Iron Speciation at the Critical Zone: Controls on Organomineral Complexation and Soil C

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Oscillations in redox state accelerate weathering of the substantial Fe-bearing mineral phases present in tropical soils, producing a spectrum of crystal size and bonding environments (solid-phase speciation) available for C complexation. While the importance of soil Fe content to C stabilization in surface soils is well-described, the contributions of Fe-bearing minerals of varying crystallinity are not. Understanding the governance of Fe solid-phase speciation on organomineral associations may prove critical to predicting the response of C-rich tropical soils to changes in global climate and land use.

Leveraging inorganic selective dissolution techniques, ^{57}Fe Mossbauer spectroscopy (MBS), specific surface area (SSA) analyses and X-ray diffraction (XRD), we conducted a investigation of organic and mineral constituents in twenty tropical surface soils of contrasting lithologies from the Luquillo Critical Zone Observatory (LCZO). The LCZO provides a model investigatory framework in which high C inputs to surface horizons are underlain by highly-weathered, volcaniclastic Oxisols or quartz diorite-derived Inceptisols, producing a gradient of Fe content and speciation.

Results indicate (1) Fe-bearing phases contribute substantially to bulk SSA in both soils, (2) selective extraction of targeted soil Fe and C produces distinct shifts in MBS-detected Fe phase distribution in each soil type, and (3) the abundant short-range-order (SRO) Fe(III) oxyhydroxide mineral phases of Oxisol soils appear protected against reductive dissolution via physicochemical mechanisms, while those in Inceptisol soils do not. These findings suggesting that high-SSA SRO Fe(III) phases, capable of disproportionate C complexation, may be immobilized against abiotic and biotic reduction events by matrix-selective reactions. Consequently, C co-precipitated or adsorbed to these phases may be preferentially stabilized in highly-weathered tropical soils, potentially reconciling the wide range of radiocarbon ages observed in such systems.