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The influence of oscillating redox cycles on colloid composition and stability

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Repeated wetting and drying in soils create oxic-anoxic interfaces that are hotspots for biogeochemical cycling and organic matter (OM) turnover. They can generate suspended, redox-sensitive mineral-OM complexes—a type of colloid—whose composition and stability affect the fates of nutrients and contaminants in the environment. Previous studies have been too limited (*e.g.*, single redox shifts between anoxic and oxic conditions) or complicated (*e.g.*, redox cycling via microbial activity) to yield clear, comprehensive information on colloid chemistry and behavior. We use a novel abiotic oscillating-redox experiment to address: *How do repeated redox cycles influence the composition and stability of colloids?*

To assess the influence of redox cycling on colloid composition and stability, we are using ferrihydrite (Fh) and birnessite (Bir) as model minerals to undergo serial redox cycles in the presence of OM. Fh is an iron (Fe) oxide and Bir a manganese (Mn) oxide commonly found in the environment; both are redox-active minerals that can bind OM to form OM-mineral complexes. We synthesize and subject the minerals to three experimental conditions: Control (no OM), Low OM, and High OM. Samples from each condition undergo one of three redox treatments: reducing, oxidizing, or oscillating redox. Additionally, we are using a modified asymmetric flow field-flow fractionation (AF4, Postnova, Salt Lake City, UT) system we developed to preserve redox integrity while separating colloids according to their physico-chemical compositions. This novel setup enables us to discretize colloid populations under oxic vs. anoxic conditions for deep molecular-scale characterization. Coupling this technique with microscopy- and X-ray-based analyses allows us to understand the redox-driven differences in AF4-partitioned colloids mineralogy, crystallinity, chemical composition, OM-binding, and spatial distributions of metals and their oxidation states. We hypothesize that 1) *OM coating protects Fh and Bir from reduction*, 2) *redox-active OM functional groups mediate redox-induced mineral changes*, and 3) *repeated redox cycles increase the stability of colloids with lower OM:mineral ratios*. This research expands our understanding of colloid chemistry and behavior and informs predictive models of abiotic-driven subsurface micronutrient cycling and transport.