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Ferrihydrite mineral transformations in the presence of Fe(II) and organic ligands

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In soils and sediments, poorly-crystalline, short-range order (SRO) iron minerals constitute one of the most abundant and reactive components. With high surface areas, SRO minerals like ferrihydrite ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2 + m\text{H}_2\text{O}$) influence the biogeochemical cycling of trace elements and nutrients, particularly in redox dynamic environments. While under oxic conditions SRO iron mineral adsorption capacity is high, in the absence of O_2 , Fe^{III} acts as an electron acceptor during microbial respiration. Electron transfer induces transformations in pure iron minerals, impacting the release and re-distribution of SRO-associated trace elements and nutrients.

In nature, however, pure SRO iron minerals rarely form. Rather, the ubiquitous presence of natural organic matter (OM) in soils and sediments promotes the formation mineral-organic associations. Coprecipitation of ferrihydrite with OM decreases particle size and alters the mineral susceptibility towards microbial reduction. Thus, under reducing conditions, an increased rate and extent of mineral transformation could be expected for OM-associated ferrihydrite. However, in the presence of abiotic reductants, mineral transformation rates and extents in OM-associated ferrihydrite are markedly inhibited when compared to that of a pure ferrihydrite. Using polygalacturonic acid (PGA) as a proxy for acid carbohydrate fraction found in exopolymeric substances, we reacted ferrihydrite-PGA coprecipitates of varying C:Fe molar ratios (0-2.5) with ferrous Fe (Fe(II), 0.5-5.0 mM) at neutral pH for up to 5 weeks. Through a combination of XRD and ^{57}Fe Mössbauer spectroscopy, we showed that at all Fe(II) concentrations, the kinetics and extent of mineral transformation decreased with increasing C content of the coprecipitates. Similarly, ferrihydrite-OM coprecipitates comprising PGA, citric acid (CA), or galacturonic acid (GA) of similar C:Fe molar ratios (~ 0.6) also showed inhibited mineral transformations compared to a pure ferrihydrite, whereby the extent of inhibition of mineral transformations followed the order $\text{GA} \gg \text{CA} > \text{PGA}$. In addition, electron microscopy imaging showed that the crystal morphology of the secondary mineral phases varied with the varying chemical structure of the coprecipitating organic ligands. Despite this, applications of stable Fe isotope tracers revealed that all OM-associated ferrihydrite actively partook in iron atom exchange, suggesting that the presence of OM inhibited crystal growth of more crystalline phases, therefore again leading to SRO phases during iron atom exchange. Collectively, the stabilization of high surface-area ferrihydrite under reducing conditions via recrystallization has implications for the release and re-distribution of ferrihydrite-associated trace elements and nutrients in redox-dynamic environments.

