



Experimental evidence for Mo isotope fractionation between metal and silicate liquids



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ABSTRACT

Stable isotope fractionation of siderophile elements may inform on the conditions and chemical consequences of core–mantle differentiation in planetary objects. The extent to which Mo isotopes fractionate during such metal–silicate segregation, however, is so far unexplored. We have therefore investigated equilibrium fractionation of Mo isotopes between liquid metal and liquid silicate to evaluate the potential of Mo isotopes as a new tool to study core formation. We have performed experiments at 1400 and 1600 °C in a centrifuging piston cylinder. Tin was used to lower the melting temperature of the Fe-based metal alloys to <1400 °C, while variable Fe-oxide contents were used to vary oxygen fugacity in graphite and MgO capsules. Isotopic analyses were performed using a double spike technique. In experiments performed at 1400 °C, the ⁹⁸Mo/⁹⁵Mo ratio of silicate is $0.19 \pm 0.03\%$ (95% confidence interval) heavier than that of metal. This fractionation is not significantly affected by the presence or absence of carbon. Molybdenum isotope fractionation is furthermore independent of oxygen fugacity in the range IW –1.79 to IW +0.47, which are plausible values for core formation. Experiments at 1600 °C show that, at equilibrium, the ⁹⁸Mo/⁹⁵Mo ratio of silicate is $0.12 \pm 0.02\%$ heavier than that of metal and that the presence or absence of Sn does not affect this fractionation. Equilibrium Mo isotope fractionation between liquid metal and liquid silicate as a function of temperature can therefore be described as $\Delta^{98/95}\text{Mo}_{\text{Metal-Silicate}} = -4.70(\pm 0.59) \times 10^5 / T^2$. Our experiments show that Mo isotope fractionation may be resolvable up to metal–silicate equilibration temperatures of about 2500 °C, rendering Mo isotopes a novel tool to investigate the conditions of core formation in objects ranging from planetesimals to Earth sized bodies.

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1. Introduction

The segregation of a metallic core from a silicate mantle is arguably the largest differentiation event in growing planetary objects. Core formation in terrestrial planets may have involved merging of metal cores derived from already differentiated objects added during accretion (Karato and Murthy, 1997; Rubie et al., 2011; Taylor et al., 1993). Alternatively or complementary, it may have been associated with metal–silicate equilibration in a deep magma ocean (e.g. Li and Agee, 1996; Righter and Drake, 1996; Wood et al., 2006). In the former case, the chemical signatures of core formation would reflect those of the relatively low tem-

peratures and pressures characteristic for the planetesimals and planetary embryos constituting the building blocks of the Earth. In the latter case, they would be the result of metal–silicate equilibration at the high pressures and temperatures prevailing in the deep Earth. Most of the information about the conditions of core formation has come from studies of elemental distributions combined with experimental studies of element partitioning between metal and silicate liquids (e.g. Li and Agee, 1996; Righter and Drake, 1996; Wood et al., 2006). As a result of these studies, equilibrium models of core formation in growing planets have become favoured over disequilibrium models, because the observed abundances of siderophile elements in the Earth's mantle match those predicted for metal–silicate equilibration at high temperatures and pressures in a deep magma ocean (Corgne et al., 2008; Righter et al., 2010; Wood et al., 2006). However, more recently it was shown that disequilibrium models provide an equally good match to the observed siderophile element abundances, indicat-

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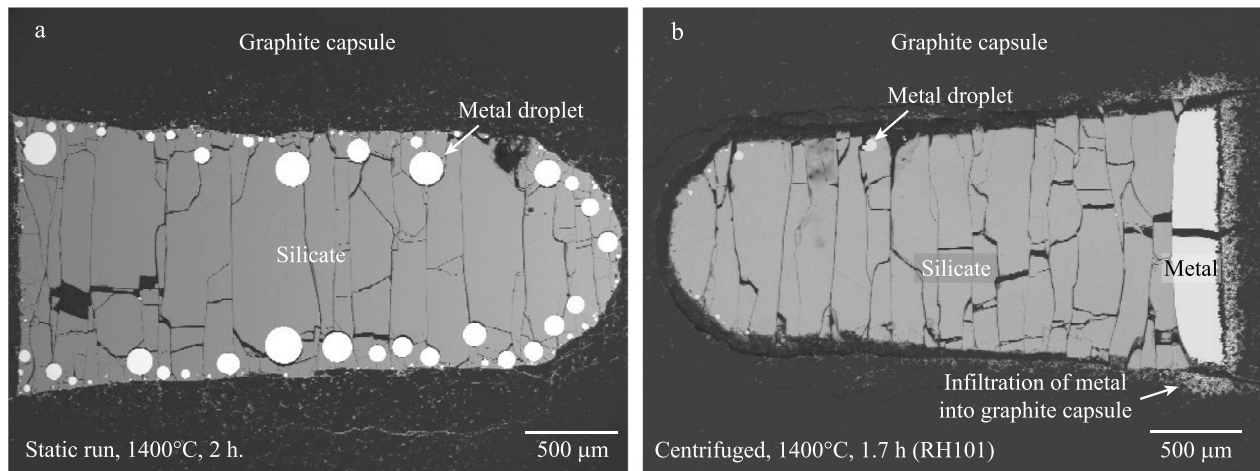


