ABSTRACT: There is increasing evidence that the fate of Fe and organic matter are intimately linked. However, much of this evidence comes from bulk scale observations from which mechanisms must be inferred. Our work has provided mechanistic insights into the coupling of Fe and OM cycling in very geochemically diverse microenvironments. In one case, precipitation of Fe is used to remove DOM from an agricultural drain. The resulting Fe-OM co-precipitates are shown to be resistant to reductive dissolution and to maintain low solution DOM concentrations. Solution concentrations of Fe and DOM were monitored, floc crystallinity was determined using X-ray diffraction, and the composition and distribution of functional groups was assessed using scanning transmission X-ray microscopy (STXM) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. Results indicate co-precipitation of Fe with DOM forms a non-crystalline floc that prevents further Fe crystallization regardless of pH, Fe:DOM ratio, and type of reductant added. There was no evidence that exposure to reducing conditions led to release of DOM from the floc, indicating that co-precipitation with complex natural OM in aquatic environments may stabilize Fe hydroxides against crystallization upon reaction with reduced species and lead to long term sequestration of the DOM. STXM analysis identified spatially distinct regions with remarkable functional group purity, contrary to the model of DOM as relatively uniform complex polymer lacking identifiable organic compounds. Polysaccharide like OM was strongly and directly correlated with the presence of Fe but showed different Fe binding strengths depending on the presence of carboxylic acid functional groups, whereas amide and aromatic functional groups were inversely correlated with Fe content. In a second microenvironment of a fungi-dominated O-horizon of old-growth forest soils thin organic coatings on Fe (hydr)oxides containing soil microstructures are enriched in aliphatic C and amide N, suggesting a concentration of microbial lipids and proteins on these surfaces. A possible explanation for the results of our micro-scale investigation of chemical and spatial patterns is that amide N from chitinuous fungal cell walls was assimilated by hyphae-associated bacteria, resynthesized into proteinaceous amide N, and subsequently concentrated onto Fe (hydr)oxide surfaces. These data provide mechanistic support for recent work proposing the importance of roots and fungi in long-term carbon stabilization. Taken together the two studies show the general importance of Fe redox cycling to understanding the fate of OM in natural systems.