

NATURAL NANOPARTICLE SHAPE, STRUCTURE, PROPERTIES AND REACTIVITY FROM X-RAY STUDIES

G.A. Waychunas¹, B. Gilbert¹, H. Zhang², C. Kim³, Y-S. Jun^{1,2}, and J.F. Banfield^{1,2}

¹Lawrence Berkeley National Laboratory, Earth Sciences Division, Berkeley CA 94720, ²University of California, Berkeley, Dept. of Earth and Planetary Sciences, Berkeley CA 94720, ³Chapman University, Dept. of Physical Sciences, Orange CA 92866

Natural nanoparticles and synthetically-prepared analogs are being studied to understand their functionality in environmental processes, especially those connected with acid mine drainage (AMD) and other inorganic toxic contaminant sources. Additional processes involving the creation, dissolution or sequestration of nanoparticles by natural biota feature nanoparticle-organic interactions that are poorly understood, but of prime interest in predicting biogeochemical mechanisms and environmental impact of biological remediation schema.

Our efforts have been focused on ZnS, TiO₂ and Fe oxyhydroxides. ZnS nanoparticles have high sensitivity to the type of surface ligand binding, and adopt a core-shell type structure with varying core size and extent of shell distortion directly equitable to the strength of ligand bonds⁴. Exchange of surface ligands can have dramatic effects on the nanoparticle structures, as can aggregation and disaggregation. These changes are best studied by a combination of MD simulation and high energy PDF analysis, with supplemental SAXS, TEM and X-ray spectroscopic measurements.

α -FeOOH nanoparticles undergo changes in growth mode as they progress from few to 100 nm dimensions⁵. At the smallest sizes there is evidence for several structural transformations. Studies of sorption behavior indicate deviations from larger particle behavior. Aggregation/sorption processes can encapsulate toxics making them difficult to localize or remove by remediation efforts. Other Fe oxide nanoparticles may be unstable as larger single crystals and adopt nanocluster structures, e.g. ferrihydrite⁶. Crystal truncation rod diffraction work suggests deviations from stoichiometry at α -Fe₂O₃ surfaces, which could affect nanoparticle stability. Fe oxide nanoparticles nucleated on surfaces and examined via GISAXS show evidence for varying growth modes depending on size and ionic strength. Such particles can effectively activate or passivate environmental surfaces, leading to changes in reactive transport predictions.

⁴Zhang et al. Nature 424, 1025-1029 (2004)

⁵Waychunas et al. J. Nanoparticulate Res. 7, 409-433 (2005)

⁶Michel et al. Science 316, 1726-1729 (2007)