Structural aspects and surface reactivity of aluminous ferrihydrite precipitates

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Ferrihydrite (Fh), a hydrated, nanoparticulate, high surface area, reactive Fe-oxide, impacts the mobility of inorganic and organic pollutants through sorption reactions in a variety of natural environments. Aluminous Fh is common in nature primarily because of the natural abundance of Al. However, few studies have dealt with Al-Fh, and thorough structural analyses of this phase are lacking. The mode of association of Al with Fh may vary from true chemical substitution, to surface precipitation, to formation of a mixture of two (or more) individual nanoscale phases. This may have a considerable effect on the composition and/or structure of Fh nanoparticle surfaces, and thus on their surface reactivity and their interaction with pollutant species.

Here we used a variety of laboratory (TEM, NMR), and synchrotron-based techniques (X-ray total scattering and PDF analysis, scanning transmission x-ray microscopy) to characterize two Al-Fh series synthesized at variable precipitation rates in the presence of 5 to 40 mol % Al. We find that roughly 25 mol % Al is incorporated in Fh, regardless of the synthesis method we used. Phase separation (formation of Al-hydroxides, e.g., gibbsite) was most significant at Al concentrations above 30 mol % Al. However, Al-hydroxide phases were also detected in samples of lower Al content (as low as 15 mol % Al), particularly in the slowly precipitated series; this finding may be a result of the kinetics of co-precipitation. Furthermore, it appears that the amount of Al incorporated in Fh is not affected by the synthesis method and is more likely controlled by the accumulated strain caused by Al in the Fh lattice. Finally, the surface reactivity of selected Al-Fh samples was investigated by Zn-adsoprtion experiments, which indicate a slight decrease in overall Zn adsorption in comparison to pure Fh. Our results provide an in-depth look at the structure and surface of Al-Fh, as well as insights about the interaction between Al and Fe during co-precipitation.

Re-partitioning of Fe and Cu during the oxidation and acidification of acid sulfate soil materials

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Drainage and excavation of coastal lowlands for agricultural and urban development often results in the oxidation of underlying Fe-rich sulfidic sediments. Exposure and subsequent dissolution of these sulfide minerals creates acidity in the form of sulfuric acid and ferrous Fe [1]. The coupled processes of oxidation and acidification result in the release and re-partitioning of Fe and associated trace metals from stable, reduced mineral phases to more mobile, oxidised forms. Elevated metal concentrations are commonly associated with the drainage waters of these landscapes [2]

We followed the partitioning changes to Fe and Cu during the short-term oxidation and acidification of two acid sulfate soil materials. The “labile”, “acid-soluble”, “organic”, “crystalline oxide”, pyritic” and “residual” metal pools were measured sequentially [3].

Initially Fe and Cu were stored in the “pyritic”, “acid-soluble” and “residual” metal fractions. The “residual” fraction measured changed little during the 90-day oxidation experiment, indicating that it was not a major source for Fe and Cu to more mobile fractions during short-term oxidation events. The “pyritic” fraction, however, is dominated by minerals which undergo oxidative dissolution when exposed to atmospheric oxygen. Major re-partitioning of Fe and Cu was expected and observed - metals initially associated with the “pyritic” fraction were re-distributed to more environmentally available fractions i.e. the “acid-soluble” and “labile” fractions. The “acid-soluble” fraction was a major source of metals both initially and as oxidation progressed. The shift to “labile” and thus leachable metal pools did not occur until conditions of extreme acidification (i.e. pH <4) were reached.

As the “labile” fraction poses the most immediate environmental hazard, managing soil acidity will be the most effective means for reducing Fe and Cu mobility in acid sulfate soils.

[1] Sundström and Åström (2006) *Bor. Environ. Res.* **11**, 275-281[2] Nordmyr *et al.* (2008) *Est. Coast. Shelf Sci.* **76**, 141-152 [3] Claff *et al.* (2010) *Geoderma* **155**, 224-230.