Critical zone weathering hotspots

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The critical zone is a heterogeneous system where local hotspots of activity dominate many processes but critically impact functions in other parts of the system. Here we compare weathering rates and mechanisms at hotspots in the humid, tropical Luquillo Critical Zone Observatory in Puerto Rico to watershed- and regolith profile-integrated rates and the mechanisms interpreted from them.

Micro-scale analysis of weathering profiles across rinds developed on the surfaces and fractures of andesitic volcaniclastic corestones embedded within thick (37+ m in some areas) regolith document dramatic mass losses and mineralogical transformations across core-rind boundaries. Although weathering rinds make up a much smaller volume of the watershed than the regolith, they represent hotspots of mass transfer. For example, ca. 40% of protolith Mg is lost over ca. 3 mm of weathering rind, reflecting significantly more and faster weathering than the final 20% of protolith Mg, which is lost over 8 m of regolith in one ridgetop profile.

Furthermore, these two weathering profile types (rind and regolith) reflect different weathering mechanisms: in fractured subsurface rocks, minor sulfide and sulfate phases are associated with early weathering of silicate minerals, reflecting a weathering mechanism involving sulfuric acid, whereas carbonic acid weathers minerals in the regolith, with help from organic acids in the surficial layers. In the regolith, chlorite, plagioclase and clays weather whereas in the hotspots, pyroxenes and other minerals also contribute to weathering fluxes. Regolith formation and silicate weathering exports from the watershed are controlled by weathering at these deep critical zone hotspots.

In addition to the deep hotspots signified by weathering rinds, another weathering hotspot occurs at the soil-saprolite transition in the shallow critical zone. In the LCZO, this transition (at ca. 1-2 m depth) marks a decoupling of surficial mineral nutrient cycles from deep cycles. Here fluctuating redox conditions affect secondary phases (Fe(III)-hydroxides and microcrystalline disordered clays) that are largely stable elsewere in the regolith, creating local isotopic excursions and leading to dramatic changes in the microbial community [1] and oxygen partial pressures below about 2 m depth.

[1] Liermann *et al* Subm. to *Geomicrobiol. J.*