

## **Fe(II)-catalyzed ligand-controlled dissolution of FeOOH: ATR-FTIR, isotopic, and kinetic studies**

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The dissolution of iron (oxyhydr)oxides is one of the widely investigated biogeochemical processes, due to its importance in the bioavailability, cycling of iron and trace elements. Earlier studies have demonstrated synergistic effects on ligand-controlled FeOOH dissolution with two or multiple ligands of synthetic and/or natural origin. Strongly accelerated dissolution rates have been reported when traces of Fe(II) were added in the presence of a ligand at pH 3-5. However, the effect of Fe(II) and the mechanisms involved in the dissolution are still not clear in the more relevant circumneutral pH range. In this study, we address these questions with Attenuated Total Reflectance Fourier Transform infrared spectroscopy (ATR-FTIR) and with <sup>57</sup>Fe(II) isotope exchange experiments, as new approaches for understanding the mechanism of FeOOH dissolution.

ATR-FTIR studies show that added and photochemically produced (0.2-10 μM) Fe(II) can significantly accelerate the overall non-reductive dissolution of lepidocrocite (γ-FeOOH) in the presence of 50 μM EDTA under anoxic conditions at pH 6 and 7. Isotope experiments show that added <sup>57</sup>Fe(II) remains in solution in the presence of EDTA and exchanges with natural abundance Fe released from lepidocrocite in the absence of EDTA. Addition of EDTA during isotope exchange leads to accelerated dissolution of lepidocrocite and to a quick re-appearance of added <sup>57</sup>Fe in the solution. A kinetic model that is able to fit the experimental data explains the catalytic effect in terms of electron transfer from adsorbed Fe(II)EDTA to surface Fe(III) sites and rapid detachment of Fe(III)EDTA from the reduced sites.

This study contributes to the mechanistic understanding of charge transfer to the surface of FeOOH and the increasing rates of overall non-reductive dissolution in anoxic environments by traces of Fe(II), or in oxic environments where Fe(II) is continuously produced photochemically or by reducing ligands.