Oxygen: Coupling and controlling critical zone weathering hotspots

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Mineral reaction mechanisms, their rates and rate-limiting steps must be known in order to predict changes in nutrient supply, solute export or soil formation under environmental changes, such as land use. Moreover, it is essential to identify and quantify these reactions in the context of their distribution in space and time and of the question being posed. For example, weathering mechanisms in a soil may be critical to forest productivity, while weathering mechanisms at the bedrock-regolith interface may control watershed solute export and critical zone formation.

The critical zone is extremely heterogeneous and hotspots dominate many processes although they may only comprise minor volumes of material within a watershed. We will present weathering mechanisms of two types of hotspots in the wet, tropical Luquillo Critical Zone Observatory in Puerto Rico, alongside mechanisms in other parts of the critical zone. The first hotspots are often 10s of metres deep, along bedrock and corestone fracture surfaces [1]. The second hotspots are the soil-saprolite transitions, ca. 1-2 m deep.

The deep hotspots effectively create the critical zone, produce the vast majority of exported cations, and strongly impact the Mg isotopic composition of the river [2]. Weathering is initiated within the visibly fresh rock when oxidative dissolution of trace sulfide phases produces acid that attacks nearby silicate grains [3]. The shallower hotspots, driven by oscillating redox conditions, largely decouple the surface and subsurface biogeochemical cycles and produce Mg isotopic fractionations that are likely ephemeral [2]. Therefore, both hotspots appear to be governed by the partial pressure and transport of O_2. Among other implications, this means that the reduction of O_2 by (bio)geochemical processes (e.g., weathering, respiration) within the soil and regolith may decrease the supply of O_2 to deep hotspots. An O_2 gradient with depth is key to maintaining steady-state regolith thickness when weathering begins with an oxidation reaction [4]. Furthermore, chemoheterotrophic microbial respiration in these C-poor soils consumes most organic acids, limiting the impact of vegetation on deep hotspot weathering rates and the flux of silicate weathering solutes out of the watershed.

[1] Buss *et al*. (2013) *ESPL* **38,** 1170-1186. [2] Chapela Lara *et al*. (2014) *PEPS* **10,** 200-203. [3] Moore *et al*. (2015) this volume. [4] Fletcher *et al*. (2006) *EPSL* **244,** 444-457.