

## Relating siderophore-promoted dissolution to properties of ferrihydrite-exopolysaccharide coprecipitates

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Little is known about the properties and reactivity of Fe oxyhydroxides formed in the presence of exopolymers of microbes and plants. We synthesized ferrihydrite (Fh) in the presence and absence of acid polysaccharides (polygalacturonic acid, PGA; alginate, xanthan) and characterized the solids with micro-spectroscopic techniques, gas adsorption, and electrophoretic light scattering. The desferrioxamine B (DFOB)-promoted dissolution of the solids was studied in batch experiments at pH 7 in the presence and absence of citrate or malate. The total ligand concentration was  $\leq 100 \mu\text{M}$ . In all cases 2-line ferrihydrite (Fh) was the main product of the synthesis. Mössbauer spectroscopy indicated a smaller particle size and a magnetic dilution of Fh in the coprecipitates. The embedding of Fh clusters in the polysaccharide matrices was confirmed by C-1s NEXAFS images. Compared to pure Fh, the coprecipitates comprised an up to 84% lower microporosity. Pure Fh sorbed about four times less DFOB than a PGA-Fh coprecipitate, and its ligand-promoted dissolution in the presence of  $50 \mu\text{M}$  DFOB was two orders of magnitude slower. Our dissolution experiments indicated that, due to Fh coagulation ( $\text{pH}_{\text{iep}} = 7.1$ ), only a small fraction of the Fh surface was accessible to ligands. In contrast, Fh in the coprecipitates was sterically and/or electrostatically stabilized by the polymers. We show that 'ligand-accessible surface area' was the key control of the dissolution reaction and that ligand/adsorbent charge or crystallinity/particle size effects were of minor importance. The solubility of biogenic Fe oxyhydroxides may thus exceed that of pure phases by several orders of magnitude at circum-neutral pH.

## History of trace metal contamination in Tagus prodelta cores, Portugal

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Favourable oceanographic and environmental conditions allow the formation of a fine-grained deposit (Tagus prodelta) located at the mouth of the Tagus river. This fine-grained deposit results from the sink and accumulation of terrestrial and marine derived materials. Three short sediment cores dated with <sup>210</sup>Pb were analysed to determine historical trends in trace metal concentrations in the Tagus prodelta. The geochemical composition of this fine-grained deposit reflects the accumulation of marine biogenic materials, terrestrial and anthropogenic materials transported by the Tagus river. Historical trends indicate significant anthropogenic enrichments for Hg, Pb, Zn, Cu, Sb and Sn since the fifties. Hg presents the highest level of anthropogenic enrichment (ca.  $E_{\text{F}_{\text{Hg}}=20}$ ) in cores PO287-26-1B and PO287-27-1B. Core PO287-28-1B is characterised by high Ca contents that acts as a diluting factor of trace metal concentration derived from anthropogenic activities. Despite the improvement in the treatment of domestic and industrial effluents since the eighties, only slightly decreases in up-core metal trends were observed, revealing the importance of sediment re-working.