

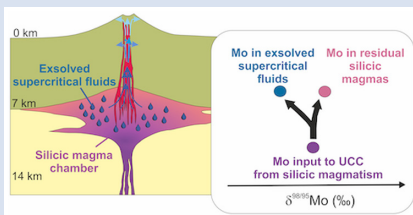
Fluid-melt Mo isotope fractionation: implications for the $\delta^{98/95}\text{Mo}$ of the upper crust

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Abstract



The isotopic composition ($\delta^{98/95}\text{Mo}$) of the modern upper continental crust (UCC) remains uncertain. A UCC estimate modelled from the $\delta^{98/95}\text{Mo}$ of igneous rocks does not converge with constraints derived from the $\delta^{98/95}\text{Mo}$ of magmatic-hydrothermal molybdenite (MoS_2), 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 ($\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$) in shallow felsic magmatic systems. We show that light Mo isotopes are preferentially incorporated in aqueous supercritical fluids in equilibrium with silicic melts, with $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ ranging from -0.43‰ to -0.17‰ . The $\delta^{98/95}\text{Mo}$ of exsolved fluids equilibrated in upper crustal silicic reservoirs should therefore be lighter than co-existing silicic melts. Since felsic plutonic rocks make $\sim 50\%$ of the UCC, estimates of UCC $\delta^{98/95}\text{Mo}$ entirely based on igneous rock compositions or based on minerals (MoS_2) growing in magmatic-hydrothermal systems alone will lead to divergent values. Our results can therefore explain the discordance between current UCC $\delta^{98/95}\text{Mo}$ constraints and provide new ones, representing a key step toward the determination of a robust estimate.

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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 ($\delta^{98/95}\text{Mo} = 1000 \times [({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{sample}}/({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{standard}}] - 1$) 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; $\sim 2.4\text{--}2.2$ Ga) exists ($\delta^{98/95}\text{Mo} = +0.03\text{‰}$; Greaney *et al.*, 2020), constraints on post-GOE UCC $\delta^{98/95}\text{Mo}$ are scarce and conflicting. The difficulty in constraining the $\delta^{98/95}\text{Mo}$ 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 $\delta^{98/95}\text{Mo}$ of modern UCC has been to use the signatures of molybdenites (MoS_2), 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, MoS_2 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 MoS_2 , a global average for MoS_2 $\delta^{98/95}\text{Mo}$ 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 ($\delta^{98/95}\text{Mo} = +0.14 \pm 0.07\text{‰}$; Yang *et al.*, 2017), since the latter is visibly heavier than the most recent MoS_2 $\delta^{98/95}\text{Mo}$ averages ($+0.04\text{‰}$ 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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$\delta^{98/95}\text{Mo}$ 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 (Greber *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 MoS_2 measured thus far have crystallised from fluids exsolved from silicic magmas or melts highly enriched in those fluids (Breillat *et al.*, 2016), a preferential enrichment in light Mo isotopes in the fluids could explain the lighter $\delta^{98/95}\text{Mo}$ of MoS_2 averages, compared to average silicic rocks ($\delta^{98/95}\text{Mo} = +0.16 \text{ ‰}$ 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 ($\Delta^{98/95}\text{Mo}_{\text{fluid-melt}} = \delta^{98/95}\text{Mo}_{\text{fluid}} - \delta^{98/95}\text{Mo}_{\text{melt}}$) 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 (~FMQ+3). Powders of Mo-doped haplogranitic glasses ($n = 11$) or non-doped natural obsidian ($n = 1$) were loaded into gold capsules together with Mo-free fluids in similar proportions (1:1) (see Supplementary Information for details on the experimental approach). The experiments were equilibrated at 200 MPa, a pressure relevant for most long lived magma chambers (*e.g.*, Huber *et al.*, 2019). At such conditions, a single magmatic fluid phase with low to intermediate salinity (*e.g.*, 1–5 wt. % NaCl in Rusk *et al.*, 2004), a supercritical fluid, exsolves from magmas (Burnham, 1979). We therefore set the range of salinity of our experimental fluids accordingly (0.5–1.5 M (Na,K)Cl). The effects of changing temperature, melt aluminium saturation index (ASI) and oxygen fugacity ($f\text{O}_2$) on $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ were also assessed over ranges relevant for 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 $\delta^{98/95}\text{Mo}$ of each sample corresponds to twice the standard deviation of the replicate analyses of the Japan Geological Survey reference materials ($\pm 0.05 \text{ ‰}$).

