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Unravelling the controls on the molybdenum isotope ratios of river waters

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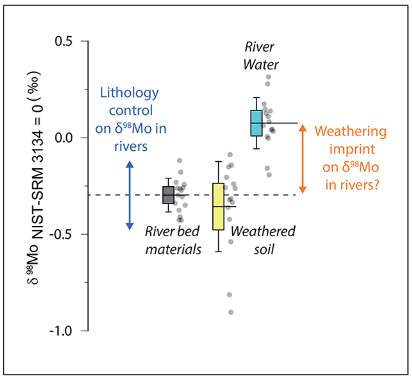
Abstract



The molybdenum (Mo) isotope ratios ($\delta^{98/95}$Mo) of river waters control the $\delta^{98/95}$Mo values of seawater and impact on the use of Mo isotope ratios as a proxy of past redox conditions. The $\delta^{98/95}$Mo values of river waters vary by more than 2 ‰, yet the relative roles of lithology *versus* fractionation during weathering remain contested. Here, we combine measurements from river waters ($\delta^{98/95}Mo_{diss}$), river bed materials ($\delta^{98/95}Mo_{BM}$) and soils from locations with contrasting lithology. The $\delta^{98/95}$Mo values of river bed materials ($\delta^{98/95}Mo_{BM}$), set by rock type, vary by ~1 ‰ between rivers in New Zealand, the Mackenzie Basin, and Iceland. However, the difference between dissolved and solid phase Mo isotopes ($\Delta^{98/95}Mo_{diss\text{-}BM}$) varies from +0.3 ‰ to +1.0 ‰. We estimate Mo removal from solution using the mobile trace element rhenium and find that it correlates with $\Delta^{98/95}Mo_{diss\text{-}BM}$ across the sample set. The adsorption of Mo to Fe-Mn-(oxyhydr)oxides can explain the observed fractionation. Together, the amount of Mo released through dissolution and taken up by (oxyhydr)oxide formation on land may cause changes in the $\delta^{98/95}$Mo values of rivers, driving long term changes in the Mo isotope ratios of seawater.

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Introduction

The cycling of molybdenum (Mo) in Earth's surface environments holds key information on the weathering and redox reactions that control atmospheric gas concentrations (Arnold *et al.*, 2004; Dickson, 2017). This is because Mo isotopes (reported here as $\delta^{98/95}Mo = [((^{98}Mo/^{95}Mo)_{sample}/\ (^{98}Mo/^{95}Mo)_{NIST\text{-}SRM\text{-}3134}) - 1\ ] \times 1000$ [‰]) can be fractionated during Mo removal from seawater, depending on the redox conditions of the sediment pore waters and overlying water column, and dissolved Mo speciation (Kerl *et al.*, 2017). Reconstructing the $\delta^{98/95}$Mo values of seawater is a recognised method for assessing the extent of past euxinic conditions and is linked to ocean oxygenation (Pearce *et al.*, 2008). Rivers are the largest input flux of Mo to oceans (~3.1×10^8 mol yr^{-1}). Consequently, the isotope ratios of dissolved Mo in rivers ($\delta^{98/95}Mo_{diss}$) control the $\delta^{98/95}$Mo values of seawater and estimations of the extent of past seawater euxinia from geochemical records (Archer and Vance, 2008).

The measured range of $\delta^{98/95}Mo_{diss}$ values in rivers is >2 ‰ (Fig. 1). Some of this variability has been linked to the Mo isotope fractionation occurring during chemical weathering and the formation of secondary minerals, such as iron (Fe) and manganese (Mn) (oxyhydr)oxides (Pearce *et al.*, 2010; Wang *et al.*, 2015, 2018). However, other studies have emphasised the role of lithology and weathering of labile phases, such as sulfide minerals, in setting the $\delta^{98/95}Mo_{diss}$ of rivers (Voegelin *et al.*, 2012; Neely *et al.*, 2018). It is important to constrain their relative importance to understand how and why $\delta^{98/95}Mo_{diss}$ values of rivers might change. For instance, changes in the extent of primary and secondary weathering could lead to changes in the $\delta^{98/95}Mo_{diss}$ of rivers over geological timescales, which may leave an imprint on seawater chemistry (Dickson, 2017). Untangling the dual controls of source and process on river $\delta^{98/95}Mo_{diss}$ values is challenging (King and Pett-Ridge, 2018). This is primarily because we lack information on the $\delta^{98/95}$Mo values of rocks and soils in many river catchments (Archer and Vance, 2008).

