Interpreting silicon isotopes in the weathering zone

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There is considerable interest in developing geochemical tools that can help unravel the complexity of the weathering zone. In recent years, metal(loid) stable isotope ratios have emerged as potential proxies for aspects of weathering, element cycling and export – but their interpretation is not always straightforward. The simplest interpretative framework for these novel isotope systems - the "batch-model" - has three parameters: (i) the isotope ratio of the primary minerals in the parent bedrock, (ii) the partitioning of the element between solute and secondary phase(s), and (iii) the fractionation(s) associated with this partitioning.

Using the example of silicon, we show how all three of these parameters vary systematically along a gradient of weathering intensity defined by three sites located on granitoid bedrock. These run from the tectonically inactive and supply-limited Sri Lankan highlands to the kinetically limited Rhone Valley in the Swiss Alps, with the Sierra Nevada mountains as a site of intermediate weathering intensity in between. At each site, *in situ* determinations of primary mineral Si isotope ratios span >0.6 ‰. Combined with differential weathering rates, the 30Si/28Si ratio of silicon being solubilised from primary minerals differs between kinetically limited and supply limited weathering regimes. The partitioning of silicon between secondary clay and solute is governed by clay mineralogy, with more intense weathering producing Si-poor clays. We finally show that the Si isotope fractionation associated with clay formation also depends on clay mineralogy. We relate both the partitioning and fractionation dependence on clay mineralogy to aluminium availability, emphasising the crucial role aluminium geochemistry plays in silicon mobility. Taking these issues into account, we present an empirical model that reproduces literature data for soil and river sediment clay Si isotope ratios well and represents a step towards the establishment of Si isotopes as a quantitative weathering proxy.