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Molybdenum isotope fractionation between Mo⁴⁺ and Mo⁶⁺ in silicate liquid and metallic Mo

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Mo isotope fractionation; Mo valence state; metal-silicate experiments; core formation

Highlights

- Experiments in gas mixing furnaces show that Mo isotope fractionation between metal and silicate is a function of Mo⁶⁺/Mo⁴⁺ in the silicate liquid
- Tetrahedrally coordinated Mo⁶⁺-species have ~0.5‰ heavier ⁹⁸Mo/⁹⁵Mo than octahedrally coordinated Mo⁴⁺-species in silicate liquid at 1400°C
- Terrestrial core formation most likely left a terrestrial mantle with Mo isotope ratios undistinguishable from the core

Abstract

Previous work has shown that Mo isotopes measurably fractionate between metal and silicate liquids, even at temperatures appropriate for core formation. However, the effect of variations in the structural environment of Mo in the silicate liquid, especially as a function of valence state, on Mo isotope fractionation remained poorly explored. We have investigated the role of valence state in metal-silicate experiments in a gas-controlled furnace at 1400°C and at oxygen fugacities between 10^{-12.7} and 10^{-9.9}, i.e. between three and 0.2 log units below the iron-wüstite buffer. Two sets of experiments were performed, both with a silicate liquid in the CaO-Al₂O₃-SiO₂ system. One set used molybdenum metal wire loops as the metal source, the other liquid gold alloyed with 2.5 wt% Mo contained in silica glass tubes. X-ray absorption near-edge spectroscopy analysis indicates that Mo⁶⁺/ΣMo in the silicate glasses varies between 0.24 and 0.77 at oxygen fugacities of 10^{-12.0} and 10^{-9.9} in the wire loop experiments and between 0.15 and 0.48 at 10^{-11.4} and 10^{-9.9} in the experiments with Au-Mo alloys. Double-spiked analysis

of Mo isotope compositions furthermore shows that Mo isotope fractionation between metal and silicate is a linear function of $\text{Mo}^{6+}/\Sigma\text{Mo}$ in the silicate glasses, with a difference of 0.51‰ in $^{98}\text{Mo}/^{95}\text{Mo}$ between purely Mo^{4+} -bearing and purely Mo^{6+} -bearing silicate liquid. The former is octahedrally and the latter tetrahedrally coordinated. Our study implies that previous experimental work contained a mixture of Mo^{4+} and Mo^{6+} species in the silicate liquid. Our refined parameterisation for Mo isotope fractionation between metal and silicate can be described as

$$\Delta^{98/95}\text{Mo}_{\text{metal-silicate}} = \frac{-1.43(\pm 0.14) \times 10^6 \left[\text{Mo}^{6+} / \Sigma\text{Mo} \right] + 8(\pm 6) \times 10^4}{T^2}$$

Molybdenum isotope ratios therefore have potential as a proxy to constrain the oxygen fugacity during core formation on planetary bodies if the parameterisation of $\text{Mo}^{6+}/\Sigma\text{Mo}$ variation with oxygen fugacity is expanded, for instance to include iron-bearing systems. On Earth literature data indicate that the upper mantle is depleted in heavy Mo isotopes relative to the bulk Earth, as represented by chondrites. As previously highlighted, this difference is most likely not caused by core formation, which either enriches the mantle in heavy Mo isotopes or causes no significant fractionation, depending on temperature and, as we determined here, Mo^{6+} content. We reaffirm that core formation does not account for the Mo isotope composition of the modern upper mantle, which may instead reflect the effect of fractionation during subduction as part of global plate recycling.

1 Introduction

Molybdenum is an element with an oxidation state that is variable in nature and most commonly thought to be Mo^{6+} , Mo^{5+} , Mo^{4+} or Mo^0 (e.g. O'Neill and Eggins, (2002); Farges et al., (2006)). For instance, at the oxygen fugacity of Earth's mantle, hexavalent Mo is the most stable Mo species (Farges et al., 2006; Leitzke et al., 2017; O'Neill and Eggins, 2002). Under conditions at which metallic iron occurs, however, tetravalent Mo has been shown to be the dominant Mo species in silicate liquids (Holzheid et al., 1994; O'Neill and Eggins, 2002; Wade et al., 2012). Consequently, the partitioning of Mo between various phases in planetary bodies is expected to vary as a function of oxygen fugacity. This has been observed experimentally for partitioning between metallic and silicate liquids (Wade et al., 2012; Walter and Thibault, 1995) as well as between silicate minerals and liquids (Leitzke et al., 2017). Farges et al. (2006) furthermore determined that hexavalent Mo forms tetrahedrally coordinated moieties in silicate liquids, while tetravalent Mo is octahedrally coordinated, a conclusion also reached by Calas et al. (2003) and Sawaguchi et al. (1996). This difference in bonding environment between Mo species in different valence states should give rise to mass-dependent fractionation of its isotopes. Higher oxidation and lower coordination states are generally associated with stiffer bonds (Schauble, 2004), which favour the heavier isotopes of an element (Bigeleisen, 1965)

Molybdenum is a refractory element under solar nebula conditions, except under relatively oxidising conditions as evidenced by Mo depletion in refractory metals in calcium-aluminium-rich inclusions in some carbonaceous chondrites (Fegley and Palme, 1985). Its refractory nature accounts for an absence of mass-dependent Mo isotopic variability among a collection of chondrites and iron meteorites, with the exception of CM and CK type carbonaceous chondrites and non-magmatic iron meteorites (Burkhardt et al., 2014). This homogeneity motivated Burkhardt et al. (2014) to propose a mean Mo isotope composition for the Solar System that can be used as reference for the Mo isotope composition of the bulk planets such as Earth. Molybdenum is also a siderophile element, such that it is useful for studying core formation. Experimental metal/silicate partition coefficients of Mo mostly vary between 100 and 1000 (Richter et al., 2010; Wade et al., 2012; Walter and Thibault, 1995), such that generally >98% of the Mo budget in a planetary body resides in its core. Mo isotope compositions of planetary cores are therefore indistinguishable from Mo isotope composition of the bulk body (Burkhardt et al., 2014; Hin et al., 2013). Consequently, an isotopic fractionation effect of core formation is directly recorded by the mantle as a dilute tracer and not affected by mass balance with the core. Determining conditions of core formation with Mo isotopes can hence be done without mass balance models, which require knowledge of currently uncertain Mo contents in the mantle as well as of metal/silicate partition coefficients as a function of pressure, temperature, composition and oxygen fugacity with their inherent uncertainties. A study by Hin et al. (2013) showed experimentally that Mo isotopes do indeed fractionate between metal and silicate, highlighting their potential as a proxy of core formation conditions in planetary bodies. The observed isotopic difference between metal and silicate ($\Delta^{98/95}\text{Mo}_{\text{metal-silicate}}$) was $-0.19 \pm 0.03\text{‰}$ at 1400°C and 1 GPa. Extrapolating to terrestrial core formation at $\sim 3000\text{ K}$ (Wade and Wood, 2005), this work implies differences in $^{98}\text{Mo}/^{95}\text{Mo}$ between silicate mantle and chondrites of ~ 0.05 . This difference is close to currently achievable analytical precision ($\sim 0.04\text{‰}$ 2sd, e.g. Willbold et al. (2016)).

Studies of the Mo isotope composition of (ultra-)mafic rocks have since led to variable conclusions about the average Mo isotope composition of the silicate portion of the Earth. Bezard et al. (2016) found that the $^{98}\text{Mo}/^{95}\text{Mo}$ of the mid-ocean ridge basalts (MORB) they studied as representative of the depleted mantle, uncontaminated by recycled crustal sediments, was slightly sub-chondritic by $0.05 \pm 0.03\text{‰}$ relative to the mean Mo isotope composition of the Solar System proposed by Burkhardt et al (2014). Compared to that same Solar System mean, Liang et al. (2017) found MORB to be $0.16 \pm 0.03\text{‰}$ super-chondritic, but their data also hint at the mantle potentially being slightly sub-chondritic by $0.06 \pm 0.07\text{‰}$ based on their observations on ultra-mafic xenoliths from the sub-continental lithospheric mantle. Greber et al. (2015) inferred a similar difference of $0.05 \pm 0.06\text{‰}$ between Earth's mantle and chondrites based on analysis of Archaean komatiites. Although the apparent inconsistencies in MORB data have yet to be settled, it appears that the terrestrial upper mantle might have a slightly sub-chondritic Mo isotope composition (Willbold and Elliott, 2017). A potentially $\sim 0.05\text{‰}$ sub-chondritic modern mantle would thus be enriched in light Mo isotopes by $\sim 0.10\text{‰}$ relative to a post-core formation mantle.

Given how small these isotopic differences are, it is important to ascertain that there are no currently known scenarios under which core formation can cause a sub-chondritic post-core formation mantle. Unfortunately, the proportions of Mo^{6+} and Mo^{4+} in the silicate liquids in equilibrium with iron-rich metals were not determined in Hin et al. (2013). To calibrate the potentially important effect of oxygen fugacity on Mo isotope fractionation between metal and silicate, we have equilibrated metallic Mo with silicate liquids with variable $\text{Mo}^{6+}/\text{Mo}^{4+}$.

2 Methods

2.1 Experimental

We performed experiments with Mo wire loops at 1400°C in gas-controlled furnaces at a range of oxygen fugacities at which variable Mo^{6+} abundances occur in equilibrium with metallic Mo (Farges et al., 2006; Holzheid et al., 1994; O'Neill and Eggins, 2002). Molybdenum wire loops were made from ribbons of Mo metal that were cut from a sheet of high purity Mo metal. The loops were equilibrated with an initially Mo-free silicate liquid containing 43.0% SiO_2 , 44.0% CaO and 13.0% Al_2O_3 by weight, which is slightly modified from the CAS1 and CAS2 compositions of O'Neill and Eggins (2002). These Ca-rich starting mixtures were chosen because their liquids are relatively depolymerised. A depolymerised structure greatly reduces the presence of metal nuggets in the silicate melt (O'Neill and Eggins, 2002), which is important to prevent overprinting of the metal-silicate fractionation factor due to metal contamination in the silicate. The silicate starting material was prepared from purified SiO_2 , Al_2O_3 and CaCO_3 powders that were ground and mixed in an agate mortar. These mixtures were decarbonated, followed by heating to 1400°C to exceed the liquidus. After quenching, the two starting glasses were again melted, quenched and ground to obtain homogeneous silicate starting mixtures.

