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Influence of size, morphology and aggregation state on reductive dissolution of hematite nanoparticles

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Nanoscale iron (oxyhydr)oxide minerals are omnipresent in natural environments and initial studies have found their size can influence chemical reactivity, e.g., dissolution kinetics. Their dissolution behavior is important because it influences the bioavailability of nutrients for plant growth and the migration of pollutant metals and organic compounds. In natural environments, reductive dissolution is the most important dissolution mechanism (Sulzberger et. al. 1989). Madden and Hochella (2005) reported the oxidation of Mn2+ catalyzed by hematite nanoparticles depended upon nanoparticle size. These results suggest that other redox reactions occurring on hematite surfaces may be size-dependent as well. In this study, we have investigated the size dependence of the reductive dissolution of hematite with ascorbic acid using two types of nanoparticles with average diameters of 7 nm and 30 nm.

Hematite nanoparticles were synthesized by forced hydrolysis of ferric nitrate and characterized with powder XRD, TEM, and BET surface area measurements. Reductive dissolution experiments were carried out in continuously stirred Teflon beakers at 302 K in the absence of light under approximately 1 atm nitrogen gas. Aqueous [Fe(II)] was measured by the ferrozine assay. The evolution of crystal morphology by reductive dissolution was examined by high resolution TEM (HRTEM). In addition, electron tomography technique was employed to understand the real three-dimensional structure of individual particles and aggregates. This technique allows us to reconstruct 3D images from a series of TEM images taken from an area of interest. HRTEM revealed that the 7 nm hematite crystals are pseudo-hexagonal plates and the 30 nm hematite crystals are rhombohedral. Hematite nanoparticles of both sizes have defective surfaces. The two types of dissolution rates, initial rate and steady state rate, were determined and compared after surface areanormalization. The surface area-normalized initial rates of reductive dissolution are more than 2 times greater in 7 nm hematite. However, no significant size dependence is observed for steady state rates. TEM observation of individual crystals and aggregates of partially-dissolved hematite reveal that dissolution initiates from surface defects or sharp edges on crystals. Also, aggregation state changes as the dissolution progresses. This study directly showsthe importance of surface roughness, defects, crystal morphology and aggregation states on dissolution rates.

Keywords: Hematite, dissolution kinetics, particle size, crystal morphology, aggregation state, transmission electron microscory