Here, we measure $\delta^{98/95}Mo_{diss}$ in river water alongside solid products of erosion and weathering found in river bed materials, suspended sediments and soils (Tables S-1–S-4). We focus on three sets of rivers that have contrasting bedrock geology (albeit with heterogeneities in each location): 13 rivers from the Southern Alps, New Zealand (metasedimentary);

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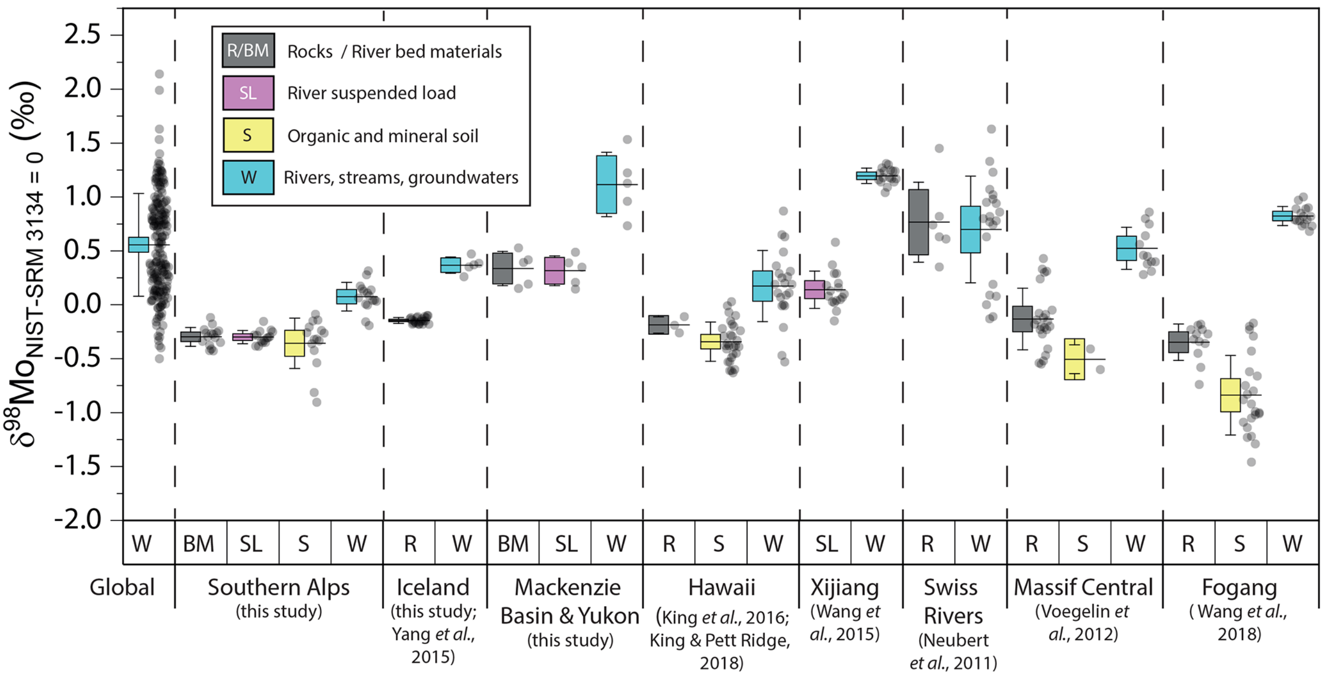

Figure 1 Molybdenum isotope ratios ($\delta^{98/95}$Mo, NIST-SRM3134 = 0 ‰) for this study (Southern Alps, Iceland, Mackenzie Basin and Yukon), alongside published measurements with: R = rocks, BM = river bed materials (grey); SL = suspended load (pink); S = soils (yellow); W = water (blue). Measurements are shown as grey dots, bars show the ±2 s.e. and whiskers ±2 s.d.

the Skaftá River, Iceland (volcanic); and the Mackenzie River and Yukon Rivers, Canada (sedimentary dominated) (Supplementary Information). We use the trace element rhenium (Re), which is hosted in similar phases as Mo but is not susceptible to uptake during Fe-Mn-(oxyhydr)oxide formation (Miller *et al.*, 2011), to help track the imprint of Mo isotope fractionation during chemical weathering.