Additionally, two Mo^{6+} -bearing glasses were prepared as standards for X-ray absorption near-edge spectroscopy (XANES) to minimise the effects of bonding environment and matrix elements on the amplitude of the pre-edge feature. They consisted of the two silicate starting mixtures used in the two sets of experiments doped with 1400 ppm and 3200 ppm MoO_3 in SiO_2 -rich and CaO -rich mixtures, respectively. These mixtures were homogenised in a pestle and mortar prior to melting in air at 1400°C followed by quenching.

The wire loop experiments contained solid metal and liquid silicate. In addition to these, we performed a second set of experiments for which we selected a different system containing an Au-Mo alloy and SiO_2 -rich silicate that are both liquid at 1400°C. There are indications that the effects of metal alloy composition may affect isotopic fractionation between metal and silicate (Elardo and Shahar, 2017; Shahar et al., 2015), so we suspected that this system might have a different fractionation factor, but that any effect of Mo valence state in the silicate should be independent of such potential effects.

The experiments with Au-Mo alloy were performed in open-ended SiO_2 glass tubes. They contained a more SiO_2 -rich silicate starting material of 62.0% SiO_2 , 29.3% CaO and 8.7% Al_2O_3 to increase the activity of SiO_2 from ~0.1 in the other starting material to ~0.9 (Eriksson and Pelton, 1993)

and thereby minimise reactivity with the SiO₂ glass tubes. One experiment with this SiO₂-rich starting material was performed on a Mo wire loop to investigate potential effects of silicate composition on Mo isotope fractionation. In the Au-Mo alloy experiment, the silicate was equilibrated with alloy beads of 97.5% Au and 2.5% Mo by weight. The alloy beads were pre-synthesized by heating a mixture of pure Au and Mo powders in a SiO₂ glass tube to 1400°C, i.e. ~150°C above the alloy liquidus (Massalski et al., 1986), for about 38 hours at an oxygen fugacity of 10^{-11.4}, i.e. 1.7 log units below the iron-wüstite buffer (IW-1.7; we will use this abbreviation in the remainder of the text to indicate oxygen fugacity). Upon quench, the alloy separated into various small beads.

All experiments were performed at 1400°C in a gas-controlled tube furnace at Imperial College London. Run durations varied from ~34 to 67 hours to ensure elemental and isotopic equilibrium, as assessed from the following previous works. Hin et al. (2013) observed that Mo isotope equilibrium between liquid metal and liquid silicate was attained in <1.5 hours at 1400°C. To choose an appropriate run duration for our Mo wire loop experiments we used an observation of O'Neill and Eggins (2002). Based on their time series experiments, elemental equilibrium in wire loop experiments was attained within 4 to 14 hours. Mo isotope equilibrium should thus be reached well within 14 hours in all experiments we performed. We have opted for ~34 to 67 hour run durations because O'Neill and Eggins (2002) observed that, compared to run durations of 14 hours, experiments run for ~45 hours resulted in better separation of metal nuggets from the silicate liquid. Such separation is important to reduce contamination effects on the isotope fractionation factor.

The oxygen fugacity of the experiments varied between IW-0.2 and IW-3.0 and was set by fluxing variable CO₂/CO gas ratios at a flow rate of 100 ml min⁻¹. The temperature profile in the furnace was carefully checked using a height adjustable Pt-Rh thermocouple and all samples were placed in the hotspot. Oxygen fugacity was found accurate to better than 0.05 log units based on calibration with an yttria-stabilised zirconia sensor (Mendybaev et al., 1998) and FeO solubility in the An-Di eutectic at oxygen fugacities of 10^{-11.1} and 10^{-12.3} (IW-1.4 to -2.6). All samples were loaded at 600°C, followed by heating at 200°C/hour to 1400°C. At the end of each run, samples were drop-quenched into a water bath. We note here that the wire loop experiment at the highest *f*O₂ of IW-0.2 had to be performed twice, because the wire loop ruptured under its own weight during the first run. Such failure did not occur in any other experiment. We therefore speculate that an oxygen fugacity of IW-0.2 may have been so close to the Mo-MoO₂ reaction (occurring at ~IW+0.5) that it oxidised the wire, causing it to weaken and fail.

2.2 X-ray analysis

Au-Mo alloy compositions were analysed on a Cameca SX-100 microprobe at the University of Bristol after synthesis prior to the experiments, using pure Au and Mo metals as standards and a 20 kV, 10 nA beam with 10 µm spot size. Quenched glass from both sets of metal-silicate equilibration experiments was separated from coexisting metal, embedded in epoxy and polished. Elemental compositions of all glasses were analysed on a Cameca SX-100 either at the University of Bristol or at

the Natural History Museum. They were analysed with a 40 nA beam and 20 μm spot size. Under these conditions the glass was observed to be stable and count rates were sufficiently high to determine Mo contents. The elements Ca, Al and Si were analysed for 20 s using wollastonite and corundum as standards, while Mo was analysed for 240 s on two spectrometers resulting in a detection limit of approximately 70 ppm. Typically, these measurement conditions lead to a standard deviation of about 60 ppm on a single analysis for glasses with contents above ~ 300 ppm. Between eight and 15 spots were analysed on each sample.

Molybdenum oxidation state variations were investigated by XANES at the Diamond Light Source synchrotron facility. Beam line I18 was operated with a Si<111> monochromator and an incident energy around 20 keV. Platinum coated Si mirrors were used for improved reflectivity in this energy range compared to common Si mirrors. All samples were analysed in fluorescence mode using a 13-element Ge detector with a Zr foil filter and a window applied at a fluorescent energy of 16.90-17.80 keV. We performed scans from 19950 to 20400 eV incident energy with 0.5 eV steps over the entire energy range and a dwell time of 0.29 s. The penetration length of X-rays at the Mo K-edge is sufficiently large that the beam energy could be calibrated by simultaneous analysis of Mo foil, which was used as reference to correct for monochromator drift during analysis of samples. Test measurements were performed for 60 and 90 s at two spots on a Mo^{6+} -bearing glass to investigate whether redox reactions occurred during analysis due to interaction with the X-ray beam. The intensity at the energy corresponding to the pre-edge feature (20005 eV) did not change during these two measurements, implying that our analyses are not affected by such beam damage.

Energy scans were post-processed in the Athena software package (Ravel and Newville, 2005). All scans were corrected for background with a linear interpolation. Sample spectra were subsequently aligned with the energy spectrum of the reference Mo foil and normalised to the intensity obtained on the reference foil. For all sample glasses, the relative intensity at the energy of the pre-edge feature (20005 eV) was determined as a deviation from a fit to the absorption edge step. The edge step for each spectrum was fitted up to a normalised height of 0.8 (excluding the range 19996.8 – 20012.6 eV, where the pre-edge peak occurs) using a Gaussian function (centre ~ 20250 eV, HWHM ~ 50 eV). This procedure is analogous to that used for Fe by Berry et al. (2018). These intensity deviations were compared to those of Mo^{6+} -bearing standards to determine abundances of Mo^{6+} relative to all other Mo species ($\text{Mo}^{6+}/\Sigma\text{Mo}$). This procedure is analogous to that used in Burnham et al. (2015). As we do not have a spectrum for glass containing only Mo^{4+} , we do not exactly know whether it contributes a minor signal to the background intensity at the energy of the pre-edge feature. We therefore calculated the intensity deviations of the pre-edge feature in two different manners. One approach calculated the intensity deviation of the pre-edge feature relative to a pure background signal, i.e. assuming no contribution of Mo^{4+} . The other approach allowed for a minor, unconstrained contribution to the peak height by Mo^{4+} . We present the mean of the $\text{Mo}^{6+}/\Sigma\text{Mo}$ values obtained by these two approaches and give errors that reflect the range of these different results (Table 1).

Metal contamination occurred in the glass areas that had been in contact with the metal during the experiments. For samples indicated with superscripts *d* and *e* in Table 1, this contamination was inadvertently not avoided during XANES analysis and these spectra were too contaminated to obtain information on relative Mo⁶⁺ abundances. We calculated Mo⁶⁺/ΣMo in these samples based on their oxygen fugacity by fitting Mo⁶⁺/ΣMo of the uncontaminated spectra and their oxygen fugacities to a similar thermodynamic model as O'Neill and Eggins (2002):

$$Mo^{6+} / \Sigma Mo = \frac{1}{1 + 10^{n/4 \log fO_2 + a}} \quad (1)$$

where *n* is the number of electrons exchanged in the redox reaction (e.g. two for a change from Mo⁶⁺ to Mo⁴⁺) in the silicate liquid and *a* is a fitted parameter relating to melt composition.

2.3 Isotope ratio analysis

Molybdenum isotope compositions were determined for all glasses. Metal-free glass material was handpicked under a binocular microscope; metal contamination was restricted to the areas in direct contact with the metal phase during the experiments. Owing to the high Mo metal/silicate partition coefficient, the metal dominated the Mo isotope composition of the bulk system in all experiments. The Mo isotope compositions of metal phases were analysed on selected samples to verify their homogeneity. Chemical protocols are based on those presented in Willbold et al. (2016), which are summarised below.

Silicate samples were weighed in pre-cleaned PFA beakers followed by addition of a ⁹⁷Mo-¹⁰⁰Mo double spike. The samples were digested in 3:1 mixtures of ~15.5 M HNO₃ and ~28 M HF on a hotplate, usually for two days. After drying, they were treated with about two drops each of ~15.5 M HNO₃ and 30% H₂O₂ to attack any organic material and then re-dissolved in 6 M HCl prior to drying and re-dissolution in 3 M HCl in preparation for ion exchange chromatography. Pure Mo metal samples were dissolved in 6 M HCl with a few drops of ~15.5 M HNO₃, while Au-Mo alloys were digested in aqua regia. Double spike was added to an aliquot of these metal sample solutions prior to drying, re-dissolving in 6 M HCl and subsequently in 3 M HCl. Our ion exchange chromatography requires adding ascorbic acid to reduce Fe³⁺ to Fe²⁺ prior to loading on an Eichrom 200-400 mesh 1x8 anion exchange resin, in order for Fe to elute immediately upon loading (Willbold et al., 2016). As all experiments were designed to be iron-free, minimal quantities of ~50 µl 1 M ascorbic acid were added to the samples analysed here, which compares to ~250 µl ascorbic acid for 200 mg of natural basaltic rock powder. Gold was separated from Mo because it is strongly retained on the resin throughout the ion exchange protocol. Although all matrix elements present in the experimental charges should have separated after eluting with 3 M HCl, the further steps used in our regular chemistry procedure of eluting with 0.5 M HCl – 0.5% H₂O₂, and 1 M HF were also followed to remove any contaminants prior to collecting Mo in 1 M HCl. Molybdenum cuts were then dried, and any resin material that had run through was attacked

with two drops each of ~15.5 M HNO₃ and 30% H₂O₂ prior to dissolution in a drop of ~15.5 M HNO₃ that was subsequently diluted to a mixture of 0.4 M HNO₃ and 0.05 M HF for analysis.

