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# Establishing a reactive transport framework for lithium isotope signatures of weathering in a first-order hillslope

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The stable isotopes of lithium (Li) in the dissolved load of large rivers have been increasingly utilized as a proxy for both past and present silicate weathering conditions. This riverine measurement is the integrated signal of water-rock reactions that took place as fluid infiltrated through the subsurface of the Critical Zone. Deconvolving from the net isotopic signal into the multiple individual contributing fractionating pathways, which may compete with or compound one another, requires a mechanistic framework grounded by direct observations. Here, we leverage unique sampling techniques to capture fluids as they transit between soil and groundwater over the intact weathering profile of an actively-eroding, first-order hillslope. The Li isotope ratios ($\delta^7$Li) of these waters are used to validate a reactive transport model that considers the distribution and contemporaneous formation of multiple lithium-bearing minerals to parse the relative effects of dissolution and precipitation on $\delta^7$Li in the dissolved load ($\delta^7Li_{diss}$).

The $\delta^7Li_{diss}$ signatures continue to evolve across the entire flow path from infiltration and drainage to groundwater and ultimately the stream at the terminus of the hillslope. In the vadose zone, there is a transition from net dissolution of weathered material (as low as $\delta^7Li_{diss}$ = -9‰) to the increasing influence of secondary mineral formation (as much as +18‰ change in $\delta^7Li_{diss}$) with depth. Beyond the water table, the increase in $\delta^7Li_{diss}$ of groundwater laterally draining through the hillslope (from +13‰ to +24‰) is associated with the shift to precipitation of metastable secondary phases and thus the continuation of silicate weathering. We use this current framework to demonstrate novel application of a data-validated, multicomponent reactive transport model predicting variability in silicate weathering exports from the Critical Zone under transient hydrologic forcing.