Lithological Imprint on River Water $\delta^{98/95}$Mo

Chemical weathering can oxidise Mo in rocks to the soluble MoO_4^{2-} anion, which can be leached from soils and delivered as dissolved Mo to rivers (Miller *et al.*, 2011). The starting isotope ratios of Mo-bearing phases can vary, with contrasts between igneous and sedimentary rocks, where the $\delta^{98/95}$Mo values of the latter depend on the redox state of the depositional environment, and can vary by ~2 ‰ at the outcrop scale (Pearce *et al.*, 2010; Yang *et al.*, 2015; Kendall *et al.*, 2017; Neely *et al.*, 2018; Li *et al.*, 2019).

To constrain the composition of the rocks undergoing weathering, the most unweathered parts of river sediment loads can be used; these are typically found in the sand and silts of river bed materials in erosive settings (*e.g.*, Hilton *et al.*, 2010). In the western Southern Alps, bulk river bed material samples across 11 catchments have relatively homogenous isotope ratios, with a mean $\delta^{98/95}$Mo value (NIST-3134 = 0 ‰; Supplementary Information) of -0.30 ± 0.05 ‰ (n = 11, mean ± 2 s.e. unless otherwise stated). These contrast with published rocks from Iceland (-0.15 ± 0.01 ‰; Yang *et al.*, 2015) and our river bed materials from the Mackenzie Basin (0.38 ± 0.14 ‰, n = 4) (Table S-1). The differences are consistent with the relatively organic carbon and sulfide poor greywacke of the Southern Alps (Roser and Cooper, 1990), which may represent oxic depositional conditions favouring lower $\delta^{98/95}$Mo values. In the Mackenzie Basin, black shales deposited under euxinic conditions may have higher $\delta^{98/95}$Mo (Johnston *et al.*, 2012). When we compare $\delta^{98/95}Mo_{diss}$ values of rivers at our study sites alongside published measurements, we find that river water $\delta^{98/95}Mo_{diss}$ values are ~0.2 ‰ to >1 ‰ higher than their complementary solids (Fig. 1). General shifts in $\delta^{98/95}Mo_{diss}$ values between locations can be explained by shifting rock compositions, but the systematically higher $\delta^{98/95}Mo_{diss}$ values in streams and rivers requires further explanation.

Previous work has suggested that incongruent weathering of phases, such as sulfide and sulfate minerals, may play a role in setting the $\delta^{98/95}Mo_{diss}$ values of rivers (Neubert *et al.*, 2011; Voegelin *et al.*, 2012) and groundwaters (Neely *et al.*, 2018). To explore this, we examine $\delta^{98/95}$Mo values alongside concentration ratios of [Mo] to rhenium, [Re], in rivers, soils and sediments from the Southern Alps (Fig. 2). Rhenium is a mobile and soluble element that is also sourced from organic and sulfide phases, yet in contrast to Mo, Re is not thought to be incorporated into secondary weathering products (Miller *et al.*, 2011). If preferential weathering of sulfide phases is responsible for the fractionation patterns, we would expect waters to have sulfide-like compositions (high $\delta^{98/95}$Mo, high [Mo]/[Re]) (Miller *et al.*, 2011; Neely *et al.*, 2018), while the residue in soils would have lower $\delta^{98/95}$Mo and [Mo]/[Re] values than parent materials. Our data lie perpendicular to this (Fig. 2), with soils having Mo enrichment relative to Re when compared to river bed materials. A negative pattern between $\delta^{98/95}$Mo and [Mo]/[Re] across our sample set is consistent with a process that preferentially removes light Mo isotopes from waters, and leaves a complementary pool of light Mo isotopes in soils.

