

## Discovering environmentally-critical nanomineralogy: Highly reactive Mn-oxyhydroxide nanofiber nucleation and growth catalyzed by nanoematite

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Manganese oxides typically form by the oxidation of aqueous Mn(II) catalyzed by mineral surfaces and are non-specific but potent redox-active mineral components commonly found in the environment. They therefore participate in a wide array of reactions with organic and inorganic compounds. They often exhibit high sorptive reactivities and capacities exceeding those exhibited by iron oxides. When present, they can play a key role in the mobility and bioavailability of important aqueous ions.

The present study investigates abiotic Mn(II) oxidation catalyzed by nanoparticulate hematite in the presence of molecular oxygen in batch reactors. The kinetics of the reaction is studied as a function of the hematite particle size and the presence of organic ligands. The effect of organic ligands on the morphology of Mn-oxides is also studied.

Surface-area normalized rate constants suggest differences in reactivity of hematite depending on its particle size. The end product of Mn(II) oxidation, a higher valent manganese oxyhydroxide identified as the mineral hausmannite, has been characterized by employing a suite of analytical techniques including high-resolution TEM, EELS mapping, SAED and SEM. The resultant Mn-oxyhydroxides have a unique nanosized, fiber-like morphology. SEM analyses were used to describe the formation and growth of Mn-oxyhydroxides fibers over time. Mössbauer analysis on nanoparticulate hematite after complete Mn(II) oxidation indicate small detectable amounts of Fe(II) suggesting hematite reduction and resorption of ferrous iron.

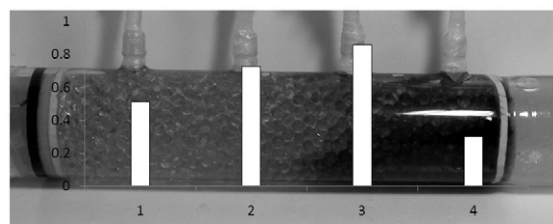
These findings suggest that the formation of Mn-oxides can be influenced by the bulk mineralogical and geochemical composition of the surrounding environment, as well as by the interfacial solute–solid nanochemistry of the solid-phase oxidant. This study further signifies the relevance of low-temperature interfacial geochemistry in the formation and the transformation of environmentally pertinent nanominerals.

## Arsenic partition in redox gradients systems with iron and sulfur presence

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In many cases the fate of arsenic (As) is controlled by its interaction with iron (Fe) and sulfur (S) species at the mineral-water interface. Although redox gradients are ubiquitous in aqueous systems, fewer controlled experimental studies have been performed on As-Fe-S systems. The interaction between diffusion-limited transport and the kinetics/equilibrium of chemical reactions was studied using redox gradient columns and batch sorption/coprecipitation experiments. The column was filled with a glass porous media, 1 mM FeCl<sub>2</sub> and 0.1 mM As(III) or As(V). Boundary redox conditions were controlled at each end (oxygen saturated water and 3 mM sulfide). Batch experiments used ferrihydrite and mackinawite as models for Fe and Fe/S precipitation under oxic and anoxic environments, respectively. A PHREEQC model was calibrated with the results from the batch experiments and it was used to assess As speciation scenarios in the column. Arsenic (0.1 mM) is effectively removed from solution by reaction with ferrihydrite (As(V): 99% As(III): 98%) and mackinawite (As(V): 45% As(III):93%) at oxic and anoxic conditions, respectively. Similar As removal from solution was observed when mackinawite and ferrihydrite were formed before and after As was added to the solution. The only exception was when mackinawite reacted with As(V). In the redox gradient column As is immobilized at oxic ( $pe = 0.3$ ) and anoxic ( $pe = -3$ ) conditions, whereas at intermediate redox potentials As is mobile (see Figure 1), showing that Fe and S have a buffer effect on the fate of As. The PHREEQC model shows that equilibrium conditions are not attained in the column.



Oxic boundary Anoxic boundary

**Figure 1:** Redox gradient column. At the oxic boundary As immobilization on Fe oxides was favoured while As immobilization on Fe-S minerals was favoured at the anoxic boundary. Bars depict the As concentration in solution.

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