

Rhizogenic C-Fe Redox Cycling: Sleeping Couple No Longer

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Nearly all soil data derive from bulked collections that homogenize soil heterogeneity [1, 2]. We therefore have limited understanding of biogeochemical processes, properties, and gradients that may contrast greatly amongst the many micro-environments that exist within soil profiles. Rooting can affect the upper several meters of soils and especially subsoil rhizospheres are hotspots of biological and chemical activity. In upland soils, distinctive redoximorphic features often visually illustrate microenvironments that contrast not only in color, but in chemistry, physics, and biology. Such redoximorphic features are often interpreted as being relic features of past ecosystems [3]. We hypothesize that mottles are both relic and active microsites in which organic-reductant enriched rhizospheres are periodically reduced when saturated, when the C-Fe redox cycle is associated with carbon stabilization, FeIII reduction, mineral dissolution reactions, and colloidal translocation.

Depth-dependent sampling of redoximorphic microsites in three upland soils was combined with chemical and physical analyses to investigate processes, properties, and time scales on which these rhizogenic microsites operate. In all three soils, we attribute C enrichment and Fe depletion in rhizospheres to result from electron acceptors periodically switching from O₂ to FeIII and other redox-active species, when subsoils become periodically saturated due to wet conditions and low hydraulic conductivity. Both $\Delta^{14}\text{C}$ and $\delta^{56}\text{Fe}$ [4] data indicate that the rhizogenic C-Fe redox cycle operates in the contemporary forest ecosystem, thus redoximorphic features are both relic and active. Large contrasts in clay and crystalline Fe concentrations among these microsites demonstrate large but local-scale mobility of Fe and colloidal materials. The significance of the upland rhizogenic C-Fe redox cycle is underscored by the deep and extensive rooting and mottling of many upland soils across a range of plant communities, lithologies, and climatic regimes.

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Kinetic isotope fractionation at the frontier of modern geochemistry

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Geochemistry can claim a special place in the Earth sciences because it provides distinctive insight into both processes and the time scale over which they operated. I will review recent developments both from experiments and natural settings that illustrate how stable isotope fractionations are being used to identify the process responsible for chemical zoning, and that when the zoning is unambiguously shown to be due to diffusion, can it be used to provide a measure of time. To make this case for the role of stable isotopes the first thing one needs to demonstrate is that mass transport by diffusion in silicate systems is easily recognized by the fact that it produces isotopic fractionations that are large compared to modern analytical methods. The state of affairs in terms of the results of laboratory experiments involving chemical diffusion in melts [1-4], minerals [5], and metal alloys [6] is that in every case so far studied large kinetic isotope fractionations were found and thus they do provide a "fingerprint" with which to distinguish mass transport by diffusion from other mechanisms. What makes this especially relevant is that what has been found in the laboratory experiments has also been found in numerous natural settings ranging from quenched contacts between mafic and silicic melts [7], minerals from mantle xenoliths [8], from lava flows both on Earth and from Mars [9,10] and from a lava lake [11]. A corollary to the above arguments is that when one finds chemical zoning that does not have correlated stable isotope fractionations, one should avoid any temptation to interpret these as providing a measure of time. Thus kinetic isotope fractionations can both give special insight into the causes of chemical zoning, but equally importantly, spare us from the embarrassment of using diffusion kinetics to infer cooling rates from chemical zoning caused by some process other than diffusion.

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