Table 1 Experimental conditions and results.

Experiment ID	Starting material*	T (°C)	Duration (days)	Starting glass ASI	(Na,K)Cl in fluid (mol/L)	$f\text{O}_2$	$\delta^{98/95}\text{Mo}_{\text{melt}}$ (‰)**	$C_{\text{Mo,melt}}$ (µg/g)	$\delta^{98/95}\text{Mo}_{\text{fluid}}$ (‰)**	$C_{\text{Mo,fluid}}$ (µg/g)	$D_{\text{fluid-melt}}$	$\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ (‰)**
Mo15	HG 1A	700	20	1	1	~FMQ+1	0.12	171	-0.31	47	0.28	-0.43
Mo22	HG 1A	800	1	1	1	~FMQ+1	0.08	197	-0.23	43	0.22	-0.30
Mo02	HG 1A	800	5	1	1	~FMQ+1	0.06	184	-0.25	48	0.26	-0.31
Mo03	HG 1A	800	10	1	1	~FMQ+1	0.09	176	-0.24	56	0.32	-0.32
Mo16	HG 1A	800	10	1	1	~FMQ+1	0.07	188	-0.26	52	0.28	-0.33
Mo07	HG 1A	800	20	1	1	~FMQ+1	0.09	171	-0.26	52	0.30	-0.36
Mo21	HG 1A	900	7	1	1	~FMQ+1	0.11	175	-0.24	59	0.34	-0.35
Mo05	HG 1A	800	10	1	0.5	~FMQ+1	0.07	187	-0.24	51	0.27	-0.32
Mo33	HG 1A	800	11	1	1.5	~FMQ+1	0.05	170	-0.26	63	0.37	-0.31
Mo27	HG 1B	800	10	1	1	~FMQ+3	0.03	269	-0.19	102	0.38	-0.22
Mo08	HG 0.8	800	10	0.80	1	~FMQ+1	0.05	245	-0.13	148	0.60	-0.17
Mo24	Nat. obsi.	800	10	0.85	1.5	~FMQ+1	0.19	5.8	-0.04	2.4	0.40	-0.23

Abbreviations: ASI, aluminum saturation index; $f\text{O}_2$, oxygen fugacity relative to the fayalite-magnetite-quartz buffer (FMQ).

* HG 1A: haplogranite with ASI = 1, 254 µg/g Mo and $\delta^{98/95}\text{Mo} = -0.01 \pm 0.05 \text{ ‰}$; HG 1B: haplogranite with ASI = 1, 383 µg/g Mo and $\delta^{98/95}\text{Mo} = -0.01 \pm 0.05 \text{ ‰}$; HG 0.8: haplogranite with ASI = 0.8, 421 µg/g Mo and $\delta^{98/95}\text{Mo} = -0.01 \pm 0.05 \text{ ‰}$.

** Error on $\delta^{98/95}\text{Mo}$ is 0.05 ‰; error on $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ is propagated (0.07 ‰).



