

## **Impact of phosphate and silicate on the stability and environmental fate of iron oxides**

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Ferrihydrite (Fh) is a ubiquitous, highly reactive ferric iron (oxyhydr)oxide that helps control the mobility and eventual sequestration of nutrients and contaminants in aquatic systems. The interaction with nutrients such as phosphorus (P) and silicon (Si) can alter the structure of iron (oxyhydr)oxides. How such structural changes translate into altered environmental behavior is poorly understood. Here, we combine structural analyses (X-ray absorption spectroscopy, high-energy X-ray scattering) with laboratory-based acidic and reductive dissolution experiments (abiotic and microbial) and field-based incubation experiments to shed light on the environmental behavior of P- and Si-bearing Fh. We find that the presence of P and Si during Fh synthesis (Fe(III) hydrolysis) had relatively limited impact on its structure. However, P or Si coprecipitation during Fh formation led to a decrease in the chemical stability of Fh. In contrast to coprecipitation, adsorption of P and Si onto pre-formed Fh enhanced its stability. Chemical modelling indicates the latter is due to surface stabilization by P and Si coordination to the low-coordinated surface Fe ions. In addition to the chemical dissolution experiments, incubation experiments showed that coprecipitation of P and Si enhanced the rate of Fh dissolution by microbial dissimilatory iron reduction. Contrasting with these observations of increased reactivity of Fh with coprecipitated P or Si, novel diffusive gel-based experiments, in which (P- and Si-bearing) Fh was deployed in natural reducing sediments over a period of two weeks, showed that PO<sub>4</sub> coprecipitation decreased Fh sulfidation while SiO<sub>4</sub> coprecipitation had little effect.

Our work indicates complex effects from the interaction of Fh with PO<sub>4</sub> and SiO<sub>4</sub>. Combining the experimental results with reactive transport modelling, we aim to assess net effect of Fh – nutrient interactions on trophic state. These findings contribute to a better understanding of the geochemical chain of events in aquatic coastal system undergoing eutrophication.