The influence of valence state on molybdenum isotope fractionation

REMCO C. HIN[1*], ANTONY D. BURNHAM[12],
MICHAEL J. WALTER[1] AND TIM ELLIOTT[1]

[1]University of Bristol, School of Earth Sciences, Bristol, UK.
(*Correspondence: remco.hin@bristol.ac.uk)
[2]Research School of Earth Sciences, The Australian National University, Canberra, Australia.

Mass-dependent fractionation of 'non traditional' stable isotopes has emerged as a tool to investigate a variety of geological processes. Important driving forces for mass-dependent isotopic fractionation are variable valence or coordination states between different phases. Owing to its various valence states, molybdenum is an attractive element to investigate for mass-dependent fractionation of its isotopes during geological processes. Recent contributions have studied Mo isotope fractionation during core formation, mantle differentiation, and crust formation [1-3].

In silicate rocks, 6+ and 4+ are the most common valence states of Mo, with the change occuring at an oxygen fugacty around one log unit below the iron-wüstite buffer [4] [5]. Although an experimental study [6] found 0.19±0.03‰ fractionation in $^{98/95}$Mo isotope ratios between liquid metal and liquid silicate, it remains unexplored whether Mo isotope fractionation can occur between Mo^{6+} and Mo^{4+} in the silicate portions of planetary objects.

To investigate the effect of valence state on Mo isotope fractionation, we have conducted a series of metal-silicate liquid equilibration experiments between oxygen fugacties of $10^{-12.7}$ and $10^{-9.9}$ at 1400°C. XANES analyses of the silicate glasses indicate a change in $Mo^{6+}/\Sigma Mo$ from ~0.66 to ~0.07 between oxygen fugacities of $10^{-9.9}$ and $10^{-10.8}$, based on pre-edge peak amplitudes indicative of Mo^{6+}.

Preliminary analyses of Mo isotope compositions by solution MC-ICPMS, emplying a double spiking technique, reveal that silicate liquids have ~0.20‰ heavier $^{98/95}$Mo compared to Mo metal, which is within error of a previous study [6]. This indicates that no resolvable fractionation between Mo^{6+} and Mo^{4+} occurs to a precision of ~0.04‰. An implication is that variations in Mo isotope compositions observed between silicate rocks are probably not driven by fractionation between Mo^{6+} and Mo^{4+}.

[1] Burkhardt *et al*. (2014) *EPSL* **391**, 201-211. [2] Voegelin *et al*. (2014) *Lithos* **190**, 440-448. [3] Liang *et al*. (2013), Mineral Mag *77*, **1607**. [4] O'Neill and Eggins (2002), *Chem Geol* **186**, 151-181. [5] Farges *et al*. (2006), *Can Min* **44**, 731-753. [6] Hin *et al*. (2013), *EPSL* **379**, 38-48.