Investigating molybdenum availability across a Hawaiian climate gradient

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Molybdenum (Mo) isotope fraction is a novel and powerful tracer for quantifying paleoredox states of marine sediments and could potentially be used similarily in soils. A critical assumption ocean paleoredox studies make is that Mo entering the oceans has been constant throughout geological history. A number of studies have recently disproven this assumption [1]. However, the processes that control Mo concentrations in soils and ultimately input into riverine systems remain poorly understood. Mo behavior is commonly thought to be a function of the oxygen availability of its surrounding environment and adsorption onto phases like iron (Fe) and manganese (Mn) oxyhydroxides. Organic matter (OM) also plays a role, although the processes underlying Mo-OM interactions are not yet understood [2]. This study investigates the fate of Mo in soils of varying oxygen status, OM content, and Fe and Mn oxyhydroxide content. Samples were collected along the Maui soil climate gradient (2200 to 5050 mm yr^{-1} mean annual precipitation), which exhibits a well-correlated decrease in soil Eh and Fe content with increasing rainfall. Along this gradient, we measured Mo concentrations in a 0.001M HCl extraction of the soil before and after exposure to Fe reducing conditions in field-placed N_2-flushed vials. Mo concentrations increased as Eh decreased at higher rainfall both before and after Fe reduction. This deviates from the hypothesis that in highly reducing environments we expect initial Mo concentrations to be low as Mo is lost from soils along with the reductive dissolution of Fe. Increasing extractable Mo concentrations with decreasing Eh can be explained by increasing Mo-OM interactions. This study is the first of its kind to examine Mo availability across a soil rainfall gradient. These patterns in Mo concentrations illustrate the potential of this tracer for recording weathering fluxes, reductive Fe conditions, and biologic activity in soils.

[1] Archer & Vance (2008) *Nature Geosciences* **1**, 599. [2] Siebert *et al* (2011) *Mineralogical Magazine* **75** (3), 1872.