Isotopic compositions were measured on a Thermo Finnigan Neptune (s/n 1020) multi-collector inductively coupled plasma mass spectrometer at the University of Bristol. Sample solutions containing approximately 150 ppb sample Mo were aspirated with a 50 µl min⁻¹ Savillex PFA nebuliser into a Cetac Aridus desolvator, resulting in total Mo intensities of ~1.5-3×10⁻¹⁰ A. The instrument was operated in low resolution mode with a normal sampler and H-skimmer cone and, in addition to ^{92,95,96,97,98,100}Mo, we collected ⁹¹Zr as well as ^{99,101}Ru to monitor possible isobaric interferences. We applied a ^{95,97,98,100}Mo double spike inversion on a cycle-by-cycle basis. Ruthenium is the only element with isobaric interference on any of these four Mo isotopes, but the monitored Ru/Mo ratios were always <2×10⁻⁵, which leads to insignificant interference corrections. Residual non-exponential fractionation during analysis was corrected for with an external normalisation to the session mean of the reference standard NIST SRM3134, as previously done, for instance, in Hin et al. (2013).

Molybdenum isotope compositions are reported as the relative difference of isotope ratios to the reference standard (delta notation), following IUPAC recommendations (Coplen, 2011): $\delta^{98/95}Mo_{SRM3134} = \left(\frac{{}^{98}Mo / {}^{95}Mo}{\text{sample}} \right) / \left(\frac{{}^{98}Mo / {}^{95}Mo}{SRM3134} \right) - 1$. The presented data are means of repeated analysis and are reported in per mil. Uncertainties are given as standard error of the mean (2*se*; i.e. 2*s*/√*n*) and represent analytical variability. We have used the standard deviation (2*s*) of geological reference material JB-2 of 0.028‰ as best estimate of the population standard deviation. This uncertainty is based on a total of twelve analyses from three JB-2 digestions and agrees well with the 2*s* of our NIST SRM3134 analyses (0.031‰, *n*=119). The mean $\delta^{98/95}Mo_{SRM3134}$ of JB-2 during this study is 0.046±0.008‰ (2*se*, *n*=12), which agrees well with the value of 0.05±0.03‰ (2*s*, *n*=4) obtained by Willbold et al. (2016). We also analysed molybdenite sample AJ011, for which we obtained a Mo isotope composition of -0.687±0.009‰ (2*se*, *n*=9) which compares to values of -0.70±0.06‰ (2*s*, *n*=12) in Hin et al. (2013) and -0.7±0.1‰ (2*s*) in Greber et al. (2011).

Together with a piece of metal, left-over shards of silicate glass from samples IW-0.2, IW-0.5 and IW-1.7 were also analysed for mass-independent isotopic anomalies to determine nuclear field shift effects, which are usually visible between even and odd masses (Bigeleisen, 1996a; Bigeleisen, 1996b; Schauble, 2007). The chemical protocol was identical to that described above, except that no ⁹⁷Mo-¹⁰⁰Mo double spike was added to the samples. All samples were also digested and processed with materials that had not previously been used for spiked samples. Our samples have high Mo contents and a simple matrix consisting principally of Al, Si, Ca. We therefore used a Mo ICP standard solution (CPI) as secondary solution instead of a geological reference material to verify the accuracy of our analyses. NIST SRM3134 was used as reference standard for external normalisation. All analyses were internal normalised to a ⁹⁸Mo/⁹⁴Mo reference ratio of 2.630639 using the exponential law. Results are

presented as epsilon-units, which are calculated in the same manner as delta-values but presented in parts per ten-thousand instead of per mil.

3 Results

All glasses were found to have homogeneously distributed elemental abundances based on multiple spot analyses, confirming previous observations that ~40-65 hour run durations are ample for chemical equilibrium in these types of experiments (Holzheid et al., 1994; O'Neill and Eggins, 2002). The mean compositions and standard errors of the glasses are presented in Table 1 and Mo contents are plotted against oxygen fugacity in Figure 1. Molybdenum contents in experiments performed on Mo wire loops, which are represented by squares in Figure 1, decrease from 21043 ± 26 ppm (2 σ based on multiple spot analyses) to below the 70 ppm detection limit with decreasing oxygen fugacity. Glasses equilibrated with Au-Mo alloys in SiO₂-glass tubes, represented as circles in Figure 1, have Mo contents ranging from 1354 ± 15 ppm to below the detection limit of our microprobe analyses. Glass from the experiment with the SiO₂-rich starting mixture on a Mo wire loop (open square in Figure 1) has a Mo content of 530 ± 14 ppm. This concentration compares to 2675 ± 66 ppm in a wire loop experiment at the same oxygen fugacity (IW-0.8), but with a silicate liquid containing less SiO₂ and more CaO. It furthermore compares to 75 ± 11 ppm in an experiment equilibrated with Au-Mo alloy at the same oxygen fugacity. Considering that the silicate liquid compositions of the SiO₂-rich wire loop experiment and the Au-Mo alloy experiment are similar, and that the Au-Mo alloy contains about 2.5% Mo by weight, the difference in Mo content implies that the activity coefficient of Mo in Au is about 0.35.

The spectra obtained by XANES show a resolvable pre-edge feature indicative of Mo⁶⁺ in all wire loop experiments with the Ca-rich silicate that were performed at an oxygen fugacity more oxidising than IW-1.4 (Figure 2a). The relative amplitudes of the pre-edge features in these experiments indicate an increase in Mo⁶⁺/ΣMo from 0.55 to 0.77 (see also Table 1). Spectra from glasses of the same type of experiments but performed at oxygen fugacities between IW-1.4 and IW-3.0 show contamination by metallic (or carbide) particles, as is easily identified from the sharp peak in all these spectra at an energy of ~20035 eV directly following the edge (Figure 2a). This contamination has obscured the pre-edge feature, except in the spectrum of the experiment performed at a fO_2 of IW-2.3 where the contamination was sufficiently small that a minor pre-edge feature could be identified. The relative amplitude of the pre-edge feature of this spectrum corresponds to Mo⁶⁺/ΣMo of 0.44. However, after subtracting a minor metallic contribution based on the spectrum of the Mo reference foil, we obtain a more realistic value of 0.24, which we use for the remainder of our work (Figure 2a, Table 1). Relative Mo⁶⁺ abundances on all other wire loop experiments were obtained through interpolation using a thermodynamic fit (see section 2.2) through the oxygen fugacity and relative Mo⁶⁺ abundances of the samples described above (Figure 3).

Glass from experiments equilibrated with Au-Mo alloys in SiO₂ glass tubes do not display significant metal contamination. The spectra of all these glasses have resolvable pre-edge features that

correspond to an increase in $\text{Mo}^{6+}/\Sigma\text{Mo}$ from 0.15 to 0.48 for an increase in oxygen fugacity from IW-1.7 to IW-0.2 (Figure 2b, Table 1).

Isotopic compositions of metals have been determined for four wire loop and four Au-Mo alloy experiments. For both types of experiments, the isotopic compositions of the four metals were within error of each other, as expected from the fact that they derive from the same metal source and that the metal dominates the isotopic composition of the bulk system due to the high metal/silicate partition coefficient of Mo. We therefore used the mean $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of $-0.098\pm0.005\text{‰}$ for the Mo wires and $-0.381\pm0.006\text{‰}$ for the Au-Mo alloys (Table 2) as reference metal compositions for calculating metal-silicate fractionation factors. We also note that the mean Mo isotope composition of the Au-Mo alloys is within error of the $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of $-0.39\pm0.02\text{‰}$ determined in Hin et al. (2013) for their starting mixture, which was prepared with the same Mo metal powder as used in this study.

Glasses from the Mo wire loop experiments have heavier $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ than the metal it coexisted with, varying between $0.215\pm0.008\text{‰}$ and $-0.011\pm0.012\text{‰}$ (Table 2). Metal-silicate fractionation factors ($\Delta^{98/95}\text{Mo}_{\text{metal-silicate}}$) in most wire loop experiments thus vary from $-0.313\pm0.009\text{‰}$ to $-0.087\pm0.013\text{‰}$ (Table 2, Figure 4). Glass from one wire loop experiment at the lowest oxygen fugacity, however, is depleted in heavy Mo isotopes compared to coexisting metal, given a $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of $-0.302\pm0.012\text{‰}$ and a fractionation factor of $0.203\pm0.013\text{‰}$ (Table 2).

The $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of glass chips from experiments equilibrated with Au-Mo alloys, in contrast, are always lighter than those of their coexisting metal alloys, ranging from $-0.468\pm0.007\text{‰}$ to $-0.679\pm0.008\text{‰}$ (Table 2). Metal-silicate molybdenum isotope fractionation factors in these experiments with Au-Mo alloys thus vary between $0.087\pm0.009\text{‰}$ and $0.298\pm0.010\text{‰}$ (Figure 4).

Finally, our analysis of unspiked samples did not result in resolvable mass-independent anomalies (Table 3, Figure 5). This result implies that nuclear field shift effects on Mo isotope fractionation are smaller than our precision of about 0.1 epsilon-units and that our assessment of mass-dependent Mo isotope fractionation is not affected by such nuclear field shifts.

4 Discussion

4.1 Molybdenum valence states as a function of oxygen fugacity

The Mo contents in our wire loop experiments are similar to those obtained by O'Neill and Eggins (2002) for their CAS1 and CAS2 compositions at the same oxygen fugacity, as expected given the similarity in compositions. An initial investigation of the slope of 1.31 on a log Mo content against log $f\text{O}_2$ plot (Figure 1) suggests mixed Mo^{4+} and Mo^{6+} valence states, which would have ideal slopes of 1.0 and 1.5, respectively.

