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Mo Isotope Partitioning Between Aqueous Fluids and Felsic Melts: Implications for the Mo Isotopic Composition of the Upper Continental Crust

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The Mo isotopic composition ($\delta^{98/95}$Mo) of the modern upper continental crust (UCC) is key for the main applications of the Mo stable isotopic system, such as the reconstruction of paleo-redox conditions of oceans. Yet, it remains uncertain due to the discrepancy between constraints obtained from different approaches: the $\delta^{98/95}$Mo of the UCC determined from exposed igneous rocks (e.g., $\delta^{98/95}$Mo = +0.14 ± 0.07‰ in [1]) is heavier than the maximum UCC values derived from global averages for molybdenite (MoS_2; e.g., $\delta^{98/95}$Mo = -0.04‰ in [2])), a mineral used as a proxy for UCC lithologies [3]. Igneous UCC rocks are dominantly felsic and MoS_2 measured for their $\delta^{98/95}$Mo mostly crystallized from magmatic-hydrothermal fluids in differentiated systems [e.g., 2]. Therefore, the derivation of a more robust UCC estimate will require a better understanding of the behaviour of Mo isotopes in silicic magmatic-hydrothermal systems. To this end, we experimentally investigated the fractionation of Mo isotopes between aqueous fluids and silicic melts at T (700-900ºC), P (2 kbar) and fO_2 (from ~FMQ+1 to ~FMQ+3) relevant for typical shallow magma chambers.

Our results show significant isotopic fractionation between equilibrated fluids and melts with $\Delta^{98/95}Mo_{fluid\text{-}melt}$ ranging from -0.43‰ to -0.17‰. No correlation between $\Delta^{98/95}Mo_{fluid\text{-}melt}$ and fluid salinity (0.5-1.5 mol/L (Na,K)Cl), T or fO_2 can be resolved. On the other hand, $\Delta^{98/95}Mo_{fluid\text{-}melt}$ correlates negatively with melt alumina saturation index (ASI; 0.8-1) implying a strong impact of this parameter. Our results suggest that the $\delta^{98/95}$Mo of supercritical fluids exsolved from shallow silicic magmas could be lighter than co-existing silicic melts. This could, in turn, explain the lighter $\delta^{98/95}$Mo of global MoS_2 averages compared to average silicic plutonic rocks, and therefore the discrepancy between UCC constraints derived from them. Fluid exsolution therefore needs to be considered for the derivation of a more robust UCC $\delta^{98/95}$Mo estimate, and for applications of Mo isotopes in hydrothermal-magmatic systems in general.

[1] Yang et al (2017) *GCA* 205, 168-186. [2] Willbold & Elliott (2017) *Chem Geol* 449, 253-268. [3] Greber et al (2014) *Lithos* 190, 104-110.