Fluid-melt Mo isotope fractionation: implications for the δ⁹⁸/⁹⁵Mo of the upper crust

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Abstract

The isotopic composition (δ⁹⁸/⁹⁵Mo) of the modern upper continental crust (UCC) remains uncertain. A UCC estimate modelled from the δ⁹⁸/⁹⁵Mo of igneous rocks does not converge with constraints derived from the δ⁹⁸/⁹⁵Mo of magmatic-hydrothermal molybdenite (MoS₂), a mineral used as a proxy for UCC lithologies. To shed light on this discrepancy, we experimentally determined equilibrium Mo isotope fractionation values between exsolved fluids and melts (Δδ⁹⁸/⁹⁵Mofluid-melt) in shallow felsic magmatic systems. We show that light Mo isotopes are preferentially incorporated in aqueous supercritical fluids in equilibrium with silicic melts, with Δδ⁹⁸/⁹⁵Mo ranging from ~0.43‰ to ~0.17‰. The δ⁹⁸/⁹⁵Mo of exsolved fluids equilibrated in upper crustal silicic reservoirs should therefore be lighter than co-existing silicic melts. Since felsic plutonic rocks make ~50% of the UCC, estimates of UCC δ⁹⁸/⁹⁵Mo entirely based on igneous rock compositions or based on minerals (MoS₂) growing in magmatic-hydrothermal systems alone will lead to divergent values. Our results can therefore explain the discordance between current UCC δ⁹⁸/⁹⁵Mo constraints and provide new ones, representing a key step toward the determination of a robust estimate.

Introduction

The Mo stable isotopic system is a very promising tool to explore both the chemical evolution of the silicate Earth (e.g., McCoy-West et al., 2019) and the palaeo-redox conditions of oceans (e.g., Wille et al., 2007). Mass balance models associated with both types of applications strongly rely on the Mo isotopic composition (δ⁹⁸/⁹⁵Mo = 1000 x [(⁹⁸Mo/⁹⁵Moanalyte)/(⁹⁸Mo/⁹⁵Mostandard) − 1]) of the continental crust (CC), especially its upper layer (UCC), because it is highly enriched in Mo and in direct contact with the hydrosphere. While an estimate for the Mo stable isotope composition of the UCC created prior to the Great Oxidation Event (GOE; ∼2.4–2.2 Ga) exists (δ⁹⁸/⁹⁵Mo = ~0.03‰; Greaney et al., 2020), constraints on post-GOE UCC δ⁹⁸/⁹⁵Mo are scarce and conflicting. The difficulty in constraining the δ⁹⁸/⁹⁵Mo of the UCC after the GOE is a consequence of the redox sensitivity of Mo and its fluid-mobility under oxidising conditions. These properties, for instance, prevent the usage of fine grained clastic sedimentary rocks for that purpose (e.g., Greaney et al., 2020). One approach to constrain the δ⁹⁸/⁹⁵Mo of modern UCC does not involve the signatures of molybdenites (MoS₂), mostly derived from magmatic-hydrothermal fluids, as proxies for exposed rocks. It was initially thought that isotopic fractionation would be minor in high temperature systems and that, MoS₂ could therefore represent the isotopic composition of their crustal source rocks (e.g., Barling et al., 2001). As studies multiplied, it became clear that the controls on Mo isotopes in hydrothermal systems were more complex than initially thought (e.g., Hannah et al., 2007). Nevertheless, because these controls were inferred to result in progressively heavier MoS₂, a global average for MoS₂ δ⁹⁸/⁹⁵Mo was suggested to represent a maximum value for Phanerozoic UCC (Greber et al., 2014). This, however, is at odds with a recent Phanerozoic UCC composition derived from igneous rock compositions (δ⁹⁸/⁹⁵Mo = +0.14 ± 0.07‰; Yang et al., 2017), since the latter is visibly heavier than the most recent MoS₂ δ⁹⁸/⁹⁵Mo averages (+0.04‰ in Breillat et al., 2016; −0.04‰ in Willbold and Elliott, 2017). Clearly, current constraints on Phanerozoic UCC do not converge, and deriving a robust estimate will require a better understanding of magmatic-hydrothermal systems.

