

## Iron oxide nanocrystal growth and aggregation

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Iron oxide nanoparticles are a major source of reactive surface in many natural systems. These nanoparticles are dynamic from the perspectives of size, phase, morphology, reactivity, and aggregation-state. Ferrihydrite is a naturally-occurring iron oxide that typically occurs as nanoparticles in the 3-10 nm size range. Under certain conditions, these nanoparticles transform into single-crystal goethite crystals through phase transformation followed by crystal growth by oriented aggregation. Cryogenic transmission electron microscopy (cryo-TEM) is an ideal technique for observing the nanoparticles as they occur in aqueous suspension and as they transition from isolated, primary ferrihydrite particles to mesocrystals to single crystals of goethite. High-resolution cryo-TEM enables determination of the crystallographic relationships between primary particles in mesocrystals as well as oriented aggregates. Quantitative results tracking the kinetics of mesocrystal formation and conversion to single crystals will be presented.

## Sulfur biomineralisation across a spatio-temporal hydrogeochemical gradient in an acid sulfate soil wetland

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The formation of iron sulfides in wetland soils is an acid-consuming process, which can sequester a range of trace metals and metalloids. In acid-sulfate soil wetlands, iron sulfide formation can therefore aid in neutralisation of acidity and immobilization of contaminants. For this reason, iron sulfide formation as a result of reductive S biomineralisation processes is an attractive site remediation objective.

In this study, we quantified the *in situ* rates and products of dissimilatory  $\text{SO}_4^{2-}$  reduction across a landscape-scale spatio-temporal hydrogeochemical gradient in an acid-sulfate soil wetland. The study site is an 800 ha tidal wetland that was extensively drained in the 1970's. Drainage triggered *in situ* pyrite ( $\text{FeS}_2$ ) oxidation and acidification of surface-waters and shallow groundwaters. In 2001-2002, a remediation program was initiated which involved progressively re-flooding the site via controlled tidal inundation.

We examined spatio-temporal dynamics in S biogeochemistry at the current fringe of tidal inundation about 5 years after commencement of remediation activities. *In situ*  $\text{SO}_4^{2-}$  reduction was confined to near-surface soil layers (to ~60 cm below ground surface) and occurred at rates up to ~300  $\text{nmol cm}^{-3} \text{ day}^{-1}$ . Elemental S was the main short-term product of  $\text{SO}_4^{2-}$  reduction, as a result of (1) reaction between S (-II) and abundant jarosite-derived Fe (III), and (2) short-term redox oscillations near the soil surface. Sulfur K-edge XANES spectroscopy showed that S (0)<sub>(s)</sub> was abundant in near-surface soils, which corroborated selective extraction data showing S (0)<sub>(s)</sub> up to ~40  $\mu\text{mol g}^{-1}$ . The iron sulfide thiospinel, greigite ( $\text{Fe}_3\text{S}_4$ ), was also an important biomineralisation product, as evident from XRD, XANES spectroscopy and analytical electron microscopy.

The results are discussed in terms of thermodynamic and kinetic constraints on the spatio-temporal behaviour of S biomineralisation products, especially S (0)<sub>(s)</sub> and greigite. Dynamic tide-induced redox oscillations in near-surface soil have a central role in the formation and fate of these observed S biomineralisation products.