Iron and carbon dynamics during the reductive transformation of organic matter-rich Fe(III) oxyhydroxides

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The association of organic matter (OM) with Fe oxyhydroxides is suggested to shield OM from biodegradation, in addition to impacting the reactivity, transformation rate, and transformation products of OM-rich Fe oxyhydroxides such as ferrihydrite. The impact of this association on the biogeochemical Fe and C cycles is not entirely understood, and may depend on the type of OM and Fe oxyhydroxide, or on the means of association, i.e., OM adsorption vs. formation of OM-mineral co-precipitates. In an attempt to gain insight into the behavior of naturally occurring OM-bearing Fe oxyhydroxides, we examined the *in situ* reductive transformation of natural biogenic ferrihydrite, and monitored changes in mineralogy, composition, and Fe and C speciation, using several synchrotron-based diffraction, imaging and spectroscopic techniques.

Organic matter-bearing ferrihydrite precipitates (C_{org}:Fe ~0.33) that exhibit twisted stalk structures typically produced by the iron oxidizer *Gallionella ferruginea* were sampled in August 2012 from artificially aerated groundwater wells at the Rifle, CO field site. During following months, groundwater conditions became reducing, and the mineralogy of the Fe(III) precipitates was modified *in situ* by April 2013, denoted by the appearance of Fe(II)/Fe(III) phases (e.g., hydroxycarbonate green rust). Despite these changes, the stalk morphology of the original precipitates was preserved, and STXM spectromicroscopy data indicate that stalks became enriched in Fe(II). Carbon K-edge NEXAFS spectra were interpreted according to synthetic Fe(III)/alginate and albumin co-precipitates, and show that the initial Fe(III)-rich stalks are rich in organic carbon, whereas stalk-associated OM appears to be partially altered, or desorbed as Fe(III) reduction proceeds. This suggests that mineral-associated OM is partly available as an electron donor. The presence of organic matter also appears to affect secondary ferrihydrite biomineralization, as previously shown for synthetic analogs [1], and these data may be useful for interpreting the behavior of natural Fe(III)/OM precipitates under comparable aqueous conditions.

[1] Shimizu, M. *et al* (2013). *Environ. Sci. Technol.* ***47*** (23), 13375–84