Depth Variation of Soil Iron Crystallinity at the Calhoun Critical Zone Observatory

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Introduction

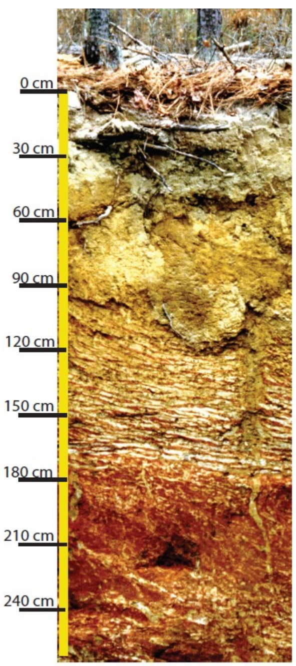
The crystallinity of iron minerals can influence iron's impact on ecosystem function. Small or disordered iron minerals (low crystallinity)—termed short-range-ordered (SRO) or poorly-crystalline—have extremely high surface area and by extension high adsorptive and electron transfer reactivity. They are a major site of carbon stabilization, but can also serve as an electron-acceptor for the conversion of organic matter to CO_2. Understanding the distribution of SRO iron is critical for predicting soil carbon cycling dynamics.

Hypothesis

As a consequence of pedogenic processes, we hypothesize that Fe phase crystallinity will increase with soil depth, yielding an greater abundance of short-range-ordered Fe phases in the surface horizons.

Methods

We tested this hypothesis using a well characterized profile of alternating Fe enriched and Fe depleted microsites (intercalated light (yellow/white) and dark (red) stripes) at the Calhoun Critical Zone Observatory (CZO) in South Carolina, USA. We sampled these microsites from 56 to 183 cm depth, and also sampled the surface (0-15 cm) and subsurface horizons (15-56 cm), which were more homogeneous in Fe abundance. We characterized these features via total elemental analysis, X-ray diffraction (XRD), and ^{57}Fe Mössbauer spectroscopy (MBS) at 295K, 77K, and 4K.



M. Hofmockel, photographer

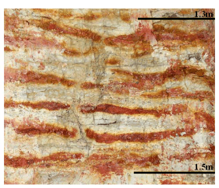


Figure 1. (Left) Soil profile showing Fe enriched and Fe depleted microsites ("tiger stripes").

Figure 2. (Top) Detail of the Fe enriched and depleted layers

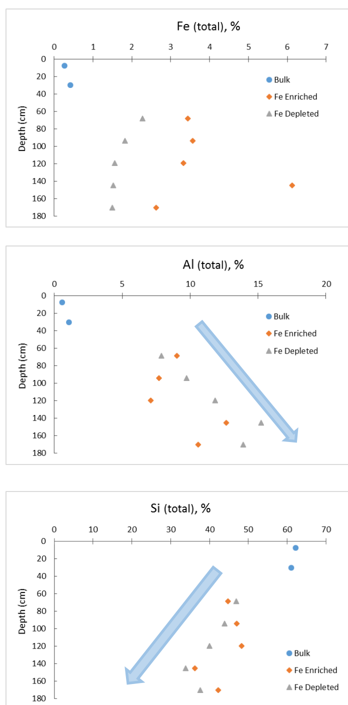
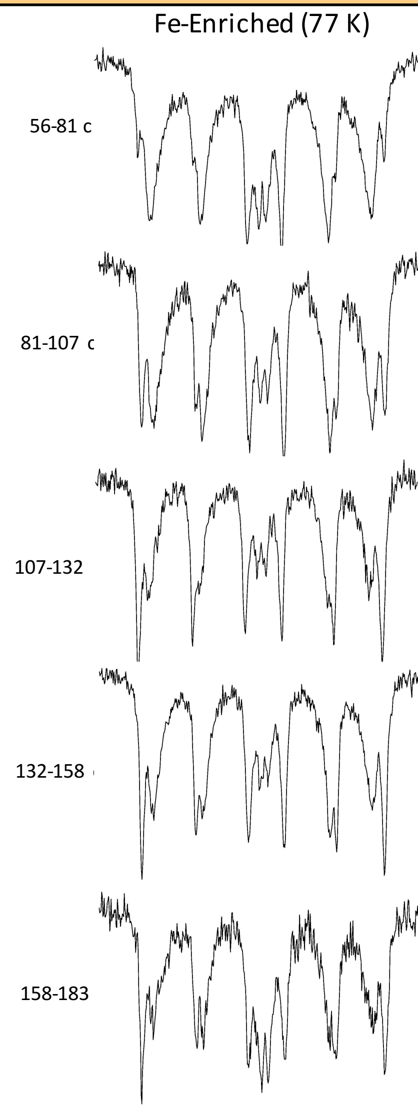


Figure 3. (Right) Total elemental analysis for framework elements (Fe, Al, and Si). Fe content is higher in Fe-enriched layers, but both Fe-enriched and -depleted sites are nearly constant down soil profile for Fe. However, Al increases and Si decreases, down profile for both Fe-enriched and depleted layers.



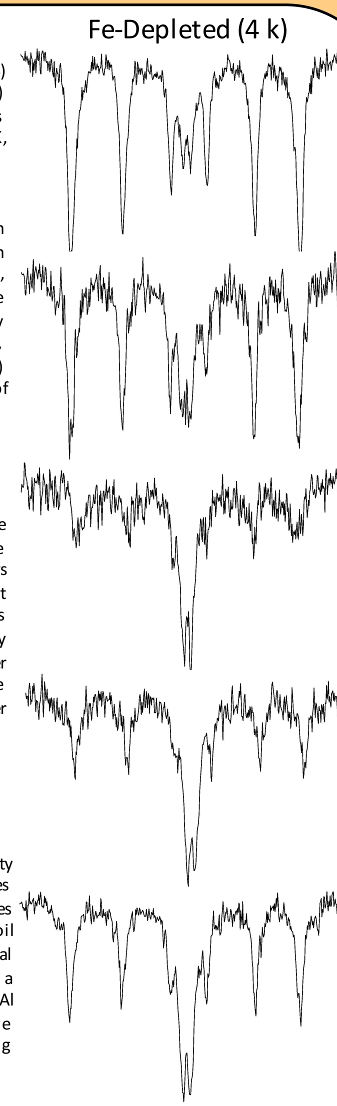


Figure 4. Mössbauer (MBS) Spectroscopy of Fe-Enriched (Left) and Fe-Depleted (right) layers collected at 77K and 4 K, respectively.

ENRICHED (left):
Targeting a MBS collection temperature where changes in crystallinity are evident (77K), Hematite (wide sextet) and goethite (slightly narrower sextet) are clearly evident in the Fe-enriched spectra, with crystallinity (sharper peaks) increasing with depth, in support of our hypothesis.

DEPLETED (right)
Targeting a MBS temp. (4K) where Fe-oxides (sextets) can be distinguished from iron in clays (center doublets). At the deepest depth, the Fe-depleted microsites contained iron primarily in clay minerals (e.g., kaolinte or other layered silicates), but became enriched in Fe (oxyhydr)oxides closer to the surface.

Conclusions

This variation in Fe phase crystallinity within similar redoxomorphic features suggests the role of surface processes (i.e., vegetation) can influence soil development well below the typical rooting zone. With increasing depth, a similar Fe content, but increasing Al and decreasing Si content three mechanisms of pedogenic weathering are acting in concert.