Our XANES analyses confirm these mixed valence states (Figures 2 and 3). They agree with previous studies (Farges et al., 2006; Holzheid et al., 1994; O'Neill and Eggins, 2002) in that the spectra imply that Mo^{6+} gradually diminishes with decreasing oxygen fugacity from an abundance of 77% to 24% between oxygen fugacities of IW-0.2 and IW-2.3. Our scans cover too short an energy range to

extract information about bond length and, by extension, details on species other than Mo^{6+} . However, as we show in Figure 3, both the wire loop and Au-Mo alloy experiments fit a change in oxidation state by two electrons according to equation (1), i.e. a change from Mo^{6+} to Mo^{4+} . This model is not parameterised for silicate composition and therefore applies only to silicate composition of wire loop experiments with CaO-rich compositions. Figure 3 also shows that the $\text{Mo}^{6+}/\Sigma\text{Mo}$ we calculated based on our XANES analysis compare well to a model of O'Neill and Eggins (2002) that includes an empirical CaO and MgO content parameterisation (see their equations 20-22 and Table 6 for their thermodynamic model and their Table 8 for the CaO- and MgO-parameterisation). This CaO- and MgO-parameterised model of O'Neill and Eggins (2002) yields maximum 0.08 higher $\text{Mo}^{6+}/\Sigma\text{Mo}$ for the CaO contents of our glasses in the wire loop experiments. We have therefore used their model to estimate the relative Mo^{6+} abundance of one wire loop experiment with an SiO_2 -rich, CaO-poor silicate liquid. The XANES spectrum of this sample was too contaminated for a direct determination of $\text{Mo}^{6+}/\Sigma\text{Mo}$. The CaO- and MgO-parameterised model estimates 0.55 but accounting for the slight offset between that model and our $\text{Mo}^{6+}/\Sigma\text{Mo}$ determined from XANES results (cf. Figure 3) we estimate a relative Mo^{6+} abundance of 47% (Table 1).

The lower Mo^{6+} abundances in the experiments with Au-Mo alloys compared to wire loop experiments at the same $f\text{O}_2$ (Figure 3) can be attributed to the higher polymerisation of the silicate liquids equilibrated with Au-Mo alloys in open-ended SiO_2 -glass tubes. Farges et al. (2006), for instance, suggested that such higher polymerisation lowers the solubility of Mo in silicate liquid because of the reduced availability of non-bridging oxygen ions, although O'Neill and Eggins (2002) hinted at the importance of molecular complexes of Mo with Ca and Mg.

We also note here that the edge of the XANES spectrum we obtained for the most reduced, wire loop experiment at a $f\text{O}_2$ of IW-3.0 has a strikingly shallower edge slope than all other spectra. One plausible explanation for this relatively shallow slope is self-absorption of the X-ray beam on Mo-rich nuggets in the silicate glass. Although we observed metallic particles in the glass, the volume fraction is likely not large enough to explain the shallow slope solely by self-absorption. This can be concluded from the observed isotope fractionation (Table 2, Figure 4), because any isotopic difference between glass and metal would be erased by $>0.04\%$ metal contamination by volume in the glass. Furthermore, our attempts to fit a Mo metal spectrum to the extended range of energies we analysed beyond the edge of this XANES spectrum have failed to reproduce the observed features at these energies of ~ 20020 to ~ 20200 , unlike the case for the other contaminated spectra (e.g. compare the spectra of IW-2.0 and IW-3.0 in Figure 2). Instead, some other Mo compound is likely responsible for the self-adsorption phenomenon, which we attribute to molybdenum carbide (Mo_2C). This phase is likely to occur given the affinity of these elements for each other at the reducing conditions of this experiment, in which the gas in the furnace consisted nearly 100% CO with which Mo metal can react to form molybdenum carbide. We were unable to find a model reference spectrum for Mo_2C to compare the spectrum of this glass. However, wavelength dispersive scans (WDS) on our electron microprobe on polished, gold-

coated pieces of metal from experiments IW-3.0, IW-2.0 and IW-1.1 resulted in a distinct carbon peak for IW-3.0, while the other metal pieces lack this feature (Figure 6). We estimate the carbon peak represents approximately 5 wt% carbon based on the depression in the Mo-M_L peak height of the carbon-rich sample relative to the reference. This estimated carbon content corresponds well to the 6 wt% carbon in Mo₂C, indicating that this piece of Mo metal had reacted to Mo₂C. Owing to this observation, we have excluded this sample from discussion of isotopic fractionation factors in the remainder of this work and their results are only displayed in Table 2.

4.2 Isotopic fractionation

We have shown that decreasing oxygen fugacity results in increasing Mo⁴⁺ at the expense of Mo⁶⁺ in the glasses of our experiments equilibrated with metallic Mo (Figure 3), as interpreted previously (Farges et al., 2006; O'Neill and Eggins, 2002). On a theoretical basis, octahedrally coordinated Mo⁴⁺ (i.e. MoO₆⁸⁻) likely has weaker Mo-O bonds than tetrahedrally coordinated Mo⁶⁺ (i.e. MoO₄²⁻) whose bonds are more covalent (Farges et al., 2006). Thus, Mo isotope fractionation between metal and Mo⁶⁺-bearing silicate is expected to be larger than fractionation between metal and Mo⁴⁺-bearing silicate. We can estimate the magnitude of this difference by taking advantage of the fact that the difference between these fractionation factors yields an isotope fractionation factor between Mo⁶⁺-bearing silicate and Mo⁴⁺-bearing silicate. We can quantitatively predict the magnitude of such Mo⁶⁺-Mo⁴⁺ fractionation by using the ionic model of Young et al. (2015), which has been shown to yield good first-order estimates of isotope fractionation among silicate and oxide minerals. The ionic model uses the valence difference between the bonding cation (z_i ; Mo⁴⁺ or Mo⁶⁺) and anion (z_j ; O²⁻) in a silicate or oxide and the interatomic distance of the bond (r) as main variables to determine bond force constants (K_f , in N m⁻¹):

$$K_f \approx \frac{z_i z_j e^2 (1-n)}{4\pi\epsilon^0 r^3} \quad (2)$$

where e is the charge of an electron in Coulomb, ϵ^0 the vacuum permittivity and n refers to a Born-Mayer constant for repulsion for which we adopt a value of 12 following Young et al. (2015). Using Mo-O bond lengths of 177 nm for tetrahedrally coordinated Mo⁶⁺ and 201 nm for octahedrally coordinated Mo⁴⁺ from Farges et al. (2006), we obtain force constants of 5492 and 2496 N m⁻¹, respectively. These force constants can be used to calculate an isotopic fractionation factor:

$$\Delta^{98/95} Mo_{Mo^{6+}-Mo^{4+}} \approx \frac{1}{24} \left(\frac{\hbar}{kT} \right)^2 \left(\frac{1}{m_1} - \frac{1}{m_2} \right) (K_{f,Mo^{6+}} - K_{f,Mo^{4+}}) \quad (3)$$

where $\hbar$ is the reduced Planck constant ($h/2\pi$), k is the Boltzmann constant, T the temperature in K, and m_1 and m_2 are the masses of ⁹⁵Mo and ⁹⁸Mo in kg. For 1400°C, this model predicts Mo⁶⁺-bearing species to be enriched in heavy Mo isotopes by 0.5‰ relative to Mo⁴⁺-bearing species in silicate glass. In other words, based on first-order estimates we may expect the metal-silicate fractionation factors of our experiments to vary by up to ~0.5‰ depending on Mo⁶⁺/ΣMo.

4.2.1 Wire loop experiments

The metal-silicate fractionation factors ($\Delta^{98/95}\text{Mo}_{\text{metal-silicate}}$) of wire loop experiments display a negative correlation with $\text{Mo}^{6+}/\Sigma\text{Mo}$, varying from $-0.087\pm0.013\text{‰}$ at $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.24 to $-0.313\pm0.009\text{‰}$ at $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.71 (Figure 4a, filled squares). The correlation is an important first order observation in that it implies that Mo isotope fractionation between metal and silicate is indeed a function of the structural environment, i.e. valence and coordination state of Mo in a silicate liquid. Moreover, it implies that fractionation of Mo isotopes between metal and silicate can be described as a linear mixture of a hypothetical Mo isotope fractionation factor between metal and octahedrally coordinated Mo^{4+} ($\Delta^{98/95}\text{Mo}_{\text{Mo}^0-\text{Mo}^{4+}}$) and one between metal and tetrahedrally coordinated Mo^{6+} ($\Delta^{98/95}\text{Mo}_{\text{Mo}^0-\text{Mo}^{6+}}$). A linear fit through the wire loop data in Figure 4a yields a slope of -0.51 ± 0.05 , excluding two outliers at $\text{Mo}^{6+}/\Sigma\text{Mo}$ 0.63 and 0.77 (MWSD = 1.2), with end-member fractionation factors of $+0.03\pm0.02\text{‰}$ for $\Delta^{98/95}\text{Mo}_{\text{Mo}^0-\text{Mo}^{4+}}$ and $-0.48\pm0.07\text{‰}$ for $\Delta^{98/95}\text{Mo}_{\text{Mo}^0-\text{Mo}^{6+}}$. The difference of $-0.51\pm0.07\text{‰}$ between these two end-member fractionation factors is in keeping with the fractionation factor of 0.5‰ predicted with the ionic model of Young et al. (2015). Such agreement between theoretical model predictions and experimental observations provides great confidence that substantial fractionation may be expected between Mo^{6+} -bearing and Mo^{4+} -bearing minerals or melts in nature. According to our findings, Mo isotope fractionation between metal and silicate can thus be described by the following equation:

$$\Delta^{98/95}\text{Mo}_{\text{metal-silicate}} = \frac{-1.43(\pm0.14)\times10^6\left[\text{Mo}^{6+}/\Sigma\text{Mo}\right]+8(\pm6)\times10^4}{T^2} \quad (4)$$

Importantly, the SiO_2 -rich silicate liquid equilibrated with a Mo wire loop has a fractionation factor that is statistically indistinguishable from the SiO_2 -poor, CaO-rich silicate liquids if we account for its $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.47 (Figure 4a, open square). This similarity implies an absence of silicate compositional effects on Mo isotope fractionation in our experiments.