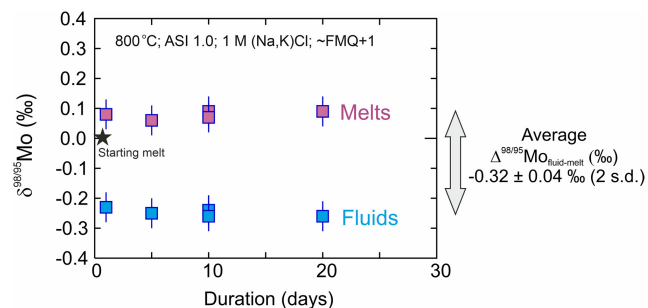


Figure 1 Mo isotopic composition ($\delta^{98/95}\text{Mo}$) of fluids and melts versus time. All experiments are identical except for their duration (days). Two experiments were performed for the 10 day duration. The average $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ (‰) for the 5 experiments is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

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 ± 0.07 ‰ to -0.17 ± 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 compositions. 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 (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 thio-molybdate at modest salinity, and as Mo-oxy-hydroxy complexes at low salinity (Zhang et al., 2012; Tattitch 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

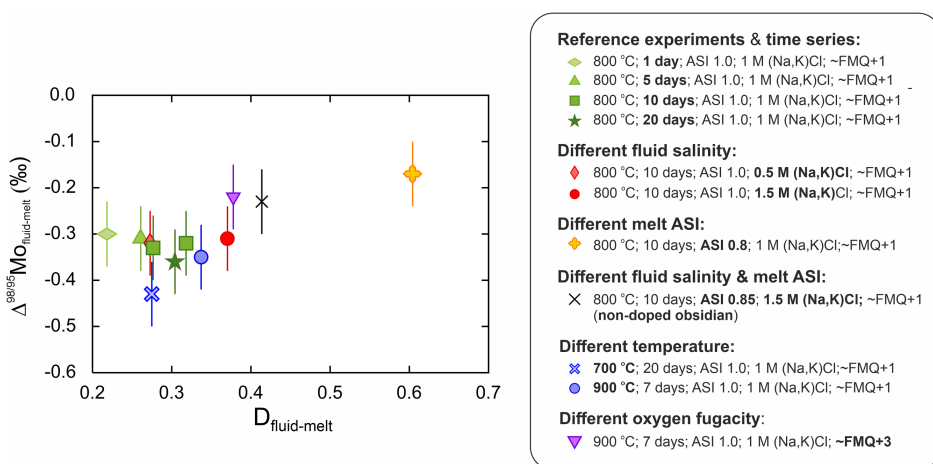


Figure 2 Mo isotope fractionation value between fluid and melt ($\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$) versus the partition coefficient ($D_{\text{fluid-melt}} = C_{\text{fluid}}/C_{\text{melt}}$) for each experiment.