One geological process having the potential to create the discrepancy described above is Mo isotopic fractionation during fluid exsolution in silicic systems. The dominant igneous rock types in the UCC are plutonic silicic rocks, and these lithologies were shown to be depleted in Mo (20–90% depletion; mean 60%) compared to fluid immobile elements of similar incompatibility (e.g., Ce and Pr; Greaney et al., 2018). In some plutonic suites, correlations between Mo and fluid soluble elements exist, suggesting fluid exsolution as a dominant control over the Mo depletions observed (Greaney et al., 2018). Significant Mo partitioning in magmatic fluids is also supported by a large number of experimental (e.g., Candela and Holland, 1984) and empirical (e.g., Zajacz et al., 2008) studies. Whether isotopic fractionation is associated with this process remains unclear, with only one empirical study suggesting a possible enrichment of heavy Mo isotopes in fluids in a Mo porphyry deposit (Questa, USA; Greber et al., 2014). This is based on the very low Mo and light

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δ98/95Mo of a porphyry rhyolite dike compared to the molybdenites in the nearby and contemporaneous Questa mineralisation. However, the porphyry dike is altered and may not derive from the same magma as that from which the fluids of the mineralisation are derived (Göber et al., 2014 and references therein). Furthermore, theoretical constraints suggest that, in the occurrence of isotopic fractionation, a preferential enrichment of light Mo isotopes in the fluids should occur. This is because Mo coordination in silicate melts is tetrahedral, while both tetrahedral and octahedral coordination have been inferred for Mo in magmatic-hydrothermal fluids (e.g., Borg et al., 2012). Given that most MoS2 measured thus far have crystallised from fluids evolved from silicic magmas or melts highly enriched in those fluids (Breilat et al., 2016), a preferential enrichment in light Mo isotopes in the fluids could explain the lighter δ98/95Mo of MoS2 averages, compared to average silicic rocks (δ98/95Mo = +0.16 % in Yang et al., 2017) and the associated discrepancies in UCC constraints. It is therefore the aim of this contribution to establish the first experimental constraints of the fluid/melt equilibrium fractionation value of Mo stable isotopes (Δ98/95Mofluid-melt = δ98/95Mofluid − δ98/95Momelt) at temperatures, fluid salinities, melt compositions and oxygen fugacities relevant to supercritical fluid exsolution in upper crustal silicic magmatic systems.

## Methods

Twelve experiments were conducted at McGill University and Institut des Sciences de la Terre d’Orléans (ISTO) to simulate the equilibration of exsolved fluids with upper crustal felsic magmas. Conditions for each experiment are shown in Table 1. Cold seal pressure vessels were used, except for two experiments (Mo21 and Mo27) requiring the usage of internally heated pressure vessels (IHPV) to allow for higher temperature (900 °C) or higher oxygen fugacity (ΦO2) (Mo21 and Mo27) requiring the usage of internally heated pressure vessels. We therefore set the aluminium saturation index (ASI) and oxygen fugacity (ΦO2) to supercritical fluid exsolution in upper crustal silicic magma chambers (see Table 1). In similar experiments, chemical equilibrium is typically reached within a maximum of 10 days (e.g., Jiang et al., 2021 and references therein). Time scales for chemical and isotopic equilibrium were therefore assessed via a series of identical experiments performed at 800 °C with durations ranging from 1 to 20 days.

Mo isotope compositions and Mo concentrations of starting glasses, final (quenched) glasses and fluids were measured using double spike MC-ICP-MS at the University of Göttingen. The detailed description of the analytical approach is shown in the Supplementary Information. The uncertainty presented for the δ98/95Mo of each sample corresponds to twice the standard deviation of the replicate analyses of the Japan Geological Survey reference materials (±0.05 %).
Results

\( \delta^{98/95} \text{Mo} \) values and Mo concentrations of starting materials and experimental results are presented in Table 1, together with the calculated Mo partition coefficients between fluid and melt \( (D_{\text{fluid-melt}} = C_{\text{Mo,fluid}} / C_{\text{Mo,melt}}) \) and the \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) for each pair. The \( D_{\text{fluid-melt}} \) and \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) of identical experiments produced at different durations (the time series experiments; Figs. 1, 2) suggest that both chemical and isotopic equilibrium were reached between 5 and 10 days at 800 °C. This is consistent with chemical equilibrium time scales observed in similar experimental studies (e.g., Jiang et al., 2021 and references therein). Therefore, with the exception of the 1 and 5 days experiments, all presented experimental data represent equilibrium values.