The deviation from the trend of the experiment with $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.63 is small and may be viewed as a poorly reproduced experiment, because the experimental reproducibility, which is difficult to assess, may be worse than the 2se analytical uncertainties we obtain from analysis of isotope ratios. The deviation of the experiment with $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.77, however, is so large that it would require an explanation. We note that this is the experiment at IW-0.2 that had to be performed twice, possibly due to weakening of the Mo wire by oxidation at this relatively high oxygen fugacity (see section 2.1). However, we did not observe any oxygen in a WDS analysis on metal from this experiment. It therefore remains unclear to us what caused the issues with performing a successful experiment at this oxygen fugacity, but it appears this issue may also have affected the isotopic fractionation.

Our results are ostensibly at odds with the results of Hin et al. (2013). They found no effect on Mo isotope fractionation between metal and silicate as a function of oxygen fugacity over a fO_2 range of about two log units and obtained an average fractionation factor of $-0.19 \pm 0.03\text{‰}$ at 1400°C . However, the Mo oxidation state in silicate liquids of Hin et al. (2013) and the extent to which it varied with oxygen fugacity remained unclear in their study. For instance, the oxygen fugacity in their experiments was calculated from FeO and Fe activities in the silicate and metal. Compositionally, their systems were rather complex and variable. They determined oxygen fugacities between about IW-1.7 and IW-0.5 for a large portion of their experiments. Another portion of experiments were calculated to be around IW+0.5 if a constant FeO activity coefficient of 1.7 (Holzheid et al., 1997) was used for all experiments. Alternatively, the fO_2 would have been close to IW in the melts with high FeO (up to 49 wt%) because Raoult's Law implies lower activity coefficients close to 1. Their silicate compositions and some of their variability (notably FeO and SnO_2) lie outside the parameter space investigated in O'Neill and Eggins (2002). However, based on CaO- and MgO-parameterised activity model of these authors, we estimate Mo^{6+} abundances in experiments of Hin et al. (2013) to have varied between 29% and 63% (Figure 7). According to our present observation, Mo^{6+} variations between 29% and 63% would affect the metal-silicate isotope fractionation factor by $\sim 0.16\text{‰}$. Although there is experimental variability beyond analytical uncertainties in the results of Hin et al. (2013) (e.g. compare results at $\text{Mo}^{6+}/\Sigma\text{Mo}$ of ~ 0.3 and ~ 0.5 in Figure 7), we would expect this difference to have been detectable. We speculate that perhaps the presence of up to 49 wt% FeO (and 3.66 wt% SnO_2) in the experiments of Hin et al. may have suppressed the relative increase in Mo^{6+} in their experiments compared to what we calculated here. Such changes in composition might have counteracted the effects of oxygen fugacity on $\text{Mo}^{6+}/\Sigma\text{Mo}$, a feature that did not occur in the experiments we performed here because of the constant composition of the silicate liquid.

The calculations above suggest that Hin et al. (2013) obtained a fractionation factor between metal and silicate containing both Mo^{4+} and Mo^{6+} . However, the $\text{Mo}^{6+}/\Sigma\text{Mo}$ variations in their glasses as calculated above are affected by the uncertainties regarding the oxygen fugacity calculations and by the dependence of $\text{Mo}^{6+}/\Sigma\text{Mo}$ on oxygen fugacity in their complex, Fe-rich systems. Instead, we can use the mean fractionation factor of $-0.19 \pm 0.03\text{‰}$ obtained at 1400°C in their work and equation (4) above to independently determine an average $\text{Mo}^{6+}/\Sigma\text{Mo}$ in their glasses. In this manner, we obtain a relative Mo^{6+} abundance of $43 \pm 10\%$. This value reassuringly falls in the 0.29-0.63 range of $\text{Mo}^{6+}/\Sigma\text{Mo}$ calculated above with the CaO and MgO contents of their glasses and the activity model of O'Neill and Eggins (2002). The agreement between these calculations of $\text{Mo}^{6+}/\Sigma\text{Mo}$ in the experiments of Hin et al. (2013) implies that changing from a solid Mo metal to liquid Fe-Mo $\pm$ Sn $\pm$ C alloy does not cause substantial changes in the fractionation of Mo isotopes between metal and silicate liquid, though with the caveat that Hin et al. (2013) did not observe an oxygen fugacity dependence of Mo isotope fractionation as discussed above.

The accuracy of the isotopic fractionation factors in our present data could be affected by contamination of metal nuggets in the silicate melt, which would lead to underestimation of the fractionation. As the Mo metal/silicate partition coefficient strongly increases with decreasing oxygen fugacity, our observed negative correlation with Mo^{6+} abundance (i.e. oxygen fugacity) could thus result from metal contamination in our silicate analyses. However, we do not think that any of the wire loop experiments are affected by such metal contamination. First, we did not observe metal nuggets on a sub-micron scale with a scanning electron microscope, except in areas directly at the contact with the Mo wire. Whilst such contaminated areas may explain some of the metal contaminated XANES spectra, these contaminated areas were avoided when picking glass for isotopic analysis. Second, our double spike analyses provide an independent measurement of the Mo content in the glasses on which we analysed Mo isotope compositions. As can be seen in Table 1, Mo contents of six of the eleven glasses for which we have determined Mo contents by both double spike ($[\text{Mo}]_{\text{D.S.}}$) and microprobe ($[\text{Mo}]_{\text{EPMA}}$) analysis are within $\pm 10\%$ of each other, which is good considering estimated weighing uncertainties of $\sim 5\%$ on our small samples (usually < 5 mg). The other samples deviate more, with $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ between 0.67 and 1.61. That these ratios vary both above and below unity implies that weighing inaccuracies in the small sample weights are a more likely cause for the concentration deviations than metal contamination. The absence of significant metal contamination in our isotopic analyses is confirmed in Figure 8 by the absence of a correlation between $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ as proxy for potential metal contamination and Mo isotope fractionation factors. If higher Mo contents determined by our double spike analyses were due to metal contamination, the data should follow the modelled curve shown as stippled arrows in Figure 8. It appears that the data do not follow this modelled contamination effect, although there is much scatter when plotting observed Mo isotope fractionation factors (Figure 8a). However, this diagram does not correct for systematic changes in $\Delta^{98/95}\text{Mo}_{\text{metal-silicate}}$ with changing $\text{Mo}^{6+}/\Sigma\text{Mo}$, as discussed above. To account for this variability, we assume that the slope of about -0.51 in Figure 3 describes the effect of such variable Mo^{6+} abundances on the isotope fractionation factors. We can then determine potential residual effects of metal contamination by normalising all isotope fractionation factors to a single $\text{Mo}^{6+}/\Sigma\text{Mo}$ of an experiment for which our isotopic analyses apparently have not been affected by metal contamination, i.e. an experiment for which $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ is close to unity. The results of this normalisation are presented in Figure 8b, which confirms that our analyses are not significantly affected by metal contamination. The negative correlation between Mo isotope fractionation factors and Mo^{6+} abundances (Figure 4) thus cannot be due to metal contamination.

4.2.2 Au-Mo experiments

The experiments with silicate liquid coexisting with liquid Au-Mo alloys were performed to verify whether Mo isotope fractionation as a function of $\text{Mo}^{6+}/\Sigma\text{Mo}$ reproduced in an independent compositional system. The glasses of these experiments display analytically significant scatter in repeated digestions of the same experiments (Table 2). Some of this poor reproducibility is also

displayed in the isotopic fractionation factors at low $\text{Mo}^{6+}/\Sigma\text{Mo}$ in Figure 4a. This scatter could indicate experimental issues, for instance with slower equilibration due to interaction with the SiO_2 glass tubes. However, a linear fit through the three Au-Mo alloy experiments with highest $\text{Mo}^{6+}/\Sigma\text{Mo}$ yields a slope of -0.52 ± 0.15 and an intercept of $0.34 \pm 0.06\text{‰}$, a slope that is indistinguishable to that of the wire loop experiments (-0.51 ± 0.05).

Interestingly, the silicates in the experiments with Au-Mo alloys are not enriched in heavy Mo isotopes, but instead are enriched in light Mo isotopes by $0.298 \pm 0.010\text{‰}$ to $0.087 \pm 0.009\text{‰}$ (Figure 4a). The change in sign of the Mo isotope fractionation factor between the wire loop and Au-Mo experiments cannot be due to the more SiO_2 -rich and CaO-poor silicate compositions because we observed no such silicate composition effect in wire loop experiments with such different compositions (cf. open and filled squares in Figure 4). The difference of 0.31‰ in the intercepts of the linear fits to the Au-Mo alloy and wire loop experiments therefore implies that the relevant bonds in an Au-Mo alloy are substantially stiffer than in pure Mo or Fe-based alloys containing Mo. This compositional effect may appear surprising given that Hin et al. (2013) observed no effect of composition in Fe-based alloys in the system $\text{Fe-Mo}\pm\text{Sn}\pm\text{C}$. Furthermore, we inferred above that changing from such Fe-based alloys to pure Mo also does not noticeably influence Mo isotope fractionation with respect to silicate liquids. However, effects of metal compositions on Fe isotope fractionation have been suggested to occur in relation to substitutional bonding of elements in Fe-based alloys (Elardo and Shahar, 2017). Crystalline Au-Mo alloys with up to 2.5 wt% Mo form a face-centred cubic (fcc) crystal structure that has a coordination number of 12, just like pure gold metal (Massalski et al., 1986). In contrast, pure Mo and Fe metals as well as Fe-Mo alloys with low Mo contents (less than ~30 wt% at ~1400°C) form eight-fold coordinated body-centred cubic crystals at high temperature (Guillermot, 1982). Given the higher coordination of the unit cell in Au-Mo alloys compared to pure Mo metal, we might expect weaker bonding and hence a more negative Mo isotope fractionation factor in the Au-Mo alloys than in pure Mo metal. This contrasts with our observations. However, the fcc structure that characterizes Au-Mo alloys with low Mo content have octahedrally and tetrahedrally coordinated interstitial sites in their crystal lattice. We therefore speculate here that Mo occupies a relatively strongly bonded, interstitial site with tetrahedral coordination in Au-Mo alloys, while it occupies the weaker bonded, 8-fold coordinated main lattice sites in pure Mo or Fe-based alloys. Although an $\text{Au}_{95}\text{Mo}_5$ alloy has no relevance for core formation, our Au-Mo alloy experiments imply that a better understanding of metal compositional effects on isotope fractionation in general may be required in future (see also review in (Bourdon et al., 2018)).

