



Elucidation of the mechanisms of non-enzymatic biological iron oxide dissolution by investigation of dissolution kinetics and iron isotope fractionation

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Dissolution of iron-bearing minerals by non-enzymatic biogeochemical mechanisms plays an important role for iron cycling in natural systems. Examples include pedogenic processes, weathering, and biological nutrient acquisition in terrestrial and marine environments. Non-enzymatic plant and microbial iron acquisition processes include the release of organic acids and siderophores as well as the acidification of the local environment. The biogenic reactants increase the solubility and dissolution rates of iron-bearing minerals and promote transport of iron toward the organisms. In this study, we investigated the mechanisms and rates of ligand-promoted and light-induced iron oxide dissolution in the presence of biogenic ligands such as organic acids (e.g. oxalate) and siderophores (e.g. DFO-B). We observed dissolution rates under steady-state and non-steady-state conditions and studied iron isotope fractionation during proton promoted, ligand-controlled, and light-induced reductive dissolution of goethite by MC-ICPMS.

Adsorbed oxalate accelerated goethite dissolution at pH 3 by a ligand-controlled dissolution mechanism in dark experiments and by light-induced reductive dissolution under simulated sunlight. At pH 6 (dark), oxalate promoted the formation of labile surface sites but did not promote dissolution due to the low solubility of goethite. DFO-B promoted iron oxide dissolution in light and dark experiments even at near neutral pH due to the high stability of soluble iron complexes.

No significant iron isotope fractionation was observed during proton-promoted dissolution with 0.5M HCl indicating that the goethite was not isotopically zoned. A strong enrichment of lighter iron isotopes (^{54}Fe) relative to the bulk mineral was observed in the early stages of ligand-controlled and reductive dissolution. We have modeled these observations using a modified Rayleigh process which takes into account that only reactive sites at the mineral surface participate in the dissolution reaction and that the isotopic composition of the bulk mineral does not change on the time-scales of the dissolution experiment.