At equilibrium, \( D_{\text{fluid-melt}} \) range from 0.27 to 0.60 and overlap the literature range for similar experiments (e.g., compilation in Fang and Audétat, 2022). \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) range from \( -0.43 \pm 0.07 \% \) to \( -0.17 \pm 0.07 \% \) (Fig. 2) and therefore indicate the preferential incorporation of light Mo isotopes in fluids under all investigated conditions, and whether or not the starting glass was doped. The data set shows a clear control of the melt ASI over \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) (linear regression with \( R^2 = 0.99 \); Fig. 3a) with the greatest isotopic differences observed in the samples with the least peralkaline composition. No effect of fluid salinity is observed (Fig. 3b). Apparent systematics suggest that \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) could be larger at lower temperatures and lower oxygen fugacities (Fig. 3c, d), but this is not resolvable in this data set, and further experimental investigation will be required to test these possible correlations.

Interpretation and Discussion of Experimental Results

The experimental data suggest that silicic melts with geologically realistic ASI will preferentially lose light Mo isotopes to exsolved supercritical fluids. In theory, both a difference in coordination and valence state of Mo between fluid and melt could induce the isotopic fractionation observed, i.e., higher coordination and/or lower valence state of Mo in the fluid than in the melt (e.g., Urey, 1947). However, thermodynamic and empirical evidence suggests that the valence state of Mo should be similar in silicate melts and associated magmatic-hydrothermal fluids, i.e., hexavalent (e.g., Kaufmann et al., 2021; Willbold and Elliott, 2017 and references therein). Therefore, the most likely driver behind the \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) observed in our experiments is higher Mo coordination in the fluid compared to the melt. In silicate melts, Mo dominantly occurs as tetrahedral molybdate species (\( \text{MoO}_4^{2-} \)). On the other hand, in high temperature fluids, the coordination of Mo remains debated. Some studies suggested that Mo dominantly occurs as Na-K molybdate, monochloride or thiomolybdate at modest salinity, and as Mo-oxy-hydroxy complexes at low salinity (Zhang et al., 2012; Taititch and Blundy, 2017). In such cases, Mo would be tetrahedrally coordinated, and no isotopic fractionation should be observed between fluids and melts, which is inconsistent with our experimental results. However, others have suggested the occurrence of species involving octahedrally coordinated Mo. For instance, Ulrich and Mavrogenes (2008) suggested the presence of a chloro-oxo Mo (VI) complex in high salinity (>20 % KCl) fluids (at 490 °C and ≥150 MPa). Borg et al. (2012), based on experiments performed at lower temperatures and pressures (up to 385 °C, 60 MPa), found that octahedral species were becoming predominant in increasingly acidic solutions (\( pH < 5 \)), with species such as molybdic acid and chloro-oxo Mo complexes. They also showed that increasing temperature favoured the formation of oxo-chloro complexes and suggested that these could be responsible for Mo transport in less acidic solutions at higher temperature (e.g., 700 °C), as proposed by Ulrich and Mavrogenes (2008). Based on the lack of correlation between \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) and starting fluid salinity in our experiments, a control of Mo isotopes by chloro-oxo Mo complexes alone seems unlikely. Hence, at least one other species in which Mo coordination is greater than tetrahedral, perhaps molybdic acid, is required in

![Figure 1](https://example.com/fig1.png)Mo isotopic composition (\( \delta^{98/95} \text{Mo} \)) of fluids and melts versus time. All experiments are identical except for their duration (days). Two experiments were performed for the 10 day duration. The average \( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \) (%) for the 5 experiments is also shown.

![Figure 2](https://example.com/fig2.png)Mo isotope fractionation value between fluid and melt (\( \Delta^{98/95} \text{Mo}_{\text{fluid-melt}} \)) versus the partition coefficient \( (D_{\text{fluid-melt}} = C_{\text{fluid}} / C_{\text{melt}}) \) for each experiment.
the fluids to explain the systematics observed in our experiments. Finally, the negative correlation between $\Delta^{\text{fluid-melt}}_{\text{Mo}}$ and ASI suggests that the latter exerts a strong influence on the coordination of Mo.

