Fluid-melt Mo isotope fractionation: implications for the $\delta^{98/95}$Mo of the upper crust

R. Bezard, H. Guo

Supplementary Information

The Supplementary Information includes:

- ➢ Experimental and Analytical Methods
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Experimental and Analytical Methods

Preparation of starting materials

The haplogranitic glasses used in the experiments were synthesised from SiO_2, $Al(OH)_3$, Na_2CO_3 and K_2CO_3 (analytical grade). The different alumina saturation indices (ASI = 0.8 and 1) were obtained by changing the abundances of $Al(OH)_3$, Na_2CO_3, and K_2CO_3, while keeping a constant Na/K ratio. In order to dehydrate and decarbonate them, the mixtures were loaded into Pt crucibles, heated in a muffle furnace from 21 °C to 1100 °C (100 °C/h) and kept at 1100 °C for 12 h. After cooling, the mixtures were finely ground in an agate mortar to achieve homogenisation and removal of gas bubbles. They were then doped with ~200–300 µg/g Mo in the form of MoO_3, heated at 1600 °C for 2 h (in a Pt crucible) and the resulting melts were quenched using distilled H_2O. Finally, the glasses were ground to fine powder and melted a last time at 1600 °C for another 2 h (in Pt crucibles) for homogeneity.

The fluids were prepared using deionised H_2O and analytical grade NaCl and KCl to reach (Na,K)Cl with a molar Na to K ratio of 1:1 and concentrations of 0.5, 1 and 1.5 mol/L (M).

High temperature and pressure experiments

The cold-seal pressure vessel (CSPV) experiments were conducted both at McGill University (Canada) and the Institut des Sciences de la Terre d'Orléans (ISTO, France), while the internally heated pressure vessel experiments (IHPV) were performed at ISTO only.

The rapid-quench CSPVs are made of nickel-based superalloy using water as the pressure medium, with a setup similar to that described in Matthews *et al.* (2003). For the IHPV experiments, the samples were pressurised using pure Ar or Ar-H$_2$ (0.15–0.6 MPa H$_2$ total pressure) in order to vary fO$_2$ conditions. The redox conditions used in this study are the apparent oxygen fugacity assuming a water fugacity of 1 for the system. For CSPV experiments, oxygen fugacity was not controlled in the vessels, but should be ~FMQ+1, as indicated by the reaction of water with the autoclave material (Keppler, 2010). For the IHPV experiments (Mo21 and Mo27), oxygen fugacity was controlled using mixtures of Ar and H$_2$, as mentioned above. The pressure was monitored by a transducer calibrated against a Heise Bourdon gauge with an accuracy of ±2 MPa (Gaillard *et al.*, 2001; Andújar *et al.*, 2013). The experiments were performed in double-coiled Kanthal with near-isothermal conditions (thermal gradient < 2–3 °C/cm) in the 3 cm long hotspot (Andújar *et al.*, 2013). Temperature was controlled using NiCr–Ni (K-type) thermocouples for CSPV and Pt-Pt$_{90}$-Rh$_{10}$ (S-type) thermocouples for IHPV experiments.

For all experiments, ~0.1 g of glass powder was loaded with a similar amount of aqueous fluid (~0.1 g) into Au capsules with 5.0 mm or 5.4 mm outer diameter, 0.2 mm wall thickness and ca. 2.0 cm length. After welding, capsules were put in an oven at 120 °C to check for potential leaks, and faulty capsules were discarded. The sealed capsules were then loaded into the CSPV or IHPV. Experiments were run at 700–900 °C and 200 MPa for 1–20 days (Table 1) and then quenched by dropping into a cold zone within a few seconds. Variable durations for otherwise identical experiments allowed the assessment of the timing of chemical and isotopic equilibrium at 800 °C, which was achieved between 5 and 10 days. Based on this, the duration was set to 20 days for 700 °C and 7 days for 900 °C experiments (*e.g.*, Guo *et al.*, 2020a). Capsules were weighted before and after experiments, to identify any obvious weight loss.

