

## Relating grain-scale weathering observations to catchment-scale critical zone morphology

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It is well known that chemical weathering and porosity development in rocks are coupled. It is less understood how these coupled processes, which operate at the mineral grain-scale, impact larger-scale phenomena such as watershed fluxes and regolith and landscape development. The Bisley watershed in the Luquillo Critical Zone Observatory (Puerto Rico) is formed on meta-volcaniclastic bedrock that is blanketed by thick regolith comprised of thin soil overlying saprolite embedded with corestones. Saprolites here are highly leached; as a result, most chemical weathering fluxes are attributed to weathering at the bedrock-saprolite interface. However, corestone surfaces and fractures represent multiple “bedrock-saprolite interfaces” distributed throughout the regolith profile. Here we compare macro-scale weathering profiles (m’s thick) in saprolite to micro-scale (mm’s thick) profiles across corestone weathering rinds. Buried corestones were sampled by drilling two boreholes (27 and 37 m deep).

Weathering fronts are most dramatic in rinds on corestone fractures and surfaces. For example, ~40% of the protolith Mg is lost over ~3 mm of rind. In saprolite hand-augered to a corestone at 9.3 m, the final 20% of protolith Mg is lost over ~8 m. These fronts may reflect different weathering mechanisms as well as different weathering rates.

Pyrite crystals, which are of low abundance in these rocks and not detected by powder XRD, were identified by SEM in many of the thin sections and appear to be the first mineral to weather. In thin sections containing fracture surfaces, pyrite is associated with increased porosity and dissolving plagioclase and amphibole grains. These associations are observed even cm’s inboard of the visible weathering rinds. Although present only in trace amounts, pyrite appears to play a controlling role in secondary porosity development and weathering of the major minerals by releasing sulfate during oxidative dissolution, creating micro-environments of highly reactive, low pH fluid within the corestones. Where the bedrock contains more pyrite, corestones may split and shrink more readily, affecting mineral weathering rates and larger-scale phenomena such as the size and distribution of corestones within the regolith profile.

## Organic geothermometry: Defining metamorphic grades in coal

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Mechanical and chemical variations created during metamorphism of organic compounds is an overlooked subject. The fundamentally structure of organic materials is analogous to that of inorganic materials such as minerals and rocks, but the organic equivalents are subject to generalities of both structure and chemistry which has left the interpretation of the metamorphic products of these materials vague and unspecific. The physicochemical nature of the coal and its macerals is currently quantified using thermogravimetric proximate analysis, which aims define the properties of coal through the quantification of moisture %, ash%, volatile% and calorific value.

A new approach was used to analyse the physicochemical character of the coal in close proximity to a dolerite intrusion on both macro and micro scales. Macro scale structural analysis has been done through the use of a Schmidt hammer to quantify *in situ* physical variation within the coal. In conjunction, conventional proximate analysis was employed to estimate the “chemical” variations within the coal. It was expected that the fundamental link between chemical properties and physical character would be displayed in the resultant analysis, but no direct link between the proximate analysis and Schmidt hammer results was observed, either as a result of inherent heterogeneity of coal or a display of the short comings of the proximate analysis method. In light of these results, a new approach was applied by using pressurized liquid extraction (PLE) combine with two dimensional gas chromatography time of flight mass spectrometry (GC\*GCTOFMS) to produce detailed chromatograms of the organic constituents of the coal. The technique will allow quantification of the organic components within the coal. Due to the variable sensitivity of organic compounds to fluids, salinity, pressure and temperature, it may be possible to define not only the temperature of metamorphism but also the type *i.e.* metasomatic or contact and also the salinity of the metamorphic fluid.