### Implications for the Composition of the Upper Continental Crust

Most large and long lived silicic magma chambers are located at upper crustal levels corresponding to lithostatic pressures of ~200 MPa (Huber et al., 2019). There, significant amounts of exsolved supercritical fluids accumulate and equilibrate with silicic magmas. Slow fluid exsolution associated with the cooling and crystallisation of the melt is punctuated by repetitive fast exsolution events associated with decompression of incoming recharging melt (e.g., Edmonds and Woods, 2018). Our data indicate that the extraction of these exsolved fluids likely results in the removal of light Mo from magma bodies, including precursor bodies of the silicic plutonic rocks making ~50% of the UCC (e.g., Wedepohl, 1995). The Mo depletion of these plutons (e.g., Greaney et al., 2018), together with the large number of experimental constraints, suggests that a significant Mo fraction must have been removed from their precursor melts via exsolved fluids. Since UCC silicic plutonic rocks are dominantly peraluminous (ASI ≈ 1.25; Wedepohl, 1995), our experiments suggest that resolvable $\Delta^{\text{fluid-melt}}_{\text{Mo}}$ likely applied during the devolatilisation of their precursor melt. In other words, the $\delta^{\text{UCC}}_{\text{Mo}}$ of UCC silicic plutons should be heavier than their precursor, undegassed melts. Based on our $D_{\text{fluid-melt}}$, the difference between undegassed and degassed silicic magmas might, however, not be large. For instance, using the highest $D_{\text{fluid-melt}}$ in our experiments and assuming an extreme scenario whereby a hydrous melt with 10 wt. % volatiles undergoes fluid exsolution with a $\Delta^{\text{fluid-melt}}_{\text{Mo}}$ of ~0.51‰ (extrapolation of the linear regression to ASI = 1.25 in Fig. 3a), would result in a residual melt that is only 0.03‰ heavier than the undegassed melt (see Supplementary Information for calculation). This is smaller than our analytical uncertainty. However, the range of published $D_{\text{fluid-melt}}$ for similar experiments is large and includes significantly higher values (e.g., compilation in Fang and Audétat, 2022). It is therefore best to consider the average $\delta^{\text{UCC}}_{\text{Mo}}$ of UCC silicic plutonic rocks (Yang et al., 2017) as a maximum value for the signature of the total Mo contribution to the UCC from undegassed silicic magmatism. In turn, UCC $\delta^{\text{UCC}}_{\text{Mo}}$ estimates derived from igneous rocks should also be viewed as maxima.

Based on our experiments, the average $\delta^{\text{UCC}}_{\text{Mo}}$ of UCC silicic rocks should also be clearly heavier than global $\delta^{\text{UCC}}_{\text{Mo}}$ average for UCC MoS$_2$ since MoS$_2$ measured thus far are from magmatic-hydrothermal systems. There, MoS$_2$ crystallises from both brines and low salinity vapours that unmix from supercritical fluids once they reach a miscibility gap in the NaCl-H$_2$O system during ascent in the shallowest part of magmatic-hydrothermal complexes (typically <140 MPa and 400–700 °C, e.g., Bodnar et al., 1985). The average UCC silicic rock composition ($\delta^{\text{UCC}}_{\text{Mo}}$ = ±0.16‰) of Yang et al. (2017) is indeed ~0.18‰ and ~0.12‰ heavier than the two most extensive and recent MoS$_2$ global averages of Willbold and Elliott (2017) and Breillat et al. (2016) (~0.04‰ and +0.04‰, respectively), in agreement with the direction of isotopic fractionation in the experiments. The isotopic difference between UCC silicic rocks and UCC magmatic-hydrothermal MoS$_2$ averages is however smaller than suggested by the experimental $\Delta^{\text{fluid-melt}}_{\text{Mo}}$ values. In the experiments, equilibrated melts are up to 0.4‰ heavier than associated supercritical fluids, and while this will need to be confirmed in future experiments, the negative correlation between $\Delta^{\text{fluid-melt}}_{\text{Mo}}$ and ASI suggests that even greater values could apply during exsolution from more peraluminous melts, such as those of the plutons dominating the UCC. While other factors are possible, this smaller isotopic difference could simply be the consequence of the timing of fluid exsolution relative to mineral fractionation in silicic magma chambers. Most recent studies suggest that long lived silicic magma reservoirs are largely crystallised between recharge events (e.g., Schmitt et al., 2010). Hence, over the lifespan of a silicic magma body, most exsolved fluids will
equilibrate with interstitial melts of crystal mushes. These interstitial melts are expected to be enriched in Mo, since it is an incompatible element. More importantly, based on the Mo coordination (octahedral) in all minerals capable of carrying significant amount of Mo in the mush (Ti-bearing oxides, biotite, amphibole, K feldspar; Greaney et al., 2018), interstitial melts (in which Mo is tetra-

hedral) are most likely isotopically heavier than the bulk mush. Exsolved fluids in equilibrium with these melts should therefore be heavier than hypothetical fluids in equilibrium with bulk mushes or fully crystallised equivalents. This would explain the smaller isotope difference between UCC silicic rocks and UCC MoS2 averages, than expected based on the experiments herein.

