

## **Mechanisms of early stage iron(III) oxyhydroxide mineral formation in mildly acidic aqueous systems**

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Mineral formation reactions are important in a wide range of natural and engineered environments. Despite the importance of these processes, exactly how the building-block molecules arrange themselves into the highly ordered, crystalline structures known as minerals remains poorly understood. A detailed understanding of these processes is critical to enable accurate prediction of the size, structure and reactivity of environmentally and industrially important minerals under a range of different chemical conditions.

Here we describe the use of several laboratory-based techniques including UV-visible spectroscopy, low resolution proton NMR and laser Doppler electrophoresis to resolve mechanistic details of the early stages of iron(III) oxyhydroxide formation from iron(III) nitrate in mildly acidic aqueous solutions at pH 3.

Results suggest the initial rapid (within a few seconds) formation of highly kinetically labile polymers, even in systems where the concentration of iron(III) is orders of magnitude below the solubility limit of ferrihydrite. These labile polymers appear to form and rearrange through a classical inner-sphere mechanism governed by the kinetics of exchange of coordinated water.

Over longer timescales, and only at higher iron(III) concentrations, this is followed by formation of a population of kinetically highly non-labile species. The formation of the non-labile species cannot be explained by simple first or second order kinetics, implying that neither internal bond reorganisation within the polymers or dissolution-repolymerisation is solely responsible. Instead, we propose a mechanism involving collision and coalescence of precursor species, presumably being either the kinetically-labile polymers themselves or derivatives of these polymers. Further work is required to determine the precise mechanism of the latter step, and relationship of these non-labile species with the thermodynamically stable mineral end-product (ferrihydrite) in these systems.