4.3 Geological implications and conclusions

The results of our experiments refine the work of Hin et al. (2013) in the sense that we show that Mo isotope fractionation between metal and silicate liquid depends on the relative abundances of Mo^{6+} and Mo^{4+} in the silicate liquid, such that it is better described by our equation (4). Mo isotopes could

thus be used to constrain the temperature or silicate $\text{Mo}^{6+}/\Sigma\text{Mo}$ during core formation (Figure 9), if one of the two can be reasonably constrained by alternative means. The oxygen fugacity during core formation may therefore be constrained with Mo isotopes, because it can be deduced from $\text{Mo}^{6+}/\Sigma\text{Mo}$, although this may require a better understanding of Mo^{4+} and Mo^{6+} activity coefficients under the high pressure and temperature conditions of terrestrial core formation with Fe-rich metals and silicates.

Interestingly, equation (4) shows that if silicate liquid contains a relative Mo^{6+} abundance of <5.6%, the silicate liquid will be enriched in light Mo isotopes relative to the metal, but this value drops to <1.7% for the fractionation to be detectable outside analytical uncertainties. Contrary to the previous statement in Hin et al. (2013), the sense of fractionation during core formation could have led to a minor enrichment of the mantle in light Mo isotopes under highly reduced conditions. This is relevant considering that the $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of the bulk silicate Earth appears slightly sub-chondritic. However, enrichment of the mantle in light Mo isotopes following core formation seems highly unlikely. Firstly, temperatures of core formation on Earth are generally believed to have been between roughly 2000°C and 3000°C based on metal-silicate partitioning studies (Ballhaus et al., 2013; Righter et al., 2010; Siebert et al., 2011; Wade and Wood, 2005). At 2000°C, equation (4) predicts the mantle Mo isotope composition to be enriched in light Mo isotopes by $0.016 \pm 0.011\%$ for a silicate liquid with $\text{Mo}^{6+}/\Sigma\text{Mo}$ of zero. As shown in Figure 9, this shift is smaller than the uncertainty of 0.02‰ in the bulk Earth $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of $-0.16 \pm 0.02\%$, which Burkhardt et al. (2014) proposed based on Mo isotope analysis of a collection of chondrites and iron meteorites.

Secondly, it seems unlikely that silicate liquids had $\text{Mo}^{6+}/\Sigma\text{Mo}$ of zero during core formation, despite the evidence that oxygen fugacities during Earth's core formation ranged broadly between IW-4 and IW-1. Molybdenum has frequently been described as occurring dominantly as Mo^{4+} in silicate liquids at conditions of core formation based on Mo partitioning studies between metal and silicate liquids (Holzheid et al., 1994; O'Neill and Eggins, 2002; Wade et al., 2012; Walter and Thibault, 1995). But we can see in Figure 10 that, for instance, the partitioning data of the 1.5 GPa, 1650°C experiments of Wade et al. (2012) fit better with a silicate $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.2 than 0. Additionally, we can also use the CaO- and MgO-parameterised model of O'Neill and Eggins (2002) to estimate the relative abundance of Mo^{6+} in a peridotitic silicate liquid, with the caveat that this model is based on a simple, four-component silicate system containing CaO, MgO, Al_2O_3 and SiO_2 . For 1400°C and 10^5 Pa, the temperature and pressure at which their model was calibrated, we obtain a $\text{Mo}^{6+}/\Sigma\text{Mo}$ of ~0.02 and ~0.34 at oxygen fugacities of IW-4 and IW-1, respectively. Despite the inclusion of a temperature dependence in the CaO- and MgO-parameterised model, extrapolating the calculation of $\text{Mo}^{6+}/\Sigma\text{Mo}$ to temperatures and pressures of terrestrial core formation are highly uncertain. A Gibbs free energy of formation exists for solid MoO_2 , but not for liquid MoO_2 because the solid sublimates (Blackburn et al., 1958). O'Neill and Eggins (2002) used a TiO_2 -based approximation to estimate a melting correction for the Gibbs free energy of formation of MoO_2 , but its accuracy over large temperature extrapolation remains unverified. Due to the unstable nature of liquid MoO_2 , we were also unable to find any thermal

expansion data for this phase, which would be required to approximate a pressure correction term if we were to approximate core formation at high temperatures and pressures. Nonetheless, it appears that although Mo occurs dominantly as Mo^{4+} in silicate liquids under core formation conditions, it does not do so exclusively. This presence of small amounts of Mo^{6+} further minimises the likelihood that core formation could have detectably enriched Earth's mantle in light instead of heavy Mo isotopes.

Our refined parameterisation of Mo isotope fractionation during core formation therefore does not seem to affect an important consequence of Mo isotope fractionation during core formation, which has previously been highlighted (Burkhardt et al., 2014; Hin et al., 2013; Willbold and Elliott, 2017); the silicate portion of a planetary body cannot be significantly enriched in light Mo isotopes following core formation. Depending on temperature and relative Mo^{6+} abundance, core formation either does not significantly fractionate Mo isotopes, or it enriches the mantle in heavy Mo isotopes (Figure 9). If we assume that a $\text{Mo}^{6+}/\Sigma\text{Mo}$ of ~ 0.1 in silicate liquids occurred during terrestrial core formation, we obtain a $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ of $-0.15 \pm 0.02\text{‰}$ for Earth's mantle after core formation at 2000°C or 3000°C from equation (4). This value is within error of bulk Earth $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ ($-0.16 \pm 0.02\text{‰}$) proposed by Burkhardt et al. (2014). Interestingly, however, several studies have now suggested that Earth's upper mantle may in fact be slightly depleted in heavy Mo isotopes, although the difference is barely resolvable and not all studies agree (Figure 9).

Previous studies have proposed various mechanisms for such enrichment in light Mo isotopes in the terrestrial upper mantle, including partial melting of the mantle (Bezard et al., 2016) and crust formation (Greber et al., 2015; Willbold and Elliott, 2017). As the Mo isotope composition of the crust has been suggested to be relatively heavy (Voegelin et al., 2014), it may mass balance the relatively light composition of the mantle (Greber et al., 2015; Willbold and Elliott, 2017). This suggestion would fit well with observations in Freymuth et al. (2015) that arc lavas are enriched in heavy Mo isotopes compared to mid-ocean ridge basalts. These authors deduced from their observations that dehydration of subducting slabs enriches the mantle wedge in heavy Mo isotopes, leaving the residual subducting slab enriched in light Mo isotopes that recycled back into the mantle. Freymuth et al. (2015) hypothesized that rutile, which has octahedral cation coordination, might be responsible for retaining light Mo isotopes in the slab during such dehydration.

It is beyond the scope of our contribution to further assess the processes that might enrich the terrestrial, upper mantle in light Mo isotopes. However, as we have mentioned in section 4.2.2, we infer from our metal-silicate experiments that silicate liquid containing 100% Mo^{6+} , which is tetrahedrally coordinated in such silicate liquid, is enriched in heavy Mo isotopes by $0.51 \pm 0.07\text{‰}$ at 1400°C compared to silicate liquid containing 100% Mo^{4+} , which is octahedrally coordinated. By extrapolation, isotopic fractionation between tetrahedrally coordinated Mo^{6+} and octahedrally coordinated Mo^{4+} would be $\sim 1.5\text{‰}$ at 700°C , a temperature relevant for subduction dehydration. Depending on whether coordination or valence state effects dominate Mo isotope fractionation, effects that our work cannot disentangle, and depending on Mo valence in rutile, which is poorly constrained, strong enrichment in

light Mo isotopes may occur in residual rutile equilibrated with slab fluids in subduction zones, as hypothesized by Freymuth et al. (2015). The potential enrichment in light Mo isotopes in dehydrated slabs highlights the possibility that recycling such rocks (e.g. eclogites) into Earth's mantle through protracted subduction and subsequent mixing, continually enriched Earth's mantle in light Mo isotopes throughout its geologic history explaining its modern, relatively light Mo isotope composition.

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Table and Figure captions

Figure 1 (*1 column wide*). Molybdenum contents of the glasses, obtained by microprobe analysis, as a function of oxygen fugacity. Squares are for glasses from wire loop experiments, circles for glasses from experiments with Au-Mo alloys. Solid line is the best fit to the data for the high-CaO composition. Results from this study are compared with data for the two most relevant glass compositions of O'Neill and Eggins (2002). When error bars ($2se$) are not visible they are smaller than the symbols.

Figure 2 (*2 columns wide*). X-ray absorption near-edge spectra showing normalised intensities as a function of incident X-ray energy for (a) glasses from experiments equilibrated with Mo wire loops and (b) glasses equilibrated with Au-Mo alloys in open-ended silica tubes. The uppermost spectra in both panels are for the reference glass materials. Stippled line at 20005 eV indicates the energy of the pre-edge feature indicative of Mo^{6+} .

Figure 3 (*1 column wide*). Abundance of Mo^{6+} compared to all Mo ($Mo^{6+}/\Sigma Mo$) in silicate glasses as a function of oxygen fugacity. All data are obtained from XANES analyses whose spectra were sufficiently free of contamination that Mo^{6+} abundances could be determined from the pre-edge feature. Error bars indicate the range of results obtained depending on choice of Mo^{4+} peak height in the spectra, which is poorly constrained in our analyses. The solid and broken curves show a model for a change from Mo^{6+} to Mo^{4+} (see equation (1)) fitted to the two data sets. The stippled curve shows a similar thermodynamic model but based on the empirical CaO and MgO content parameterisation of O'Neill and Eggins (2002) and the CaO contents in the glasses of our wire loop experiments.

Figure 4 (1 column wide). Molybdenum isotope fractionation factors between metal and silicate as a function of $\text{Mo}^{6+}/\Sigma\text{Mo}$ determined from XANES analyses. Stippled lines are linear fits to the data (see text for details). Large grey error bars on three of the Au-Mo experiments are $2s$ based on poorly reproduced replicate digestions as opposed to $2se$ based on the long-term $2s$ of geological reference material JB-2 (see Table 2).

