Extreme Li isotope fractionation during tropical weathering: The multiple roles of secondary minerals

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We investigated the processes that fractionate Li isotopes in a regolith profile at the Luquillo CZO, Puerto Rico, which has one of the fastest silicate weathering rates on Earth [1]. This profile is highly weathered, with complete depletion of primary minerals other than quartz over 9+ m depth. We found the lowest δ^7Li values published to date for porewater (δ^7Li = –27‰) and solid regolith (δ^7Li = –38‰), representing an isotopic difference relative to the bedrock of –31‰ and –43‰, respectively. We also record a Li isotope fractionation of +50‰ *within* the regolith profile from the bottom (9.3 m) to 1.8 m depth. Contrary to the usual δ^7Li signatures of silicate weathering, porewater has lower δ^7Li than the bulk regolith for most of the profile. The exchangeable fraction has lower δ^7Li than the bulk solid, suggesting that ^{6}Li is retained preferentially in the easily exchangeable sites of the newly formed secondary minerals. We explain these observations by two consecutive weathering processes: first, a –31‰ fractionation from the fresh bedrock to the deepest regolith (9.3 m), as the last remaining primary minerals weather to kaolinite and Fe-oxides. Next, as weathering advances from the bottom to the surface of the profile, Li is leached out of the ^{6}Li-enriched secondary minerals, leaving behind a bulk regolith enriched in ^{7}Li. Despite the record-breaking low δ^7Li values in all analysed reservoirs in the profile (bulk, exchangeable, dissolved), the stream that drains this regolith has δ^7Li = +34.7‰ (at baseflow), at the upper end of tropical stream values [2], suggesting the δ^7Li signature of the stream records the weathering of the little remaining primary minerals at the bedrock-regolith interface (10 wt.% chlorite in this case), rather than secondary mineral-related processes in the regolith. This bedrock-regolith weathering hotspot also produces the δ^{26}Mg signature of the stream at baseflow [3].

[1] Dosseto *et al.* (2012) *EPSL* **337-338**, 47-55. [2] Huh *et al.* (2001) *EPSL* **194**, 189-199. [3] Chapela Lara *et al.* (2017) *GCA* **202**, 77-100.