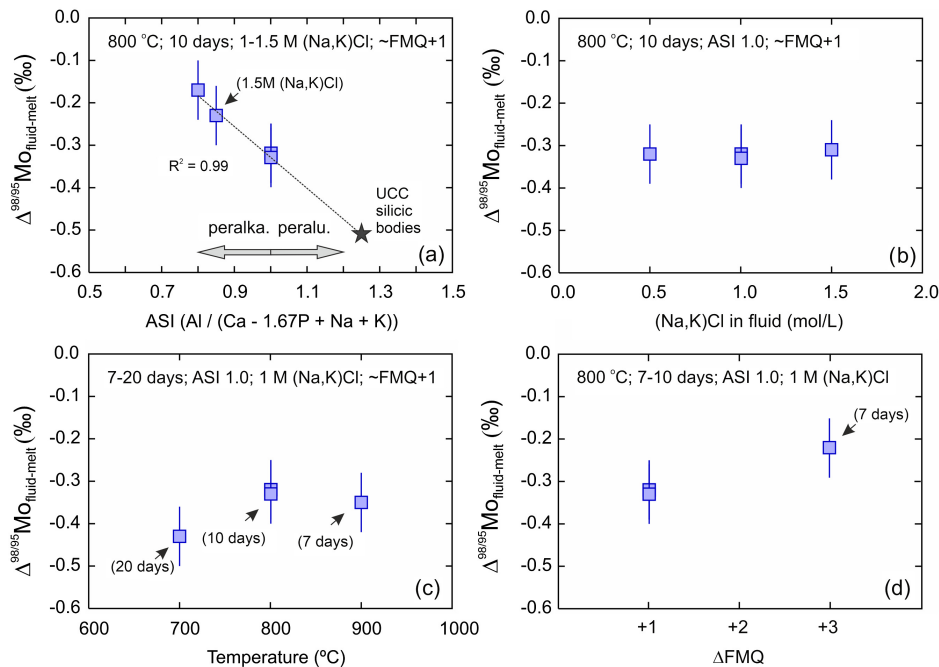


Figure 3 Evolution of the Mo isotope fractionation value between fluids and melts ($\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$) at different experimental (a) melt aluminium saturation indexes ($\text{ASI} = \text{Al}/(\text{Ca} - 1.67\text{P} + \text{Na} + \text{K})$), (b) fluid salinities, (c) temperatures and (d) oxygen fugacities ($f\text{O}_2$ relative to the fayalite-magnetite-quartz buffer, FMQ). Abbreviations: peralka., peralkaline; peralu., peraluminous.

the fluids to explain the systematics observed in our experiments. Finally, the negative correlation between $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ 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 ($\text{ASI} \approx 1.25$; Wedepohl, 1995), our experiments suggest that resolvable $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ likely applied during the devolatilisation of their precursor melt. In other words, the $\delta^{98/95}\text{Mo}$ 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 $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ of -0.51 ‰ (extrapolation of the linear regression to $\text{ASI} = 1.25$ 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 $\delta^{98/95}\text{Mo}$ 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 $\delta^{98/95}\text{Mo}$ estimates derived from igneous rocks should also be viewed as maxima.

Based on our experiments, the average $\delta^{98/95}\text{Mo}$ of UCC silicic rocks should also be clearly heavier than global $\delta^{98/95}\text{Mo}$ 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 $\text{NaCl-H}_2\text{O}$ system during ascent in the shallowest part of magmatic-hydrothermal complexes (typically <140 MPa and $400\text{--}700$ °C; *e.g.*, Bodnar *et al.*, 1985). The average UCC silicic rock composition ($\delta^{98/95}\text{Mo} = +0.16$ ‰) 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 $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ 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 $\Delta^{98/95}\text{Mo}_{\text{fluid-melt}}$ 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 tetrahedral) 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 isotopic 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 $\delta^{98/95}\text{Mo}$ estimate derived from exposed igneous UCC rocks and constraints obtained from average UCC MoS₂. They also stress the lack of straight forward assessment of the UCC $\delta^{98/95}\text{Mo}$ *via* MoS₂ and suggest that UCC $\delta^{98/95}\text{Mo}$ derived from igneous rock compositions should be considered as a maximum value.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2320>.