Chemical Weathering Imprint on River Water $\delta^{98/95}$Mo

Field observations and experiments suggest Mo can be removed from solution during Fe-Mn (oxyhydr)oxide formation (Barling and Anbar, 2004; Goldberg *et al.*, 2009; Pearce *et al.*, 2010) and can be adsorbed onto organic matter (Siebert *et al.*, 2015; King *et al.*, 2018). To explore the potential imprint of this process in both the western Southern Alps and our wider sample set,

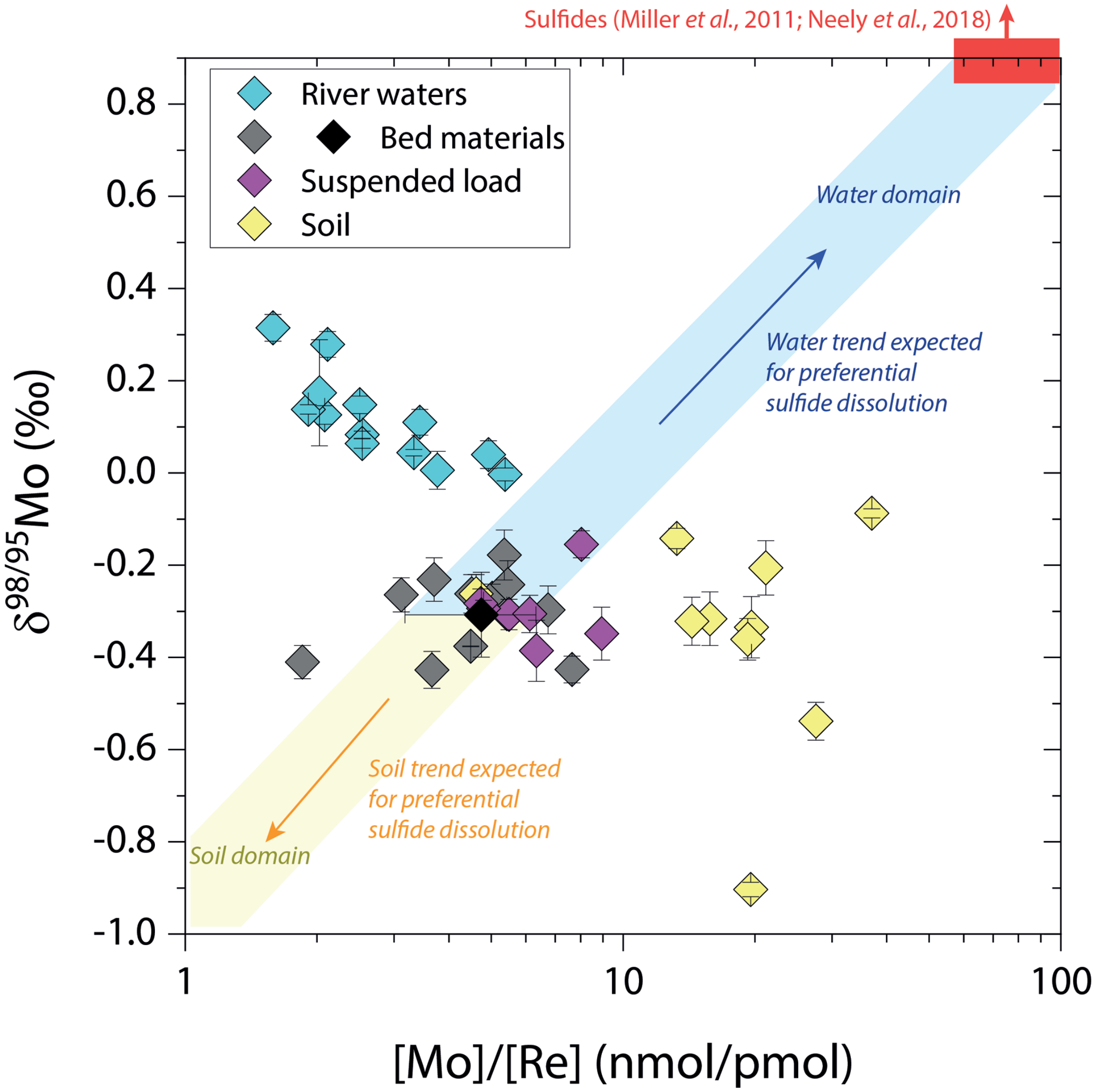

Figure 2 The Mo isotope ratios of materials from the western Southern Alps, New Zealand, *versus* the Mo to Re concentration ratios for river waters (light blue), river bed materials (grey), suspended load (purple) and soils (yellow). Black diamond is the mean of the bed material samples. Shaded domains show the expected fields of soil and water compositions if preferential dissolution of sulfides was occuring, but data lie perpendicular to this trend implying an alternative mechanism is responsible for fractionation patterns observed.

we use [Mo]:[Re] ratios to quantify Mo removal from solution (Supplementary Information). Following an approach taken for several other isotope systems (Millot *et al.*, 2010; Dellinger *et al.*, 2015), the fraction of Mo left in solution after secondary mineral formation ($f\text{Mo}_{\text{diss}}$) is:

$$f\text{Mo}_{\text{diss}} = \frac{([\text{Mo}]/[\text{Re}])_{\text{diss}}}{([\text{Mo}]/[\text{Re}])_{\text{rock}}} \qquad \text{Eq. 1}$$

