

Impacts of Adsorbed Natural Organic Matter on Ligand-controlled Iron(III) (oxyhydr)oxide Dissolution

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Soil iron (Fe) availability is often limited by the poor solubility of Fe-bearing minerals, especially under neutral or alkaline conditions. To overcome this, organisms, including bacteria, fungi, and plants, exude chelating ligands to enhance Fe bioavailability by forming soluble complexes with soil-Fe. Most research on mechanisms of ligand-mediated Fe acquisition has been conducted in simplified binary systems involving only ligands and pure Fe-minerals. In natural systems, Fe-mineral surfaces are typically covered with adsorbed humic substances (HS), but the effects of HS on ligand-controlled Fe dissolution are poorly understood. Specifically, the impact of HS type, adsorbed HS concentration, Fe(III) mineral type, ligand properties, and pH, remain largely unexplored.

This study aimed to unravel how HS adsorbed onto Fe-mineral surfaces influence ligand-controlled Fe dissolution in relation to various environmental parameters. We conducted batch dissolution experiments in ternary systems consisting of an Fe(III) (oxyhydr)oxide mineral (ferrihydrite, lepidocrocite, or goethite), HS (humic or fulvic acid (HA and FA)) at various concentrations, and a chelating ligand (N,N'-di(2-hydroxybenzyl)ethylene-diamine-N,N'-diacetic acid (HBED) or desferrioxamine B (DFOB)) over a pH range from 4 to 8.5. Initial Fe dissolution rates were determined by linear regression and compared across variables.

The effect of adsorbed HS on ligand-controlled goethite dissolution depended on ligand charge. For the negatively charged HBED, the dissolution rate decreased with increasing HA and FA loading while for the positively charged DFOB it increased. The rate of dissolution by HBED was affected more strongly by FA than by HA, while for DFOB both HS had comparable effects. Adsorbed HS affected the dissolution rate by HBED more than by DFOB. The effect of adsorbed HS also proved pH-dependent; for DFOB the extent to which adsorbed HS enhanced the dissolution rate decreased with increasing pH, from 4 to 8.5. Furthermore, the inhibiting effect of HA on Fe dissolution by HBED increased with mineral stability (ferrihydrite < lepidocrocite < goethite).

Our findings improve the understanding of how ligands increase Fe availability in natural environments, and how changes in soil organic matter content (e.g. related to agricultural practices) may affect ligand-mediated Fe acquisition.