

## Acquisition of Fe from hematite (nano)particles by an aerobic microorganism

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Although most studies of microbial interactions with Fe (hydr)oxides have focused on reducing environments, aerobic processes can also be important. All but a few unique organisms require Fe as a fundamental nutrient; yet, Fe-bearing minerals tend to be highly insoluble in circum-neutral aerobic environments. Many aerobic microorganisms overcome Fe limitation by releasing low molecular weight organic ligands known as siderophores. Siderophore-Fe (III) 1:1 complex stability constants can be extremely high ( $10^{23}$ - $10^{52}$ ). Our research focuses on determining the mechanisms of Fe acquisition from (nano)particulate hematite by a siderophore-producing bacterium in the presence and absence of other common soil organic ligands.

Results of microbial growth experiments using an obligate aerobic bacterium *Pseudomonas mendocina* ymp and a siderophore (-) mutant of the species, along with a reporter strain that signals Fe deficiency, show that Fe acquisition from hematite can involve siderophores acting in combination with other exogenous organic ligands and reductants (oxalate and ascorbate). Both *P. mendocina* wild type and mutant grow better on hematite particles < 10 nm, indicating that the smaller particles provide more readily bioavailable Fe. Abiotic experiments using the siderophore desferrioxamine B (DFOB) reveal that siderophore-mediated dissolution of hematite is sensitive to particle size, with particles < 10 nm in diameter dissolving about an order of magnitude faster than larger particles. Results of both biotic and abiotic experiments illustrate the importance of considering surface area versus mass (weight) of particles when comparing nanoparticle reactivity and bioavailability.

## In situ XAS study of Zn<sup>2+</sup> and Ni<sup>2+</sup> adsorption on Fe<sub>3</sub>O<sub>4</sub> nanoparticles in supercritical aqueous fluids

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The role played by nanoparticles in elemental transport, mineral nucleation, and geochemical reactions dominated by fluid-interface interactions in natural hydrothermal systems is poorly understood due to a lack of experimental data on the physical and chemical properties of nanoparticles in hydrothermal fluids. In addition, new experimental data on the solubility and chemical reactivity of metal oxide nanoparticles in supercritical aqueous fluids are necessary to develop a better understanding of corrosion-related processes in supercritical-water-cooled reactors. Consequently, *in situ* x-ray absorption spectroscopy (XAS) measurements were made for the first time on nanoparticle systems in supercritical aqueous fluids. XAS spectra were measured at the Advanced Photon Source (APS) from 0.05M Zn (NO<sub>3</sub>)<sub>2</sub> and from 0.05M Ni (NO<sub>3</sub>)<sub>2</sub> added to Fe<sub>3</sub>O<sub>4</sub> nanoparticles in aqueous fluids to 500 °C. The XAS data indicate that reactivity of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with Zn<sup>2+</sup> and Ni<sup>2+</sup> ions is negligible to 300 °C but becomes significant in the 400 – 500 °C temperature range. Analysis of Zn *K*-edge extended x-ray absorption fine structure (EXAFS) using a spinel-motif structure to model the Fe<sub>3</sub>O<sub>4</sub> nanoparticles shows that Zn<sup>2+</sup> adsorbs on tetrahedral sites whereas analysis of Ni *K*-edge EXAFS shows that Ni<sup>2+</sup> adsorbs on octahedral sites of the surface of nanoparticles in aqueous fluids at 400 to 500 °C. The Zn<sup>2+</sup> and Ni<sup>2+</sup> ions remain bound to the surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, as evidenced from XAS measurements made upon cooling of the aqueous nanoparticle samples. In addition to helping understand metal transport and mineralization at the nanoscale under hypogene conditions, the knowledge gained from our studies may be used to model and control corrosion in supercritical-water-cooled nuclear and conventional reactors and to achieve new insights in hydrothermal synthesis of nanostructured materials.