Tracing weathering processes in shale by Li isotopes

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Lithium isotopes provide an excellent tool to investigate weathering processes because isotope fractionation is especially pronounced during abiotic processes depending on the degree of weathering. Isotope ratios for Li are mainly controlled by the rate of mineral dissolution and precipitation of secondary phases and fractionation thus yields insights into clay mineral formation.

Here, we investigate the Li cycle in the Susquehanna Shale Hills Critical Zone Observatory (USA). It is a well-studied first-order catchment in a temperate climate [1] providing an ideal field laboratory to explore Li isotope fractionation as a proxy for shale weathering. It represents a weathering system limited by dissolution kinetics within a tectonically quiescent setting. Soil formation initiated on ridgetops after the last glacial maximum. Chemical weathering appears to take place at several reaction fronts at various depths: carbonate dissolution (20 m), plagioclase dissolution (5-6 m) and clay mineral dissolution/transformation at shallow depth. Despite a significant range in Li concentration (37 to 91 ppm), bedrock and soil samples from various depths show similar signatures with δ^7Li values around -1.5‰ revealing that the initial isotope signature is retained in bulk soil samples. Li concentrations in water samples taken in autumn increase with depth ranging from < 1 ppb for the headwater of the stream to 6 ppb for deep groundwater. The headwater (representing water from the upper soil zone) and groundwater samples show increasing δ^7Li values with depth from about 20 to 30‰ which correlates with increased time of water-solid interaction and precipitation of secondary phases. Water sampling throughout the year will reveal if processes vary with the season. This study will give important constraints on weathering mechanisms together with water pathways in shale.

[1] Brantley *et al* (2013) *ESPL* **38**, 1280-1298.