Controls on the molybdenum isotope composition of river water: Insights from Iceland and New Zealand

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The molybdenum (Mo) isotope composition of river water plays a central role in setting the $\delta^{98/95}$Mo of the oceans [1] [2]. Use of $\delta^{98/95}$Mo as a palæo-redox proxy in marine sediments requires quantification of the controls on $\delta^{98/95}$Mo in continental runoff. Additionally, Mo can be sourced from sulfides and organic carbon, and its mobilisation may help quantify oxidative weathering reactions which govern the long-term evolution of atmospheric CO_2 and O_2 [3] [4]. Here we present measurements of redox-sensitive trace elements Mo and rhenium (Re) and $\delta^{98/95}$Mo in rivers with contrasting lithology and differing erosion processes (glacial versus non-glacial) to understand dissolved $\delta^{98/95}$Mo variability.

Existing $\delta^{98/95}$Mo data from glacial rivers in basaltic catchments in Iceland [2] show $\delta^{98/95}$Mo values increase from ~0‰ close to the source to ~1‰ downstream. This is thought to reflect weathering of basalt (0‰) and isotope fractionation downstream associated with oxy-hydroxide formation or cycling of Mo through organic matter. New data from the Skaftá glacial river indicates higher $\delta^{98/95}$Mo values at the source (0.43‰) which decrease downstream (0.23‰), suggesting a role of the rhyolitic basement geology in this catchment and a predominance of sulfide weathering. A sulfidic source of Mo is supported by high sulfate concentrations. $\delta^{98/95}$Mo data from the Skaftá River also support the premise that glacial systems are isotopically heavy compared with non-glacial systems [2] with a non-glacial tributary having $\delta^{98/95}$Mo = 0.08‰. Sediment with high surface area to volume ratio in glacial catchments may facilitate increased isotopic fractionation.

Preliminary dissolved Re concentrations in rivers draining meta-sedimentary bedrock in the western Southern Alps, New Zealand, suggest that the efficiency of oxidative weathering reactions is much greater in glacial ([Re] = 1.3ppt-1.5ppt) compared with non-glacial catchments ([Re] = 0.4-0.7ppt). Application of $\delta^{98/95}$Mo in these systems will lend new insights into the role of Mo source versus isotope fractionation during weathering in these catchments.

[1] Archer & Vance (2008) *Nature Geosci.* **1**, 597-600. [2] Pearce *et al.* (2010) *EPSL* **295**, 104-114. [3] Calmels *et al.* (2007) *Geology* **35**, 1003-1006. [4] Hilton *et al.* (2014) *EPSL* **403**, 27-36.