

Unraveling the Role of Organic Ligands in Aphotic Iron Oxidation: Mechanisms, Kinetics, and Environmental Implications

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The oxidation of iron in sedimentary deposits plays a crucial role in biogeochemical cycles influencing, for example, primary production in ocean and pollutants reactivity. Yet the knowledge on the mechanisms and kinetics of its aphotic oxidation remains limited, in particular the influence of ligands which can either enhance or restrict the kinetics of oxidation. While some studies suggest that complexation with organic ligands enhances oxidation rates because iron complexes would react better with oxygen, others propose that ligands inhibit oxidation by sequestering Fe(II) and limiting its interaction with oxidants. This conflicting framework underscores the need for a comprehensive investigation into the controlling factors of iron oxidation in presence of unknown organic ligands. The present study test the hypothesis that complexation with organic ligands enhance oxidation rates by stabilizing Fe(III) species. We propose a ligand-independent oxidation scheme and explain how the greater thermodynamic stability of complexed Fe(III) can account for the faster oxidation rate observed for iron. To this end, iron oxidation was tested in laboratory experiments where various parameters were modified, including the type of ligand, Fe(II) concentration and iron to ligand ratio.

To overcome the analytical limitation of quantifying organic complexed iron; both iron species and hydrogen peroxide (H₂O₂) are measured simultaneously. H₂O₂, a reaction intermediate formed during iron oxidation, is produced in proportion to Fe oxidation and quantified using a new methodology that enables the precise determination of H₂O₂ production rate and concentration. By integrating these parallel measurements, our findings offer new insights into the pathways and rates of aphotic iron oxidation under different ligand conditions. This work advances our understanding in the extent and the factors controlling the production of reactive oxygen species produced during aphotic oxidation of iron. In the future, these results will help understand the contribution of this ROS production to the degradation of organic pollutants.