Fig. 1. Backscattered electron images of experiments performed in a standard piston cylinder (panel a) and a centrifuging piston cylinder (panel b). Although metal and silicate liquids can segregate well during standard piston cylinder runs, this is not always the case (panel a). Centrifugation ascertains good separation of the two liquids (panel b), except that surface tension often retains a few metal droplets attached to the capsule wall, particularly in graphite capsules.

ing that elemental partitioning studies alone cannot be used to constrain the degree of metal–silicate equilibration during core formation (Rudge et al., 2010). Furthermore, Rubie et al. (2011) concluded that a model with incomplete re-equilibration of the accreting material best reproduces the element budget of the silicate Earth.

Stable isotopes have emerged as a tool to constrain the conditions of core formation (e.g. Georg et al., 2007; Moynier et al., 2011; Zhu et al., 2002). Mass dependent equilibrium fractionation of isotopes occurs due to differences in the bond stiffness of isotopes between various phases and it is a strong function of temperature (Bigeleisen and Mayer, 1947; Urey, 1947). In principle, isotope fractionation factors could be calculated from vibrational frequencies of the isotopes in both phases (Bigeleisen and Mayer, 1947; Schauble, 2004; Urey, 1947), but these frequencies remain poorly constrained for most elements and phases. Thus, experimental calibration of the magnitude and direction of mass dependent isotope fractionation between metal and silicate is the best method to develop stable isotopes as tracers of core formation. For example, such experimental calibrations showed that Si isotopes fractionate between metal and silicate at conditions relevant for core formation (Shahar et al., 2011), as opposed to Fe and Ni isotopes (Hin et al., 2012; Lazar et al., 2012; Poitrasson et al., 2009).

Molybdenum is an element of interest for core formation. It is refractory in the canonical solar nebula (Fegley and Palme, 1985) and its siderophile behaviour suppresses the necessity for mass balance calculations, because bodies with core mass fractions as small as 5% will have over 90% of their Mo in the metallic core. As such, the isotopic effect is quantitatively transferred to the silicate portion, making analyses of silicate samples sufficient to study metal–silicate fractionation.

We present the first experimental study of Mo isotope fractionation between liquid metal and liquid silicate. To determine whether there is resolvable fractionation, we have performed experiments in a centrifuging piston cylinder, which separated the metal from the silicate prior to chemical processing for isotopic analyses. Controlled variables included temperature, oxygen fugacity, the metal composition, and some variation in silicate melt polymerisation. Although no data are yet available on natural rocks, our results indicate that Mo isotopes constitute a suitable tool to determine in particular temperatures of core formation in planetary bodies.

2. Methods

2.1. Experimental methods

Molybdenum is classified as a moderately siderophile element, but its metal/silicate liquid partitioning may exceed 1000 at oxygen fugacities relevant for core formation (Holzheid et al., 1994; Wade et al., 2012). Such elemental distribution implies that a silicate melt contaminated by ~0.03 vol% metal consists of an approximately 1:1 mixture by mass of metallic Mo and Mo-oxide. Segregation of the metal and silicate liquids prior to isotopic analysis is therefore essential for a reliable interpretation of the isotopic data. In standard piston cylinder experiments, the metal remains sometimes dispersed and we therefore used a centrifuging piston cylinder at ETH Zurich to ascertain good density segregation of the two synthetic liquids (Fig. 1). Such centrifugation does not cause compositional gradients that could induce isotopic fractionation, as can be deduced from the results of centrifuged and static experiments in Hin et al. (2012).

Equilibrium isotope fractionation decreases strongly as a function of temperature, favouring low temperatures to analytically resolve fractionation. We have thus performed experiments at 1400 °C and 1600 °C, at pressures of 1 GPa. The melting temperature of Fe–Mo alloys (>1500 °C) was lowered with Sn to <1400 °C (Okamoto, 1993). Both Sn-bearing and Sn-free experiments were performed at 1600 °C to control for potential effects of Sn on the Mo isotope fractionation factors (Table 1, cf. mixtures B and F). Silicates were prepared from purified oxides, except for Ca, Na and K that were purchased as carbonates and mixed with SiO₂ (and Al₂O₃) to synthesise wollastonite, albite and orthoclase after decarbonation. The silicate and metal fractions were finely mixed into a bulk powder. Graphite as well as MgO capsules were employed to establish whether carbon affects Mo isotope fractionation, because element partitioning may be affected by carbon (Jana and Walker, 1997).

Run durations were varied to assess isotopic equilibration, while oxygen fugacity was varied to potentially assess the effect of Mo⁴⁺/Mo⁶⁺ in the silicate melt on isotopic fractionation. We varied oxygen fugacity by varying the concentration of Fe₂O₃ in the oxide component of the starting material from 6.42 to 44.7 wt% (recalculated to FeO in Table 1; mixtures B, C, D). These runs were all performed at 1400 °C.

A consequence of the siderophile character of Mo is that high Mo concentrations in the metal are required to yield measurable

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