upon the Si content of the Fe metallic liquid (Ono-Nakazato et al., 2007; Tuff et al., 2011), but the magnitude of the effect is unclear, with Tuff et al. (2011) reporting a weaker effect than Ono-Nakazato et al. (2007). Additional work on the effect of Si on D(Mo) metal/silicate is important in achieving confidence in the modeling calculations of Mo in the primitive Earth's mantle.

In order to better understand the partitioning behavior of Mo between metal and silicate melt, we have undertaken a study to a) measure the valence of Mo in experimental glasses equilibrated with Fe metal liquid across a wide range of P–T–fO_2 conditions using XANES spectroscopy, b) isolate the effect of pressure on D(Mo) metal/silicate, and c) isolate the effect of Si on D(Mo) metal/silicate. The results were combined with data from previous studies of D(Mo) metal/silicate (Siebert et al., 2011; Wade et al., 2012; Tuff et al., 2011; Hillgren et al., 1996; Walter and Thibault, 1995; Righter et al., 1997; Jana and Walker, 1997a, 1997b; Wade and Wood, 2001; Righter and Drake, 1999; Righter et al., 2010) and then applied to core formation modeling for the Earth.

2. Experiments

2.1. Partitioning experiments

2.1.1. Piston cylinder (1 GPa)

Metal–silicate equilibrium experiments were carried out in a piston cylinder apparatus to investigate the effect of Si (in Fe liquid) on D(Mo) by comparison to Si-free series of Righter et al. (2010) (Tables S1 and S2). Experiments at 1.0 GPa and 1600 °C were conducted using a non-end-loaded piston cylinder apparatus at NASA-JSC. Experimental details of pressure and temperature control, and the assemblies were presented in Filiberto et al. (2008) and Righter et al. (2006). The sample used in this series of experiments was composed of 70 wt% Knippa Basalt, the composition of which is described in Lewis et al. (1993), 29 wt% Fe and 1 wt% MoO_3 (Table S1; Supplementary Information). Addition of Si metal to the mixture resulted in variable amounts of Si in the metallic liquids which in turn resulted in variable fO_2 (see fO_2 section in "Results" below) in the sample. These mixtures were ground to a powder and mechanically mixed again. Graphite capsules were used, and once samples were under pressure, they were heated to silicate superliquidus temperatures, and then equilibrated at 1600 °C. Run durations were chosen based on equilibration times from previous experiments (Righter et al., 2010; Berthet et al., 2009; Table S2). The samples were then power quenched to a silicate glass which contained large metallic liquid spheres (Fig. 1; cow 3 and cow B1).

2.1.2. Multi-anvil

To investigate D(Mo) at high pressure and temperature conditions, where there are fewer experimental data available, we carried out several experiments in a multi-anvil apparatus, between 12 and 19 GPa (Table S2). Run charges were contained in graphite and single crystal MgO capsules (Table S2). Pressure and temperature in the multi-anvil experiments were generated using COMPRES 10/5 and 8/3 assemblies, and calibrated as reported in Righter et al. (2008) and Shofner (2011). The samples were also power quenched to a silicate glass which contained metallic liquid spheres (Fig. 1; GN24). Some of the experimental glasses were used for XANES measurements as well as partitioning studies. The experiments of Shofner (2011) focused on D(W) metal/silicate partitioning, but Mo was added to many of the experimental runs; the metals were analyzed by EMPA (most contained ~0.3 wt% Mo) and reported in the thesis, but the silicates contained Mo concentrations <100 ppm. We have analyzed experiments carried out at 12 to 16 GPa, where sample starting materials consisted of natural peridotite powder (DMP56 and DMP60; Rudnick et al., 2004), mixed with Fe and W metals (Table S1).

2.2. Mo-bearing glass experiments for valence measurements

To create samples with ample Mo contents to measure XANES spectra and determine valences of Mo, we synthesized some Mo-bearing glasses at 1 bar and also elevated pressure. Two compositions were studied at 1 bar and at variable fO_2–ankaramite and basalt (Table S1). The ankaramite series was doped with 500 ppm Mo, whereas the basalt series was un-doped. For the ankaramite series the powder was pressed into a pellet and hung from a Re wire basket, whereas for the basalt (Fig. 1; Mo cow IW−0.5), the pellet was hung from a Re wire loop. Both of these samples were 3