

Ligand-controlled Fe mobilization catalyzed by adsorbed Fe(II) on Fe(hydr)oxides

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Dissolution of Fe(hydr)oxides is a key process in biological iron acquisition. Due to the low solubility of iron oxides in environments with a circumneutral pH, organisms may exude organic compounds catalyzing iron mobilization by reductive and ligand controlled dissolution mechanisms. Recently, we have shown synergistic effects between reductive dissolution and ligand-controlled dissolution that may operate in biological iron acquisition. The synergistic effects were observed in Fe mobilization from single goethite suspensions as well as in suspensions containing calcareous soil [1],[2]. However, how the redox reaction accelerates Fe(hydr)oxide dissolution by ligands is not studied intensively. In our study, we hypothesized that electron transfer to structural Fe(III) labilizes the Fe(hydr)oxide structure, and that this can accelerate ligand controlled dissolution.

Systematical batch dissolution experiments were carried out under anoxic conditions at environmentally relevant pH values in which various Fe(hydr)oxides (goethite, hematite, lepidocrocite) interacted with two different types of ligand (desferrioxamine B (DFOB) and N,N'-Di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid monohydrochloride (HBED)). Electron transfer to the structure was induced by adsorbing Fe(II) to the mineral surface at various Fe(II) concentrations. Our results show a distinct catalytic effect of adsorbed Fe(II) on ligand controlled dissolution, even at submicromolar Fe(II) concentrations. We observed the effect for a range of iron oxides, but it was strongest in lepidocrocite, most likely due to anisotropy in conductivity leading to higher near-surface concentration of reduced iron. Our results demonstrate that the catalytic effect of reductive processes on ligand controlled dissolution require a very low degree of reduction making this an efficient process for biological iron acquisition and a potentially important effect in natural iron cycling.

References

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2. Schenkeveld, W. D. C.; Wang, Z. M.; Giammar, D. E.; Kraemer, S. M. *Environ. Sci. Technol.* 2016, 50, (12), 6381-6388.