

## Reactivity of ferrihydrite nanoparticles prepared with and without added carbonate, arsenate, and other oxoanions

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Iron oxides and oxyhydroxides are common and important materials in the environment. These materials commonly occur as nanoparticles in the 3-10 nm size range and strongly impact the biogeochemical cycle of iron and other species at the Earth's surface. Surface-area normalized rates of reduction of ferrihydrite nanoparticles using hydroquinone in batch experiments enables comparisons of reactivity as a function of preparation conditions. We have used this system to characterize the reactivity of several different ferrihydrite samples. In general, ferrihydrite was synthesized by precipitation from homogeneous solution. Surprisingly, ferrihydrite nanoparticles prepared using sodium bicarbonate are substantially more reactive than ferrihydrite nanoparticles prepared using sodium hydroxide. Furthermore, the reactivity of microwave-heat treated ferrihydrite nanoparticles (after the method of Knight and Sylva, 1974) is greater than untreated ferrihydrite nanoparticles. Ferrihydrite nanoparticles prepared by coprecipitation with sodium arsenate are substantially more reactive than ferrihydrite nanoparticles that are equilibrated in solutions containing sodium arsenate, and both arsenate containing samples are substantially less reactive than arsenate-free ferrihydrite nanoparticles.

## The structural chemistry of hydroxyl moieties in ferric polymers

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### Introduction and Objectives

Ferric (oxy)hydroxy polymers are ubiquitous in surface environments and play an important role in several geochemical processes. They are short-lived intermediates produced as aqueous Fe(III) hydrolyzes to form stable crystalline Fe(III)-(oxy)hydroxides. Our goal is to examine the short range order in ferric polymers, the chemical variables that influence their structure and formation, and the relationship between structure and reactivity.

The bridging and terminal hydroxyls in ferric polymers hold the key to their reactivity in the environment. Because it is highly sensitive to small changes in hydroxyl coordination, infrared (IR) spectroscopy was used to interpret the structure of hydroxyls in ferric polymers based on well characterized crystalline Fe(III)-(oxy)hydroxides.

### Discussion of Results

Our investigation focused on the hydroxyl stretching and bending vibrations and their variations as a function of pH, ligand type, and reaction time. Since ripening of ferric polymers into nano-crystalline, and ultimately into macro-crystalline phases, is slower at room temperatures, initial studies were conducted at elevated temperatures (50-90°C).

Freshly prepared ferric polymers from the hydrolysis of Fe(III) in the pH range of 3-7.5 exhibited a broad band around 900 cm<sup>-1</sup>, corresponding to the Fe-OH bending vibrations. In time (0-144 hrs), this band gradually evolved into two distinct bands centered around 900 and 800 cm<sup>-1</sup>, similar to those observed for goethite. Ferric polymers aged in the presence of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> exhibited the greatest maturation rate at high pH. Conversely, the presence of SO<sub>4</sub><sup>2-</sup> not only accelerated polymer aging relative to the NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> systems, but also maximized the maturation rate at low pH. Ligand concentration associated with the polymers also changed with gel maturation. A mechanistic explanation for this disparity will be the focus of future research.

### References

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