

Nanoparticle Fe as a Reactive Constituent in Air, Water, and Soil

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Iron (Fe) oxide particles in the nanometer size range (< 100 nm) are ubiquitous in nature and their occurrence ranges from ultra-fine mineral dust in the atmosphere to nanocrystalline precipitates in the hydrosphere (e.g., Hochella, 2002; van der Zee et al., 2004). The goal of this project is to understand the reactivity of Fe oxide nanoparticles in air, water, and soil environments¹. Research into the reactivity of nanoparticle Fe oxides has been primarily aimed at understanding the bonding characteristics of atoms adsorbed at the surface. It is now recognized, however, that the behavior of Fe in the environment is strongly influenced by bacterially driven redox reactions, as well as the local chemistry and nature of mineral surfaces in rocks and soils, and by the presence of water. Therefore, detailed investigations of the *redox chemistry* of Fe oxide nanoparticles under conditions analogous to nature are critical to understanding the role of these tiny particles in the cycling of Fe in the environment.

Our working hypothesis is that unique reaction mechanisms occur at the surface of Fe oxide nanoparticles that do not extrapolate outside of the nanoscale domain. Our primary goal is to understand the redox chemistry of Fe oxide nanoparticles during four major components of the Fe biogeochemical cycle including (i) Fe isotope exchange, (ii) adsorption and dissolution of atmospheric Fe mineral dust, (iii) pollutant reduction, and (iv) microbial Fe oxidation. Observing these trends for four diverse, but related reactions critical to the Fe biogeochemical cycle will provide a powerful mechanism to identify new phenomena and reactions that are unique to oxide particles within the nanometer size range.

During the first year of the project, our efforts have focused on synthesizing and characterizing nanoscale Fe oxide nanoparticles at UIowa². We have synthesized and characterized nanoscale ferrihydrite, goethite and hematite particles. For both goethite and hematite, we have also synthesized larger particles to compare to the

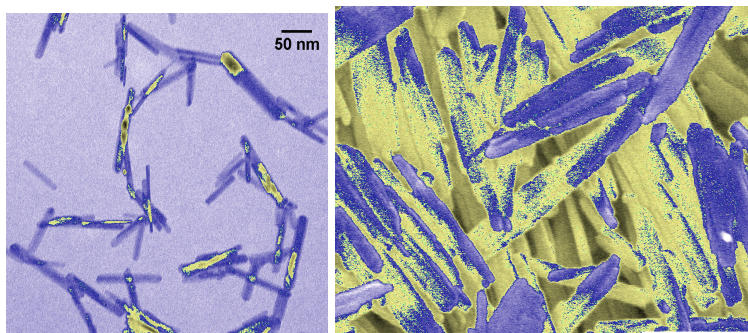


Figure 1. Left: TEM image of nanoscale goethite. Right: SEM image of conventional goethite.

behavior of the smaller particles. Figure 1 shows a TEM image of nanoscale goethite with an average particle size of 8 x 90 nm (110 m²/g) compared to an SEM image of 80 x 800 nm conventional goethite (41 m²/g). We had our first NIRT meeting in July of 2006 and distributed

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goethite particles to the UW Madison, UC Berkeley, and Coe research groups to begin size-dependent reactivity studies.

The initial size-dependent reactivity studies have focused on three Fe redox processes: (i) metal sorption and interfacial electron transfer (ii) atmospheric and microbial dissolution, and (iii) Fe isotope exchange. Interestingly, we have some results that are not consistent with the typical notion of a “nano-effect”, that is, that the smaller a particle is, the more reactive it is. Instead, results for sorption of Fe(II) on goethite shown in Figure 2 show the opposite trend with fewer Fe(II) molecules sorbed per m^2 on the small particles. A similar observation was recently made for mercury sorption on goethite (Waychunas et al., 2005). The decreased sorption does not appear to be due to aggregation effects as we have observed no influence of solids loading on the amount sorbed. We have previously shown that electron transfer occurs between sorbed Fe(II) and structural Fe(III) in iron oxides (Williams and Scherer, 2004), and we suspect that differences in redox properties or reduced energetics at the surface of the nanoparticles is responsible for the lower surface coverage. Experiments are currently underway using isotope selective Mossbauer spectroscopy to investigate the redox reaction between Fe(II) and nanoscale goethite.