where $([\text{Mo}]/[\text{Re}])_{\text{diss}}$ is the ratio of Mo to Re in the dissolved products of weathering (river water), and $([\text{Mo}]/[\text{Re}])_{\text{rock}}$ is the ratio of the elements in the unweathered parent. A value of $f\text{Mo}_{\text{diss}} = 1$ suggests Mo is released congruently to the dissolved phase alongside Re. A value of $f\text{Mo}_{\text{diss}} < 1$ suggests less Mo loss relative to Re from the dissolved phase (*i.e.* Mo retention in secondary minerals).

To account for lithological controls on $\delta^{98/95}\text{Mo}_{\text{diss}}$ between basins (Fig. 1), we calculate the difference between river water and source rock: $\Delta^{98/95}\text{Mo}_{\text{diss-BM}} = \delta^{98/95}\text{Mo}_{\text{diss}} - \delta^{98/95}\text{Mo}_{\text{BM}}$ (Table S-3). Despite the diversity of our studied catchments in terms of geology, climate and scale, the $\Delta^{98/95}\text{Mo}_{\text{diss-BM}}$ values are correlated with $f\text{Mo}_{\text{diss}}$ (Fig. 3): as the fraction of Mo left in solution decreases, $\Delta^{98/95}\text{Mo}_{\text{diss-BM}}$ values increase. Notwithstanding the uncertainties on $f\text{Mo}_{\text{diss}}$ (Supplementary Information), the data suggest a common process across all of our study sites that modifies $\delta^{98/95}\text{Mo}_{\text{diss}}$ values from those of the parent materials and decreases Mo/Re ratios as $\delta^{98/95}\text{Mo}_{\text{diss}}$ values increase (Fig. 2). Adsorption of Mo to Fe and Mn (oxyhydr)oxides and/or organic matter removes Mo from solution (Goldberg *et al.*, 1996) and preferentially scavenges light isotopes (Barling and Anbar, 2004; Goldberg *et al.*, 2009; King *et al.*, 2018). We find that experimentally derived fractionation factors for Mo uptake by Fe and Mn (oxyhydr)oxides are consistent with our new data (Fig. 3), supporting inferences from a granitic weathering profile (Wang *et al.*, 2018).