Figure 5 (1 column wide). Molybdenum isotopic data normalised to $^{98}\text{Mo}/^{94}\text{Mo}$ from unspiked analyses. The stippled curves show the $2s$ reproducibility of NIST SRM3134 based on 26 analyses of this reference standard. Note that individual points have been slightly offset from their true masses to better visualise their error bars.

Figure 6 (1 column wide). Wavelength dispersive spectrum of metals from wire loop experiments normalised (and reference to zero) to the spectrum of a reference Mo metal. A piece of metal from experiment IW-3.0 shows a distinct peak at the wavelength representing carbon as well as a significant depression at the wavelength representing Mo-M_L. Note that spectra were also collected on metals from experiments IW-2.0 and IW-1.1. Both these spectra are in marked contrast with the spectrum of IW-3.0, but they are not significantly different to each other. Only the spectrum of IW-2.0 is therefore shown to improve visibility of the features of the two shown spectra.

Figure 7 (1 column wide). Molybdenum isotope fractionation factors between metal and silicate as a function of $\text{Mo}^{6+}/\Sigma\text{Mo}$. Data from wire loop experiments of this study are compared to data from Hin et al. (2013), from whom we show all fractionation factors from experiments at 1400°C that equilibrated (i.e. run duration ≥ 1.5 hours). The $\text{Mo}^{6+}/\Sigma\text{Mo}$ of these literature data have been estimated with the CaO- and MgO-parameterised model of O'Neill and Eggins (2002), despite that their compositional parameterisation was done on silicate glasses free of FeO (and SnO_2 ; see text for details).

Figure 8 (2 columns wide). a) Molybdenum isotope fractionation factors between metal and silicate plotted against the ratio of Mo concentrations determined by double spike analysis and microprobe analysis ($[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$). Stippled arrows indicate the modelled effect of metal contamination. Error bars as in Figure 4. b) Same as a), but with normalised Mo isotope fractionation factors to correct for systematic changes with varying $\text{Mo}^{6+}/\Sigma\text{Mo}$. All Mo isotope fractionation factors of each of the two sets of experiments have been normalised to the same $\text{Mo}^{6+}/\Sigma\text{Mo}$ as an experiment with $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ near unity (i.e. wire loop IW-1.1 with $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ of 1.04 and $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.55, and Au-Mo alloy experiment IW-0.5 with $[\text{Mo}]_{\text{D.S.}}/[\text{Mo}]_{\text{EPMA}}$ of 0.98 and $\text{Mo}^{6+}/\Sigma\text{Mo}$ of 0.40). This normalisation has been made using the slope 0.51 in Figure 3 to eliminate the effect of variable

Mo⁶⁺/ΣMo on the Mo isotope fractionation factors. This normalisation visualises potential residual effects of metal contamination, which appear insignificant in our experiments given that the experiments do not significantly follow the modelled effect of metal contamination.

Figure 9 (*1 column wide*). Mo isotope composition of the terrestrial mantle predicted in a single stage core formation model as a function of metal-silicate equilibration temperature. The core formation model assumes a Mo metal-silicate partition coefficient of 100, following Willbold and Elliott (2017). The broken curves are based on equation (4) for different Mo⁶⁺/ΣMo values; an error field is shown on one curve for comparison. The composition of the core is identical to the mean chondrite composition of Burkhardt et al. (2014). Also shown are estimates of the Mo isotope composition of the upper mantle as deduced from komatiites (cross; (Greber et al., 2015)), mid-ocean ridge basalts (diamond and pentagram; (Bezard et al., 2016), and (Liang et al., 2017), respectively) and “slightly altered” mid-ocean ridge basalts (asterisk; (Freymuth et al., 2015)).

Figure 10 (*1 column wide*). Molybdenum metal/silicate partition coefficients (corrected for activity coefficients in the metal) against oxygen fugacity relative to the iron-wüstite buffer in experiments of Wade et al. (2012). Experiments contain liquid, Fe-based metal alloys with compositions thought to represent cores of planets such as Earth, coexisting with ultra-mafic silicate liquids. Although these experiments appear to fit a curve with slope -1 indicative of Mo⁶⁺/ΣMo equal to zero, they seem to fit even better to a curve with slope -1.1 indicative of Mo⁶⁺/ΣMo equal to 0.2. This confirms that Mo is dominantly tetravalent in ultra-mafic silicate melt during core formation, but that it is likely not exclusively tetravalent. Figure modified from Wade et al. (2012).

Table 1. Compositions of silicate glasses. Values are means of analyses on various spots on the glass and are wt%, except for Mo contents, which are ppm. Standard errors of the mean (2se) are also based on the various spots. Concentrations below detection limits are shown as <d.l.

<i>Sample</i>	<i>SiO₂</i>	<i>2se</i>	<i>CaO</i>	<i>2se</i>	<i>Al₂O₃</i>	<i>2se</i>	<i>Mo</i>	<i>2se</i>	<i>Total</i>	<i>2se</i>	<i>Mo^a</i>	<i>Mo⁶⁺/ΣMo^b</i>
<i>Wire loop experiments</i>												
IW-0.2	41.70	0.07	41.37	0.05	12.29	0.03	21043	87	98.17	0.09	19781	0.77(6)
IW-0.5	42.72	0.12	43.26	0.05	12.79	0.04	6952	63	99.70	0.08	11209	0.71(7)
IW-0.8	42.93	0.12	43.52	0.05	12.93	0.05	2675	66	99.74	0.10	2864	0.63(8)
IW-0.8 ^c	61.38	0.11	28.55	0.08	8.57	0.03	530	14	98.57	0.16	534	0.47 ^d
IW-1.1	43.10	0.11	43.44	0.09	12.94	0.04	1196	51	99.63	0.07	1239	0.55(8)
IW-1.4	43.53	0.07	42.51	0.07	12.62	0.04	461	33	98.73	0.07	497	0.47 ^e
IW-1.7	44.38	0.11	42.55	0.09	12.68	0.03	219	34	99.64	0.07	318	0.39 ^e
IW-2.0	43.14	0.11	43.61	0.06	13.03	0.02	84	69	99.79	0.08	126.3	0.31 ^e
IW-2.3	42.98	0.06	43.67	0.05	13.02	0.02	<d.l.		99.68	0.07	73.7	0.24(6)
IW-2.6	42.87	0.10	42.93	0.09	12.71	0.04	<d.l.		98.51	0.07	73.2	0.19 ^e
IW-3.0	43.16	0.07	43.37	0.08	12.92	0.03	<d.l.		99.46	0.08		0.13 ^e
<i>Au-Mo alloy experiments</i>												
IW-0.2	65.57	0.12	25.38	0.06	7.63	0.02	1354	15	98.76	0.18	912	0.48(10)

IW-0.5	65.70	0.07	26.42	0.06	7.83	0.02	148	66	99.97	0.04	145.6	0.40(9)
IW-0.8	65.78	0.13	25.53	0.14	7.59	0.03	75	11	98.91	0.27	92.2	0.32(8)
IW-1.1	65.89	0.06	25.51	0.03	7.63	0.02	<d.l.		99.04	0.07	63.6	0.25(7)
IW-1.4	65.80	0.06	26.49	0.05	7.82	0.01	<d.l.		100.11	0.06	23.1	0.19(6)
IW-1.7	67.30	0.06	25.33	0.04	7.47	0.02	<d.l.		100.10	0.07	42.1	0.15(5)

Footnotes: ^aMo concentration (ppm) determined by double spike analysis. Relative errors ~5% based on weighing error estimates for samples with weights <5 mg. ^bDetermined from height of pre-edge feature in XANES spectra, unless otherwise indicated. Values in brackets are errors referring to the last decimal. ^cThis wire loop experiment was performed with a more SiO₂-rich starting material. ^dThe relative Mo⁶⁺ abundance of this SiO₂-rich wire loop experiment was estimated with the CaO- and MgO-parameterised model of O'Neill and Eggins (2002) (see text). ^eRelative Mo⁶⁺ abundances obtained from a thermodynamic fit (see equation (1)) through the results obtained for the other spectra, because the XANES spectra were too contaminated to extract Mo⁶⁺ abundances. Note that this method yielded only 0.02 higher ratios than a thermodynamic fit through double spike concentration data following equations 9, 10 and 21 in O'Neill and Eggins (2002).

Table 2. Molybdenum isotope compositions relative to the international reference standard NIST SRM3134 and metal-silicate fractionation factors.

<i>Sample</i>	$\delta^{98/95}\text{Mo}_{\text{SRM3134}}$	$2se^a$	n^b	$\Delta^{98/95}\text{Mo}_{\text{metal-silicate}}^c$	$2se$
<i>Mo wire loops</i>					
Metal mean	-0.098	0.005	35,4		
IW-0.2a	0.024	0.009	9		
IW-0.2b	0.030	0.014	4		
IW-0.2 mean	0.025	0.008	13,2	-0.123	0.009
IW-0.5a	0.216	0.009	9		
IW-0.5b	0.214	0.014	4		
IW-0.5 mean	0.215	0.008	13,2	-0.313	0.009
IW-0.8	0.103	0.009	9	-0.201	0.011
IW-0.8 SiO ₂ -rich	0.134	0.012	6	-0.232	0.013
IW-1.1	0.160	0.009	9	-0.258	0.011
IW-1.4	0.116	0.009	9	-0.214	0.011
IW-1.7	0.094	0.011	7	-0.192	0.012
IW-2.0	0.009	0.012	6	-0.107	0.013
IW-2.3	-0.011	0.012	6	-0.087	0.013
IW-3.0	-0.302	0.012	6	0.203	0.013
<i>Au-Mo alloys</i>					
Metal mean	-0.381	0.006	24,4		
IW-0.2a	-0.447	0.009	9		
IW-0.2b	-0.453	0.014	4		
IW-0.2c	-0.530	0.014	4		
IW-0.2 mean	-0.468	0.007	17,3	0.087	0.009
IW-0.5a	-0.541	0.009	9		
IW-0.5b	-0.493	0.014	4		

IW-0.5 mean	-0.527	0.008	13,2	0.145	0.010
IW-0.8a	-0.548	0.009	9		
IW-0.8b	-0.546	0.014	4		
IW-0.8 mean	-0.547	0.008	13,2	0.166	0.010
IW-1.1a	-0.729	0.009	9		
IW-1.1b	-0.567	0.014	4		
IW-1.1 mean	-0.679	0.008	13,2	0.298	0.010
IW-1.4	-0.553	0.012	6	0.172	0.013
IW-1.7	-0.568	0.012	6	0.187	0.013

Standards

JB-2	0.046	0.008	12,3
AJ011	-0.687	0.009	9

Footnotes: ^aStandard error of the mean, calculated with the 2s of JB-2 (0.028‰). ^bTotal number of repeated measurements. If two numbers are listed, the second number refers to the number of replicate digestions (listed in this Table), except for metals where it represents the number of experiments of which a metal piece has been analysed (not listed). ^cFractionation factor, calculated as the isotopic composition of the metal minus that of the silicate.