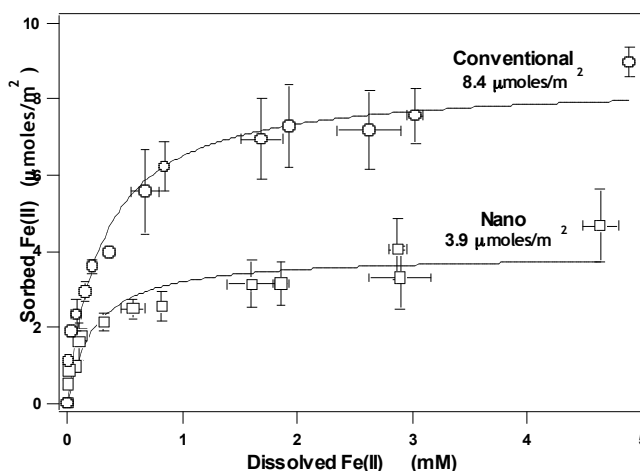


Figure 2. Isotherms for Fe(II) sorption onto conventional ($40 \text{ m}^2/\text{g}$) and nanoscale ($110 \text{ m}^2/\text{g}$) goethite particles.

Additional studies are investigating the size-dependent reductive dissolution of hematite and goethite nanoparticles resulting from their photocatalytic reaction with organic acids (e.g., oxalic and formic acid). These iron oxides are frequently encountered in mineral dust aerosols (Claquin et al., 1999), whereas simple organic acids represent anthropogenic pollutants believed to be integral to the formation of bioavailable forms of iron via redox cycling in atmospheric waters (Deguillaume et al., 2005). Preliminary results show that the surface-area-normalized rate constant for the photoreduction of nanoscale hematite ($\sim 90 \text{ m}^2/\text{g}$, $\sim 7\text{-}10 \text{ nm}$) by formic acid is nearly 3 times greater than that measured for conventional hematite particles ($\sim 30 \text{ m}^2/\text{g}$, $\sim 30 \text{ nm}$) (Figure 3). This behavior is consistent with that typically anticipated for nanoparticles, in that our smaller hematite particles exhibit enhanced reactivity that cannot be wholly attributed to their greater surface area. Experiments are being conducted to

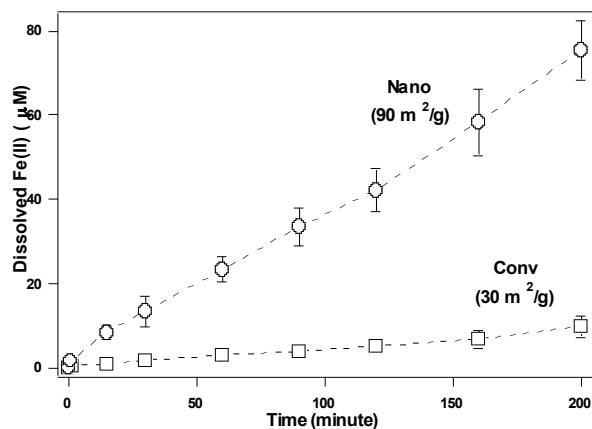


Figure 3. Photoreductive dissolution of nanoscale and conventional hematite particles via reaction with formic acid in the presence of oxygen at pH 3.5.

better understand the molecular-level processes responsible for the observed differences in nanoparticle and conventional hematite reactivity, with a particular focus on the roles that organic acid adsorption and ligand-promoted dark dissolution play in the photocatalytic reduction process.

Collaborative experiments between UIowa and UW Madison, as well as Coe College, have also been started to investigate rates of Fe isotope exchange and reductive microbial Fe respiration as a function of particle size. Preliminary experiments with reduction of goethite by a representative dissimilatory iron reducing microbe reveal less overall reduction per m² in the presence of the nanoscale particles compared to the conventional particles and additional experiments are underway at Coe College to better understand this observation. For the Fe isotope experiments, a meeting between the UIowa and UW Madison groups took place in October to finalize an experimental design and coordinate sample preparation and transfer. The next steps of our experimental plan are to synthesize Fe(II) bearing minerals as a function of particle size to investigate nano-effects in oxidative microbial Fe respiration. The goal of these size-dependent studies is to identify new phenomena and reactions that are unique to oxide particles within the nanometer size range.

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