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Molybdenum stable isotopic variations indicate Mo attenuation in sulfidic mine waste rock

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Variations in $\delta^{98}\text{Mo}$ arising from chemical reactions can yield insights into processes governing the fate of molybdenum during weathering and transport^[1]. Here, $\delta^{98}\text{Mo}$ and geochemical concentrations were measured in mine drainage, groundwater, surface water and rock samples from a Mo mine in the USA, to assess controls on Mo mobility during sulfidic waste-rock weathering. Mine drainage from two waste-rock storage facilities at this site are differentiated by acidic and alkaline pH values, providing an opportunity to contrast Mo mobility under distinct pH conditions. Surface coatings of weathered waste rock were also characterized using a two-step sequential chemical extraction to determine the distribution and isotopic composition of Mo among primary and secondary mineral assemblages.

No change in $\delta^{98}\text{Mo}$ was observed from rock samples ($0.7 \pm 1.1 \text{ ‰}$, $n = 36$) to Mo-rich ($>340 \text{ } \mu\text{g/L}$) mine process water and pit wall runoff samples that reflected molybdenite oxidative dissolution ($0.6 - 0.7 \text{ ‰}$), suggesting a lack of Mo isotopic fractionation during the dissolution process. In contrast, seepage from the base of both waste-rock storage facilities was isotopically heavier ($1.6 - 1.9 \text{ ‰}$) with Mo concentrations ranging from 4 to 79 $\mu\text{g/L}$. Coupled $\delta^{98}\text{Mo}$ and $\text{Mo}/\text{SO}_4^{2-}$ ratios in mine drainage, and sequential chemical extractions of weathered waste-rock samples indicated that Mo adsorption onto mineral surfaces was responsible for this increase in $\delta^{98}\text{Mo}$. Because aqueous Mo adsorption is known to be minimal under alkaline-pH conditions^[2], $\delta^{98}\text{Mo}$ analyses suggested that portions of the interior of the alkaline-pH waste-rock storage facility were acidic, a finding that would not have been possible without the Mo isotopic analysis.

^[1]Siebert et al. 2015. *Geochim. et Cosmochim. Acta* 162:1-24.

^[2]Goldberg et al. 1996. *Soil Sci. Soc. Am. J.* 60:425-432.