Iron and organic matter dynamics under fluctuating redox conditions

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The co-precipitation of Fe and organic matter (OM) is common in soils, sediments, surface water and subsurface aquifers, systems that experience significant variation in either redox, or pH conditions. The abundance of Fe in almost all natural soils and sediments combined with the enormous quantity of carbon stored in soils means that Fe-OM interactions likely have a quantitatively significant impact on global carbon cycling. It is suggested that the association of OM with Fe oxyhydroxides hinders its biodegradation, but the mechanism behind these reactions is not entirely understood, and may depend on the type of OM (e.g. polysaccharide-, protein-rich, etc.) and Fe oxyhydroxide, on the type of functional groups involved in Fe complexation (e.g. carboxyl), or on the means of association, (e.g., OM adsorption, formation of OM-mineral co-precipitates, OM occlusion). The goal of this work is to improve our understanding of organic matter-Fe oxyhydroxide interaction in natural settings, and propose a mechanistic example of C and Fe dynamics under fluctuating redox conditions. A series of naturally occurring ferrihydrite samples that underwent in situ reductive transformation in groundwater at the Rifle, Colorado field site were characterized in parallel with model compound/Fe(III) co-precipitates (alginate, albumin, amylose) in order to (1) examine C spectroscopic signatures that indicate Fe-OM complexation, and (2) determine OM types and their spatial distribution in relation to Fe. The mineralogy, composition, and Fe and C speciation were characterized using several synchrotron-based diffraction, nm-scale imaging and spectroscopic techniques. Results obtained for synthetic model compounds allowed us to attribute C NEXAFS spectral shifts to Fe complexation, and these were used for the interpretation of C NEXAFS obtained for the natural samples. The mineral-associated OM fraction in the natural samples exhibits variable C spectroscopic signatures as reductive transformation reactions progressed. Additional OM heterogeneity was observed in the most reduced samples in terms of OM type and association with Fe(II)/(III) phases. Possible reaction pathways between C and Fe will be discussed based on these results.