

## **Surface catalyzed Fe(II) oxidation process and its influence on ligand-controlled Fe(III) (hydr)oxide dissolution rate**

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Many plants and microorganisms exude ligands and reductants for acquiring Fe from their external environment through reductive and ligand-controlled dissolution. We previously demonstrated that under anoxic conditions and at circumneutral pH, Fe(II) can catalyze ligand-controlled Fe(III) (hydr)oxide dissolution. However, Fe availability is typically limited under oxic conditions, where Fe(II) is rapidly oxidized to Fe(III).

In this study, we examined surface-catalysed Fe(II) oxidation and its impact on the ligand-controlled Fe(III) (hydr)oxide dissolution rate. Fe(II) oxidation rates were examined in batch experiments for a range of Fe(II) concentrations, in the presence of several Fe(III) (hydr)oxide minerals (ferrihydrite, lepidocrocite, goethite and hematite), under various oxygen regimes and over broad pH range. Furthermore, we determined lepidocrocite dissolution rates by organic ligands (DFOB; desferrioxamine B and HBED; N,N'-di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid), in mineral suspension that had been spiked with Fe(II) under oxic conditions at circumneutral pH.

Fe(II) oxidation rates were strongly dependent on Fe(II) adsorption and on redox properties of the Fe(hydr)oxide minerals. We observed that even under oxic conditions, adsorbed Fe(II) can transiently catalyse ligand-controlled dissolution of Fe(III) (hydr)oxide while Fe(II) oxidation occurs; 5  $\mu$ M Fe(II) addition increased the ligand-controlled dissolution rate significantly relative to the ligand-only treatment. The catalytic effect continued until all added Fe(II) was oxidized.