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References

- BARLING, J., ARNOLD, G.L., ANBAR, A.D. (2001) Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth and Planetary Science Letters* 193, 447–457. [https://doi.org/10.1016/S0012-821X\(01\)00514-3](https://doi.org/10.1016/S0012-821X(01)00514-3)
- BODNAR, R.J., BURNHAM, C.W., STERNER, S.M. (1985) Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system H₂O–NaCl to 1000°C and 1500 bars. *Geochimica et Cosmochimica Acta* 49, 1861–1873. [https://doi.org/10.1016/0016-7037\(85\)90081-X](https://doi.org/10.1016/0016-7037(85)90081-X)
- BORG, S., LIU, W., ETSCHMANN, B., TIAN, Y., BRUGGER, J. (2012) An XAS study of molybdenum speciation in hydrothermal chloride solutions from 25–385 °C and 600 bar. *Geochimica et Cosmochimica Acta* 92, 292–307. <https://doi.org/10.1016/j.gca.2012.06.001>
- BREILLAT, N., GUERROT, C., MARCOUX, E., NÉGREL, PH. (2016) A new global database of $\delta^{98}\text{Mo}$ in molybdenites: A literature review and new data. *Journal of Geochemical Exploration* 161, 1–15. <https://doi.org/10.1016/j.gexplo.2015.07.019>
- BURNHAM, C.W. (1979) Magmas and hydrothermal fluids. In: BARNES, H.L. (Ed.) *Geochemistry of Hydrothermal Ore Deposits*. Second Edition, Wiley, New York, 71–136.
- CANDELA, P.A., HOLLAND, H.D. (1984) The partitioning of copper and molybdenum between silicate melts and aqueous fluids. *Geochimica et Cosmochimica Acta* 48, 373–380. [https://doi.org/10.1016/0016-7037\(84\)90257-6](https://doi.org/10.1016/0016-7037(84)90257-6)
- EDMONDS, M., WOODS, A.W. (2018) Exsolved volatiles in magma reservoirs. *Journal of Volcanology and Geothermal Research* 368, 13–30. <https://doi.org/10.1016/j.jvolgeores.2018.10.018>
- FANG, J., AUDÉTAT, A. (2022) The effects of pressure, f_{O_2} , f_{S_2} and melt composition on the fluid–melt partitioning of Mo: Implications for the Mo-mineralization potential of upper crustal granitic magmas. *Geochimica et Cosmochimica Acta* 336, 1–14. <https://doi.org/10.1016/j.gca.2022.08.016>
- GREANEY, A.T., RUDNICK, R.L., GASCHNIG, R.M., WHALEN, J.B., LUAI, B., CLEMENS, J.D. (2018) Geochemistry of molybdenum in the continental crust. *Geochimica et Cosmochimica Acta* 238, 36–54. <https://doi.org/10.1016/j.gca.2018.06.039>
- GREANEY, A.T., RUDNICK, R.L., ROMANIELLO, S.J., JOHNSON, A.C., GASCHNIG, R.M., ANBAR, A.D. (2020) Molybdenum isotope fractionation in glacial diamictites tracks the onset of oxidative weathering of the continental crust. *Earth and Planetary Science Letters* 534, 116083. <https://doi.org/10.1016/j.epsl.2020.116083>
- GREBER, N.D., PETTKE, T., NÄGLER, T.F. (2014) Magmatic–hydrothermal molybdenum isotope fractionation and its relevance to the igneous crustal signature. *Lithos* 190–191, 104–110. <https://doi.org/10.1016/j.lithos.2013.11.006>
- HANNAH, J.L., STEIN, H.J., WIESER, M.E., DE LAETER, J.R., VARNER, M.D. (2007) Molybdenum isotope variations in molybdenite: Vapor transport and Rayleigh fractionation of Mo. *Geology* 35, 703–706. <https://doi.org/10.1130/G23538A.1>
- HUBER, C., TOWNSEND, M., DEGRUYTER, W., BACHMANN, O. (2019) Optimal depth of subvolcanic magma chamber growth controlled by volatiles and crust rheology. *Nature Geoscience* 12, 762–768. <https://doi.org/10.1038/s41561-019-0415-6>
- JIANG, Z., SHANG, L., GUO, H., WANG, X.-S., CHEN, C., ZHOU, Y. (2021) An experimental investigation into the partition of Mo between aqueous fluids and felsic melts: Implications for the genesis of porphyry Mo ore deposits. *Ore Geology Reviews* 134, 104144. <https://doi.org/10.1016/j.oregeorev.2021.104144>
- KAUFMANN, A.K.C., PETTKE, T., WILLE, M. (2021) Molybdenum isotope fractionation at upper-crustal magmatic–hydrothermal conditions. *Chemical Geology* 578, 120319. <https://doi.org/10.1016/j.chemgeo.2021.120319>
- MCCOY-WEST, A.J., CHOWDHURY, P., BURTON, K.W., SOSSI, P., NOWELL, G.M., FITTON, J.G., KERR, A.C., CAWOOD, P.A., WILLIAMS, H.M. (2019) Extensive crustal extraction in Earth's early history inferred from molybdenum isotopes. *Nature Geoscience* 12, 946–951. <https://doi.org/10.1038/s41561-019-0451-2>
- RUSK, B.G., REED, M.H., DILLES, J.H., KLEMM, L.M., HEINRICH, C.A. (2004) Compositions of magmatic hydrothermal fluids determined by LA-ICP-MS of fluid inclusions from the porphyry copper–molybdenum deposit at Butte, MT. *Chemical Geology* 210, 173–199. <https://doi.org/10.1016/j.chemgeo.2004.06.011>
- SCHMITT, A.K., STOCKLI, D.F., LINDSAY, J.M., ROBERTSON, R., LOVERA, O.M., KISLITSYN, R. (2010) Episodic growth and homogenization of plutonic rocks in arc volcanoes from combined U–Th and (U–Th)/He zircon dating. *Earth and Planetary Science Letters* 295, 91–103. <https://doi.org/10.1016/j.epsl.2010.03.028>
- TATTITCH, B.C., BLUNDY, J.D. (2017) Cu–Mo partitioning between felsic melts and saline–aqueous fluids as a function of $X_{\text{NaCl(aq)}}$, f_{O_2} , and f_{S_2} . *American Mineralogist* 102, 1987–2006. <https://doi.org/10.2138/am-2017-5998>
- ULRICH, T., MAVROGENES, J. (2008) An experimental study of the solubility of molybdenum in H₂O and KCl–H₂O solutions from 500 °C to 800 °C, and 150 to 300 MPa. *Geochimica et Cosmochimica Acta* 72, 2316–2330. <https://doi.org/10.1016/j.gca.2008.02.014>
- UREY, H.C. (1947) The Thermodynamic Properties of Isotopic Substances. *Journal of the Chemical Society (Resumed)* 1947, 562–581. <https://doi.org/10.1039/jr9470000562>
- WEDEPOHL, K.H. (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59, 1217–1232. [https://doi.org/10.1016/0016-7037\(95\)00038-2](https://doi.org/10.1016/0016-7037(95)00038-2)
- WILLBOLD, M., ELLIOTT, T. (2017) Molybdenum isotope variations in magmatic rocks. *Chemical Geology* 449, 253–268. <https://doi.org/10.1016/j.chemgeo.2016.12.011>



