

## The effect of valence and coordination on Mo isotope fractionation between metal and silicate

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Mass-dependent fractionation of isotopes occurs during a variety of geological processes. As a rule-of-thumb, the magnitude of such fractionation increases with greater contrast in valence and coordination state between two phases increases. However, the relative effects of these structural features on isotopic fractionation have been poorly known.

Molybdenum can have variable valences in silicate liquid equilibrated with metal and, therefore, may provide information on the relative effects of oxidation state on isotopic fractionation. However, a previous study of Mo isotope fractionation between metal and silicate liquids [1] did not constrain the range of  $\text{Mo}^{6+}/\text{Mo}^{4+}$  in the melt.

To obtain a large range in  $\text{Mo}^{6+}/\text{Mo}^{4+}$  in the silicate liquid, we performed experiments at 1400°C in a controlled-atmosphere furnace.  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  mixtures were equilibrated with either pure Mo or Au alloyed with 2.5 wt% Mo. These compositions were chosen to avoid compositional changes between experiments at different oxygen fugacities.

Run products were analysed by X-ray Absorption Near-Edge Structure spectroscopy to determine Mo valences before analysis of Mo isotope ratios by multi-collector inductively coupled plasma mass spectrometry using a double spike to correct for mass fractionation during chemistry and analysis.

Results show that Mo isotope fractionation between metal and silicate varies linearly with  $\text{Mo}^{6+}/\Sigma\text{Mo}$  implying that silicate liquid containing only  $\text{Mo}^{6+}$  has ~0.5‰ heavier  $^{98}\text{Mo}/^{95}\text{Mo}$  than silicate liquid containing only  $\text{Mo}^{4+}$ . The effect of valence and coordination cannot strictly be deconvolved from these results because  $\text{Mo}^{6+}$  is tetrahedrally and  $\text{Mo}^{4+}$  octahedrally coordinated. Tantalisingly, however, insights into unravelling the effects of these structural features may come from a ~0.3‰ offset between experiments with pure Mo and Au-Mo alloys, which we speculatively interpret as an effect arising from differences in Mo coordination in the metal phase.

[1] Hin et al., 2013. *EPSL* 379, 38-48. [2] Farges et al., 2006. *Can. Min.* 44, 731-753.