Overall, our results provide a solution for the discrepancy between the UCC δ98/95Mo estimate derived from exposed igneous UCC rocks and constraints obtained from average UCC MoS2. They also stress the lack of straightforward assessment of the UCC δ98/95Mo via MoS2 and suggest that UCC δ98/95Mo derived from igneous rock compositions should be considered as a maximum value.

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References


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

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**Supplementary Information**

The Supplementary Information includes:

- Experimental and Analytical Methods
- Details for Modelled Impact of Fluid Exsolution in Discussion
- Supplementary Table S-1
- Supplementary Information References

**Experimental and Analytical Methods**

**Preparation of starting materials**

The haplogranitic glasses used in the experiments were synthesised from SiO$_2$, Al(OH)$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$ (analytical grade). The different alumina saturation indices (ASI = 0.8 and 1) were obtained by changing the abundances of Al(OH)$_3$, Na$_2$CO$_3$, and K$_2$CO$_3$, 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$_2$O. 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$_2$O 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-H₂ (0.15–0.6 MPa H₂ total pressure) in order to vary fO₂ 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 H₂, 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–Pt₀₉–Rh₁₀ (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 de-ionised H₂O. They were then cooled by liquid N₂ 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 H₂O (MQ H₂O; 18.2 MΩ cm). The supernatant (MQ H₂O) 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 HNO₃ and 29 M HF for 72 h at 140 °C. The solutions were then dried down, followed by sample re-dissolution in 14 M HNO₃. 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 HNO₃. 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 HNO₃.

Mo separation and measurement

For each fluid and glass, an aliquot from the stock was spiked with a ⁹⁷Mo-¹⁰⁰Mo mixture and equilibrated in 14 M HNO₃ 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 HClO₄ (~50 μL) and 14 M HNO₃ (~500 μL). After this, the Mo cut was equilibrated and re-dissolved in 0.4 M HNO₃-0.05 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. 95Mo, 97Mo, 98Mo and 100Mo, were measured together with 101Ru and 99Ru using Faraday cups equipped with 10¹¹Ω (Mo isotopes) and 10¹³Ω (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 HNO₃-0.05 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 δ¹⁰⁰/⁹⁵Mo 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 ± 0.05 ‰ (2 s.d.) for JB-2 (n = 5), −0.17 ± 0.03 ‰ (2 s.d.) for AGV-2 (n = 8) and −0.04 ± 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 $\delta^{98/95}\text{Mo}$ 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:

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

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

\[
\alpha = \left(\frac{^{98}\text{Mo}/^{95}\text{Mo}}{^{98}\text{Mo}/^{95}\text{Mo}}\right)_{\text{fluid}} / \left(\frac{^{98}\text{Mo}/^{95}\text{Mo}}{^{98}\text{Mo}/^{95}\text{Mo}}\right)_{\text{melt}}
\]

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:

\[
f = F \times \frac{C_{\text{Mo,melt}}}{C_{\text{Mo,initial melt}}}
\]

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:

\[
C_{\text{Mo,melt}} = C_{\text{Mo,initial melt}} \times F^{(D_{\text{fluid-melt}} - 1)}
\]

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.

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<tr>
<th></th>
<th>Initial melt</th>
<th>Magma after 10 % fluid exsolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$ (fraction of Mo remaining)</td>
<td>1</td>
<td>0.94</td>
</tr>
<tr>
<td>$F$ (fraction of melt remaining)</td>
<td>1</td>
<td>0.90</td>
</tr>
<tr>
<td>$C_{Mo}$ ($\mu$g/g)</td>
<td>1</td>
<td>1.04</td>
</tr>
<tr>
<td>$\delta^{98/95}_{Mo}$melt</td>
<td>0</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Supplementary Information References**


[https://doi.org/10.1016/j.gca.2021.06.028](https://doi.org/10.1016/j.gca.2021.06.028)

[https://doi.org/10.1016/j.gca.2009.10.010](https://doi.org/10.1016/j.gca.2009.10.010)

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