Fluid and melt extraction from experimental capsules and preparation

Capsules having preserved their initial weight were cleaned in dilute HCl, followed by at least three rinses with deionised H_2O. They were then cooled by liquid N_2 and punctured carefully with a needle prior to fluid extraction using a pipette. The capsule interiors were rinsed with hot and cold deionised water several times in a similar way to that described by Keppler and Wyllie (1991). This is to ensure full dissolution of potentially precipitated material during quenching. The recovered fluids and capsule rinses were transferred into 15 mL pre-cleaned Teflon beakers. The glasses and capsules were dried at 130 °C in the oven for at least 2 h and were weighted to determine the post-quenching fluid weight by subtraction. This approach was shown to be successful in other stable isotope studies (Guo *et al.*, 2020a, 2020b, 2021).

Glasses were crushed to fine particles in agate mortars in order to open fluid inclusions that were possibly trapped in the glass. The powders were then transferred to centrifuge tubes and were agitated and centrifuged in Milli-Q H_2O (MQ H_2O; 18.2 MΩ cm). The supernatant (MQ H_2O) was then discarded to release possible contamination from fluid inclusions. The rinsing process was repeated twice more. The powders were then dried in the oven at 60 °C for 24 h.

Digestion and preparation of stock solutions for fluids and melts

For each experiment, between 10 and 20 mg of glass powder was digested in Teflon beakers using twice distilled (2TD; using Savillex DST-1000 distillation units) 14 M HNO_3 and 29 M HF for 72 h at 140 °C. The solutions were then dried down, followed by sample re-dissolution in 14 M HNO_3. The last two steps were repeated again, this time with aqua-regia and 6 M HCl to ensure complete fluoride dissolution. Samples were then equilibrated in 0.5 M HNO_3. Fluids recovered from the capsule and capsule rinses were dried down. They were subsequently handled like the glass samples and all fluids and glasses were equilibrated in 0.5 M HNO_3.

Mo separation and measurement

For each fluid and glass, an aliquot from the stock was spiked with a ^{97}Mo-^{100}Mo mixture and equilibrated in 14 M HNO_3 at 110 °C. The solutions were then dried dry down and the solids were converted into chloride form using 6 M

HCl and then equilibrated in 3 M HCl for Mo separation. The procedure described in Willbold *et al.* (2016) was used to extract Mo from the sample matrix using a single-stage anion (AG1*8 100–200 mesh) column chemistry. After separation, organic matter introduced during chemistry was removed by passing the collected solution through ~200 μL Eichrom prefilter (100–150 μm; PF-B200-A) or by treating the dried down residues with $HClO_4$ (~50 μL) and 14 M HNO_3 (~500 μL). After this, the Mo cut was equilibrated and re-dissolved in 0.4 M HNO_3-0.05 M HF for mass spectrometric analysis.

The samples were measured using the ThermoScientific NeptunePlus MC-ICP-MS in the Isotope Geology and Geochemistry department at the University of Göttingen. The introduction system consisted in a Cetac Aridus III desolvator and a Savillex PFA nebuliser (~70 μL/min uptake rate). The Mo isotopes used in the double spike deconvolution, *i.e.* ^{95}Mo, ^{97}Mo, ^{98}Mo and ^{100}Mo, were measured together with ^{101}Ru and ^{99}Ru using Faraday cups equipped with 10^{11} Ω (Mo isotopes) and $10^{13}\Omega$ (Ru isotopes) feedback resistors amplifiers. Every sample measurement was bracketed by analyses of a spiked NIST SRM3134 standard solution. Prior to each sample or standard solution measurement, an on-peak baseline measurement on a blank 0.4 M HNO_3-0.05 M HF solution was done (15 integrations of 4 s). Sample/standard solutions were measured at concentrations of ~70 ng/g (80 integrations of 4 s). Each processed sample aliquot was measured twice. A Python script and the mathematical method described by Rudge *et al.* (2009) were used for the (off-line) data deconvolution including the correction for isobaric Ru interferences. Both the Mo isotopic compositions and Mo concentrations of the samples were derived from this spike inversion. Mo isotopic compositions are presented in $\delta^{98/95}Mo$ notation, which represents the parts per thousand deviation from the bracketing NIST SRM 3134 measurements.