- WILLE, M., KRAMERS, J.D., NÄGLER, T.F., BEUKES, N.J., SCHRÖDER, S., MEISEL, TH., LACASSIE, J.P., VOEGELIN, A.R. (2007) Evidence for a gradual rise of oxygen between 2.6 and 2.5 Ga from Mo isotopes and Re-PGE signatures in shales. *Geochimica et Cosmochimica Acta* 71, 2417–2435. <https://doi.org/10.1016/j.gca.2007.02.019>
- YANG, J., BARLING, J., SIEBERT, C., FIETZKE, J., STEPHENS, E., HALLIDAY, A.N. (2017) The molybdenum isotopic compositions of I-, S- and A-type granitic suites. *Geochimica et Cosmochimica Acta* 205, 168–186. <https://doi.org/10.1016/j.gca.2017.01.027>
- ZAJACZ, Z., HALTER, W.E., PETKE, T., GUILLONG, M. (2008) Determination of fluid/melt partition coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: Controls on element partitioning. *Geochimica et Cosmochimica Acta* 72, 2169–2197. <https://doi.org/10.1016/j.gca.2008.01.034>
- ZHANG, L., AUDÉTAT, A., DOLEJŠ, D. (2012) Solubility of molybdenite (MoS₂) in aqueous fluids at 600–800 °C, 200 MPa: A synthetic fluid inclusion study. *Geochimica et Cosmochimica Acta* 77, 175–185. <https://doi.org/10.1016/j.gca.2011.11.015>