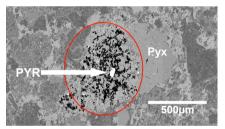
## What lies beneath: weathering in the deep critical zone

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Despite recent work pointing to subsurface weathering along fractures as the primary contributor of silicate weathering products to the world's oceans, most field studies of weathering extrapolate mechanisms and rates from soil profile or watershed-integrated data. Here we present detailed chemical weathering data of fractured metavolcaniclastic rock obtained by drilling (to 37m) in the Bisley watershed of the Luquillo Critical Zone Observatory (Puerto Rico). The thick (37+ m) Bisley 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.

We collected high resolution elemental, mineralogical and textural transects across thin sections to document mineral weathering reactions, weathering fronts and elemental fluxes. We have identified the oxidative weathering of sulfide minerals as the first weathering reaction; evidence of its dissolution occurs >30mm inboard of fractures. The release of sulfate during this reaction creates low pH microenvironments, initiating dissolution of the surrounding minerals (Fig. 1) and creating weathering fronts distinctly different from those measured in the overlying saprolite profiles that begin inboard of the visible weathering rinds.



**Figure 1**: BSE Image showing increased dissolution of a pyroxene (Pyx) grain in association with pyrite (Pyr).

We also present mineral weathering rates determined at the spatial scale over which they occur (10's mm), providing insight into the reaction mechanisms that dominate solute fluxes and initiate regolith formation. These mechanisms and their rates differ significantly from those interpreted from stream solute fluxes or whole regolith-integrated profiles.