Biological processes could influence $\delta^{98/95}\text{Mo}_{\text{diss}}$ values if plants fractionate Mo during uptake (Malinovsky and Kashulin, 2018) and previous observations on organic rich

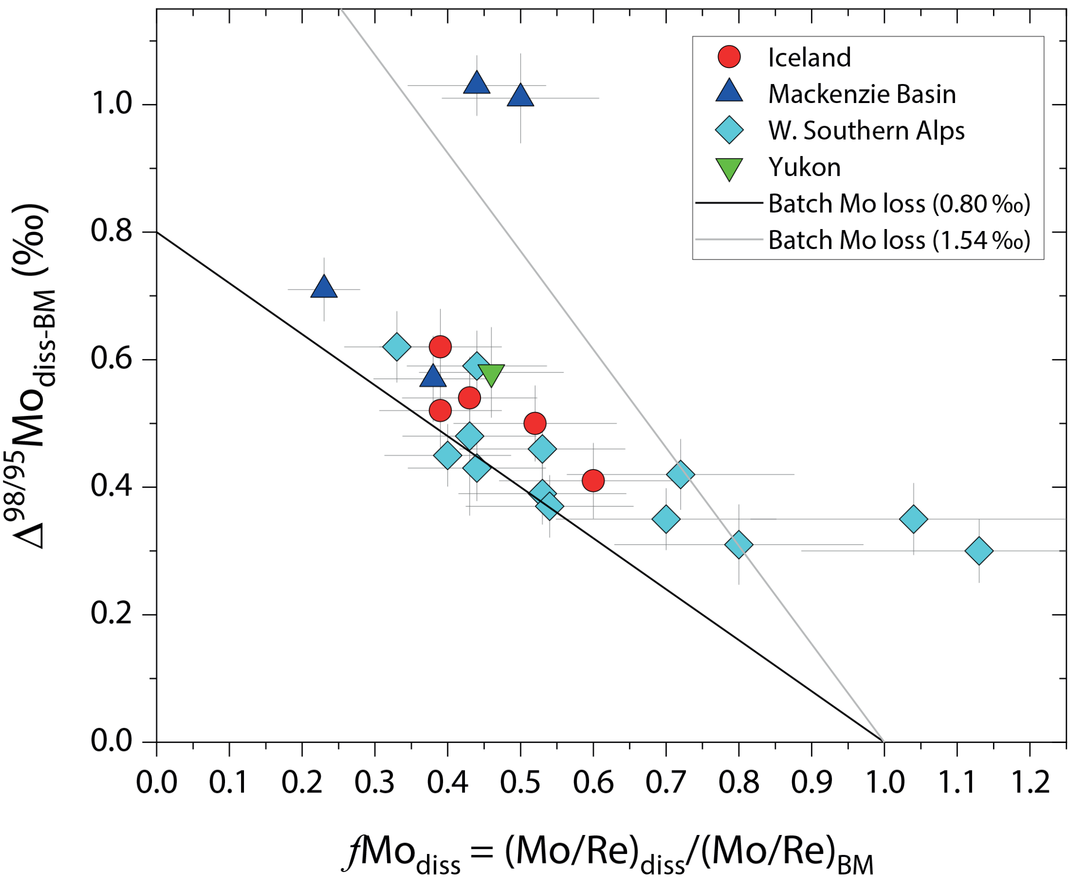

Figure 3 The fraction of Mo remaining in river water, fMo_{diss}, estimated using the ratio of Mo to rhenium (Re) in the dissolved load relative to parent materials, *versus* the difference in $\delta^{98/95}$Mo between river water and river bed materials. Lines are a batch fractionation model using fractionation factors between a solution and secondary mineral phases, based on fractionation factors of -0.8 ‰ (black) to -1.4 ‰ (grey) (Goldberg *et al.*, 2009; Barling and Anbar, 2004). Error bars indicated for fMo_{diss} are the propagated 2 s.e. errors on $(Mo/Re)_{BM}$, which is the main source of uncertainty. Error bars for $\Delta^{98/95}Mo_{diss\text{-}BM}$ incorporate the 2 s.d analytical error on $\delta^{98/95}Mo_{diss}$ and the 2 s.e. of the mean $\delta^{98/95}Mo_{BM}$.

soils document a net enrichment in heavier isotopes compared to the original bedrock (Siebert *et al.*, 2015). However, the organic rich soil layers from the western Southern Alps have similar $\delta^{98/95}$Mo values to river bed materials (Figs. 2 and S-5). Surface soil litters with organic carbon contents >4 wt. % have a mean $\delta^{98/95}$Mo = -0.23 ± 0.11 ‰ (n = 5), which is the same within uncertainty as the river bed material at this location ($\delta^{98/95}$Mo = -0.26 ± 0.04 ‰; Table S-4).