Japan Geological Survey (JGS) reference materials were prepared identically to the samples, *i.e.* stocks were prepared for each standard and were aliquoted, with each aliquot measured twice (like for the samples). This yielded isotopic compositions of $+0.03 \pm 0.05$ ‰ (2 s.d.) for JB-2 ($n = 5$), $−0.17 \pm 0.03$ ‰ (2 s.d.) for AGV-2 ($n = 8$) and $−0.04 \pm 0.01$ ‰ (2 s.d.) for JR-2 ($n = 3$). These values are identical within uncertainties to previously published averages if available (JB-2 and AGV-2; *e.g.*, in Freymuth *et al.*, 2015; Villalobos-Orchard *et al.*, 2020; Ahmad *et al.*, 2021). Based on the 2 s.d. of processed JGS reference materials, the reproducibility of our Mo isotope analyses is ±0.5 ‰. Total procedural blanks ranged between 40 and 220 pg, which amounts to less than 0.8 % of the Mo from the samples. Blank-

corrected and uncorrected $\delta^{98/95}$Mo values are identical within uncertainties, and the latter are presented in the manuscript. Mo concentrations for JB-2, AGV-2 and JR-2 (obtained from the deconvolution) were 913 ± 102 ng/g (2 s.d.), 1870 ± 80 ng/g and 2642 ± 43 ng/g, respectively, which again, are well within the range of published values when available (JB-2 and AGV-2; *e.g.*, Villalobos-Orchard *et al.*, 2020).

Details for Modelled Impact of Fluid Exsolution in Discussion

The modelling discussed in the section 'Implications for the Composition of the Upper Continental Crust' uses the equation that governs isotopic fractionation in a Rayleigh distillation process:

$$(\delta^{98/95}\text{Mo})_{\text{melt}} = [(\delta^{98/95}\text{Mo})_{\text{initial melt}} + 1000]f^{(\alpha - 1)} - 1000 \tag{S-1}$$

where $\delta^{98/95}\text{Mo}_{\text{melt}}$ is the $\delta^{98/95}$Mo of the melt after fluid exsolution, $\delta^{98/95}\text{Mo}_{\text{initial melt}}$ is the $\delta^{98/95}$Mo of the initial melt, which is set to 0 ‰ in our calculation and α is the fractionation factor, defined as:

$$\alpha = (^{98}\text{Mo}/^{95}\text{Mo})_{\text{fluid}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{melt}} \tag{S-2}$$

but set to 0.9995 in our calculation, which corresponds to a $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ (‰) = −0.51 ‰ (extrapolated value at ASI = 1.25 based on linear regression; see text for explanation).

The fraction of Mo remaining in the melt (*f*) is calculated as:

$$f = F \times C_{\text{Mo,melt}}/C_{\text{Mo,initial melt}} \tag{S-3}$$

where F is the fraction of melt remaining and is set at 0.9 to model the extraction of 10 % fluid. $C_{\text{Mo,initial melt}}$ is the Mo concentration in the initial melt and is set to 1 µg/g in our calculation and $C_{\text{Mo,melt}}$ is the Mo concentration in the remaining melt, calculated as:

$$C_{\text{Mo,melt}} = C_{\text{Mo,initial melt}} \times F^{(D_{\text{fluid−melt}}−1)} \tag{S-4}$$

where $D_{\text{fluid-melt}}$ is the Mo partition coefficient between fluid and melt, here set to 0.6, which is the maximum value obtained in our experiments.

Results of the calculations and key parameters are shown in Table S-1.

Supplementary Table

Table S-1   Calculations of the Mo isotopic composition of a melt after 10 % fluid exsolution.

	Initial melt	Magma after 10 % fluid exsolution
f (fraction of Mo remaining)	1	0.94
F (fraction of melt remaining)	1	0.90
C_{Mo} (µg/g)	1	1.04
$\delta^{98/95}Mo_{melt}$	0	0.03

Supplementary Information References

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