Table 3. Mo isotopic compositions of unspiked analysed internally normalised to ⁹⁸Mo/⁹⁴Mo of 2.630639 and externally normalised to NIST SRM3134.

Sample	ε ⁹² Mo	2s.e.	ε ⁹⁵ Mo	2s.e.	ε ⁹⁶ Mo	2s.e.	ε ⁹⁷ Mo	2s.e.	ε ¹⁰⁰ Mo	2s.e.	n
CPI	0.02	0.09	-0.02	0.05	-0.01	0.05	-0.07	0.07	-0.01	0.09	12
Metal	0.02	0.11	-0.01	0.06	0.04	0.07	0.06	0.08	0.04	0.11	6
IW-0.2	-0.09	0.12	-0.01	0.07	-0.02	0.07	-0.01	0.09	-0.02	0.12	8
IW-0.5	-0.10	0.12	0.05	0.07	0.00	0.07	0.01	0.09	-0.11	0.12	7
IW-1.7	-0.09	0.13	-0.01	0.07	0.03	0.08	0.00	0.10	0.08	0.13	7

References

- Ballhaus, C. et al., 2013. The U/Pb ratio of the Earth's mantle-A signature of late volatile addition. *Earth and Planetary Science Letters*, 362: 237-245.
- Berry, A.J., Stewart, G.A., O'Neill, H.S.C., Mallmann, G., Mosselmans, J.F.W., 2018. A re-assessment of the oxidation state of iron in MORB glasses. *Earth and Planetary Science Letters*, 483: 114-123.
- Bezard, R., Fischer-Godde, M., Hamelin, C., Brennecke, G.A., Kleine, T., 2016. The effects of magmatic processes and crustal recycling on the molybdenum stable isotopic composition of Mid-Ocean Ridge Basalts. *Earth and Planetary Science Letters*, 453: 171-181.
- Bigeisen, J., 1965. Chemistry of Isotopes. *Science*, 147(3657): 463-471.
- Bigeisen, J., 1996a. Nuclear size and shape effects in chemical reactions. Isotope chemistry of the heavy elements. *Journal of the American Chemical Society*, 118(15): 3676-3680.
- Bigeisen, J., 1996b. Temperature dependence of the isotope chemistry of the heavy elements. *Proceedings of the National Academy of Sciences of the United States of America*, 93(18): 9393-9396.
- Blackburn, P.E., Hoch, M., Johnston, H.L., 1958. The vaporization of molybdenum and tungsten oxides. *Journal of Physical Chemistry*, 62(7): 769-773.

- Bourdon, B., Roskosz, M., Hin, R.C., 2018. Isotope tracers of core formation. *Earth-Science Reviews*.
- Burkhardt, C., Hin, R.C., Kleine, T., Bourdon, B., 2014. Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation. *Earth and Planetary Science Letters*, 391: 201-211.
- Burnham, A.D. et al., 2015. The oxidation state of europium in silicate melts as a function of oxygen fugacity, composition and temperature. *Chemical Geology*, 411: 248-259.
- Calas, G., Le Grand, M., Galois, L., Ghaleb, D., 2003. Structural role of molybdenum in nuclear glasses: an EXAFS study. *Journal of Nuclear Materials*, 322(1): 15-20.
- Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Communications in Mass Spectrometry*, 25(17): 2538-2560.
- Elardo, S.M., Shahar, A., 2017. Non-chondritic iron isotope ratios in planetary mantles as a result of core formation. *Nature Geoscience*, 10(4): 317-321.
- Eriksson, G., Pelton, A.D., 1993. Critical-Evaluation and Optimization of the Thermodynamic Properties and Phase-Diagrams of the $\text{CaO-Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ Systems. *Metallurgical Transactions B-Process Metallurgy*, 24(5): 807-816.
- Farges, F., Siewert, R., Brown, G.E., Guesdon, A., Morin, G., 2006. Structural environments around molybdenum in silicate glasses and melts. I. Influence of composition and oxygen fugacity on the local structure of molybdenum. *Canadian Mineralogist*, 44: 731-753.
- Fegley, B., Palme, H., 1985. Evidence for Oxidizing Conditions in the Solar Nebula from Mo and W Depletions in Refractory Inclusions in Carbonaceous Chondrites. *Earth and Planetary Science Letters*, 72(4): 311-326.
- Frey, H., Vils, F., Willbold, M., Taylor, R.N., Elliott, T., 2015. Molybdenum mobility and isotopic fractionation during subduction at the Mariana arc. *Earth and Planetary Science Letters*, 432: 176-186.
- Greber, N.D., Puchtel, I.S., Nagler, T.F., Mezger, K., 2015. Komatiites constrain molybdenum isotope composition of the Earth's mantle. *Earth and Planetary Science Letters*, 421: 129-138.
- Guillemet, A.F., 1982. The Fe-Mo (iron-molybdenum) system. *Bulletin of Alloy Phase diagrams*, 3: 359-367.
- Hin, R.C., Burkhardt, C., Schmidt, M.W., Bourdon, B., Kleine, T., 2013. Experimental evidence for Mo isotope fractionation between metal and silicate liquids. *Earth and Planetary Science Letters*, 379: 38-48.
- Holzheid, A., Borisov, A., Palme, H., 1994. The Effect of Oxygen Fugacity and Temperature on Solubilities of Nickel, Cobalt, and Molybdenum in Silicate Melts. *Geochimica Et Cosmochimica Acta*, 58(8): 1975-1981.
- Holzheid, A., Palme, H., Chakraborty, S., 1997. The activities of NiO, CoO and FeO in silicate melts. *Chemical Geology*, 139(1-4): 21-38.
- Leitzke, F.P. et al., 2017. Redox dependent behaviour of molybdenum during magmatic processes in the terrestrial and lunar mantle: Implications for the Mo/W of the bulk silicate Moon. *Earth and Planetary Science Letters*, 474: 503-515.
- Liang, Y.H. et al., 2017. Molybdenum isotope fractionation in the mantle. *Geochimica Et Cosmochimica Acta*, 199: 91-111.
- Massalski, T.B., Okamoto, H., Brewer, L., 1986. The Au-Mo (gold-molybdenum) system. *Bulletin of Alloy Phase diagrams*, 7: 449-452.
- Mendybaev, R.A., Beckett, J.R., Stolper, E., Grossman, L., 1998. Measurement of oxygen fugacities under reducing conditions: Non-Nernstian behavior of Y_2O_3 -doped zirconia oxygen sensors. *Geochimica Et Cosmochimica Acta*, 62(18): 3131-3139.
- O'Neill, H.S.C., Eggins, S.M., 2002. The effect of melt composition on trace element partitioning: an experimental investigation of the activity coefficients of FeO, NiO, CoO, MoO_2 and MoO_3 in silicate melts. *Chemical Geology*, 186(1-2): 151-181.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation*, 12: 537-541.
- Righter, K., Pando, K.M., Danielson, L., Lee, C.T., 2010. Partitioning of Mo, P and other siderophile elements (Cu, Ga, Sn, Ni, Co, Cr, Mn, V, and W) between metal and silicate melt as a function of temperature and silicate melt composition. *Earth and Planetary Science Letters*, 291(1-4): 1-9.

- 844 Sawaguchi, N., Yokokawa, T., Kawamura, K., 1996. Mo K-edge XAFS in Na₂O-K₂O-SiO₂ glasses.
845 Physics and Chemistry of Glasses, 37(1): 13-18.
- 846 Schauble, E.A., 2004. Applying stable isotope fractionation theory to new systems. Geochemistry of
847 Non-Traditional Stable Isotopes, 55: 65-111.
- 848 Schauble, E.A., 2007. Role of nuclear volume in driving equilibrium stable isotope fractionation of
849 mercury, thallium, and other very heavy elements. Geochimica Et Cosmochimica Acta, 71(9):
850 2170-2189.
- 851 Shahar, A. et al., 2015. Sulfur-controlled iron isotope fractionation experiments of core formation in
852 planetary bodies. Geochimica Et Cosmochimica Acta, 150: 253-264.
- 853 Siebert, J., Corgne, A., Ryerson, F.J., 2011. Systematics of metal-silicate partitioning for many
854 siderophile elements applied to Earth's core formation. Geochimica et Cosmochimica Acta,
855 75(6): 1451-1489.
- 856 Voegelin, A.R., Pettke, T., Greber, N.D., von Niederhausern, B., Nagler, T.F., 2014. Magma
857 differentiation fractionates Mo isotope ratios: Evidence from the Kos Plateau Tuff (Aegean
858 Arc). Lithos, 190: 440-448.
- 859 Wade, J., Wood, B.J., 2005. Core formation and the oxidation state of the Earth. Earth and Planetary
860 Science Letters, 236(1-2): 78-95.
- 861 Wade, J., Wood, B.J., Tuff, J., 2012. Metal-silicate partitioning of Mo and W at high pressures and
862 temperatures: Evidence for late accretion of sulphur to the Earth. Geochimica et Cosmochimica
863 Acta, 85: 58-74.
- 864 Walter, M.J., Thibault, Y., 1995. Partitioning of Tungsten and Molybdenum between Metallic Liquid
865 and Silicate Melt. Science, 270(5239): 1186-1189.
- 866 Willbold, M., Elliott, T., 2017. Molybdenum isotope variations in magmatic rocks. Chemical Geology,
867 449: 253-268.
- 868 Willbold, M. et al., 2016. High-Precision Mass-Dependent Molybdenum Isotope Variations in
869 Magmatic Rocks Determined by Double-Spike MC-ICP-MS. Geostandards and Geoanalytical
870 Research, 40(3): 389-403.