In contrast, the weathered colluvium sediments with low organic matter contents (<1.5 %) have a mean $\delta^{98/95}$Mo = -0.52 ± 0.28 ‰ (n = 4), with $\delta^{98/95}$Mo values reaching -0.90 ± 0.07 ‰ (Figs. 2 and S-5). Weathered materials in the surface environment thus offer a complementary reservoir of Mo to river water (Figs. 1 and 2). These data are comparable to those of Siebert *et al.* (2015), who found lower $\delta^{98/95}$Mo in the deeper portions of soil horizons from Hawaii, Iceland and Puerto Rico. A light Mo reservoir in mineral soils is consistent with $\delta^{98/95}$Mo measurements on soil and root samples from the Massif Central (Voegelin *et al.*, 2012, Fig. 1) and soil samples paired to local bedrock samples in Hawaii (King *et al.*, 2016).

In the Mackenzie Basin, we find the highest average $\Delta^{98/95}Mo_{diss\text{-}BM}$ value (0.78 ± 0.23 ‰) (Fig. 3). This would suggest a weathering regime that promotes Mo removal from solution, potentially by Fe-Mn (oxyhydr)oxide formation. In contrast, the Southern Alps have a lower mean value of $\Delta^{98/95}Mo_{diss\text{-}BM}$ (0.42 ± 0.09 ‰). The higher erosion rates in this setting drive high oxidative weathering fluxes (Horan *et al.*, 2017) but a lower extent of primary and secondary weathering compared to the Mackenzie Basin (Supplementary Information). We acknowledge that the dataset of Mo isotope ratios is limited in size compared to other isotope systems (Dellinger *et al.*, 2015) and for the published datasets (Fig. 1) fMo_{diss} cannot be estimated without complementary Re analyses. In addition, understanding temporal and spatial changes in water flow paths and Mo flux at the catchment scale requires flux weighted $\delta^{98/95}$Mo values (King and Pett-Ridge, 2018). Nevertheless, the contrast between our study locations suggests that primary weathering coupled to the formation of specific mineral phases (which are likely to be linked to bioclimatic regimes, erosion rates, lithology) could play a role in setting differences in $\Delta^{98/95}Mo_{diss\text{-}BM}$.

Wider Implications

Our approach attempts to tease apart the source (lithology) *versus* process (secondary mineral formation) controls on $\delta^{98/95}Mo_{diss}$ in rivers. Although lithological differences account for ~1 ‰ variability (Fig. 1), we find that the partitioning of Mo between the dissolved load and solid weathering products (fMo_{diss}) can produce an additional ~1 ‰ offset (Fig. 3). These findings indicate that changes in primary and secondary weathering patterns could give rise to changes in $\delta^{98/95}Mo_{diss}$ values. Over geological time, this could influence the Mo isotope ratios of lakes, coastal regions and the $\delta^{98/95}$Mo values of seawater. Shifts of as little as ~0.3 ‰ in continental runoff impact how $\delta^{98/95}$Mo values of sedimentary rocks are used to reconstruct palaeoredox conditions (Dickson, 2017). Global changes in chemical weathering on land are reflected in seawater lithium isotope records over the Cenozoic (*e.g.*, Misra and Froelich, 2012; Dellinger *et al.*, 2015). Our data raise the intriguing possibility that secular trends in $\delta^{98/95}Mo_{diss}$ could also result from changes in the extent of primary and secondary weathering (Fig. 3), and call for future work to better constrain $\delta^{98/95}$Mo fractionation in large rivers catchments to understand spatio-temporal variability.

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Author Contributions

KH, RGH and KB conceived the research and designed the study. KH, RGH, ETT, SH and KB collected the samples. KH undertook the geochemical analyses under the supervision of AMW. KH interpreted the data with RGH and in discussion with AMW, KB, DS and ETT. KH and RGH wrote the manuscript with input from co-authors.

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article2005.

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