# Tales of the deep: Weathering at the base of the critical zone

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Despite its importance to many of Earth's biogeochemical systems, very little is known about weathering along subsurface rock fractures below the water table. To date, most field studies have extrapolated weathering mechanisms and rates from the soil profile or watershed-integrated scale, to the deep critical zone. This inference from the surface to the deep assumes the same processes act at both. Within the tropics, where some of the highest weathering rates in the world are reported, the regolith profile can be 10's to 100's of meters deep such that the weathering mechanisms at the bedrock-regolith interface may be decoupled from those at surface.

Here we present chemical weathering data from meta-volcaniclastic rock, 37m deep within a tropical watershed (Luquillo Critical Zone Observatory, Puerto Rico). The thick regolith is comprised of ca. 1m of soil overlying highly leached saprolite embedded with intact and fractured bedrock corestones. The fracture surfaces and corestone-saprolite interfaces represent weathering hotspots, where the majority of mineralogical transformations and solute production occurs.

Utilising micrometer scale elemental and mineralogical transects across thin sections, U-Th disequilibria data and reactive transport modelling we elucidate the weathering processes that occur at depth and calculate mineral specific dissolution rates. By then conducting sensitivity analysis we gain a mechanistic understanding of the profile-limiting processes that initiate regolith formation. These mechanisms and their rates differ significantly from those interpreted from stream solute fluxes or whole regolith-integrated profiles.

We have identified the oxidative weathering of sulfide minerals as the first weathering reaction; occuring >30mm inboard of fractures. The release of sulfate during this reaction creates low pH microenvironments, initiating aggressive dissolution of other minerals and creating weathering fronts distinct from those measured in the overlying saprolite profiles.