

Characterization of nanoparticle formation and aggregation on mineral surfaces

Glenn Waychunas and Young-Shin Jun, LBNL

Carmen Martinez and Katya Bazilevskaya, Pennsylvania State University (CEKA)

Research Objective

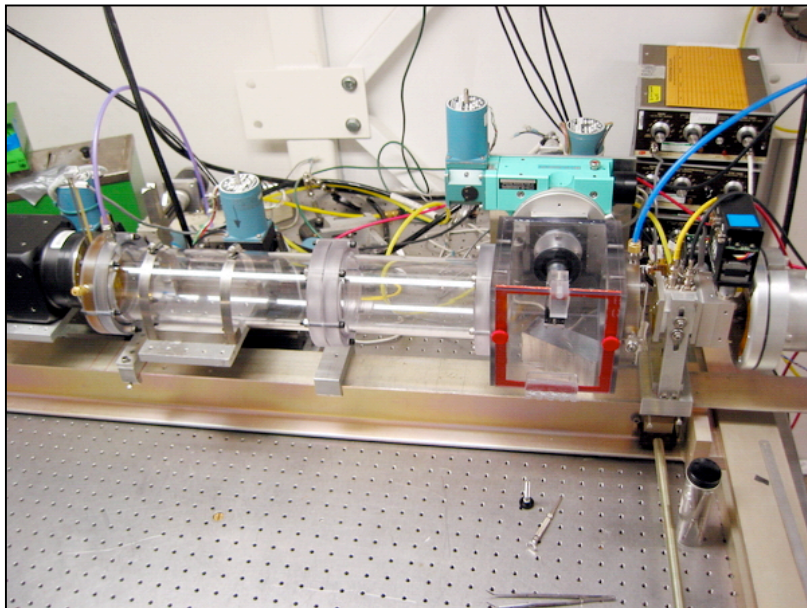
The research effort in the Waychunas group is focused on the characterization and measurement of processes at the mineral-water interfaces specifically related to the onset of precipitation. This effort maps into one of the main project groups with the Penn State University EMSI (CEKA) known as PIG (Precipitation Interest Group), and involves collaborations with several members of that group. Both synchrotron experimentation and technique development are objectives, with the goals of allowing precipitation from single molecule attachment to sub-monolayer coverage to be detected and analyzed. The problem being addressed is the change in reactivity of mineral interfaces due to passivation or activation by precipitates or sorbates. In the case of passivation, fewer active sites may be involved in reactions with environmental fluids, while in the activated case the precipitate may be much more reactive than the substrate, or result in the creation of a higher density of active sites. We approach this problem by making direct measurements of several types of precipitation reactions: iron-aluminum oxide formation on quartz and other substrates from both homogeneous (in solution) nucleation, and heterogeneous (on the surface) nucleation; precipitation and sorption of silicate monomers and polymers on Fe oxide surfaces; and development of grazing-incidence small angle x-ray scattering (GISAXS) as a tool for *in-situ* measurement of precipitate growth, morphology and aggregation. We expect that these projects will produce new fundamental information on reactive interface growth, passivation and activation, and be applicable to a wide range of environmental interfaces.

Research Progress and Implications

As of September 30, 2006 the first two years of the five year term have been completed, with a significant amount of results on all fronts. A new postdoctoral scientist was hired in the fall of 2005, Dr. Young-Shin Jun, and immediate work began on developing the GISAXS technique. The initial tests were done at SSRL with the assistance of Dr. Michael Toney and Dr. John Pople. Measurements were first conducted on dry samples run in a dry He atmosphere to gauge the signal/noise needed for single precipitate layer detection and optimize the experimental geometry. At the current date the apparatus has progressed through the 3rd generation, and has reached optimal performance on an SSRL bending magnet beamline with sensitivity of about 10% monolayer and excellent reproducibility in determination of size and shape of nanoparticles when compared to dynamic light scattering (DLS) and TEM analysis. Work on silicate sorption and precipitation has progressed through surface-diffraction (CTR) studies at the APS (three beam periods) and initial studies of Si K-edge surface EXAFS done at the ALS. Analysis of the CTR data suggest monodentate attachment of silicate monomer to the surfaces of hematite, consistent with the topology of silicate-ferric iron attachment in layer silicates, but different from that observed in chain and other silicates, and weaker in binding energy than bidentate attachment. Work on homogeneous and heterogeneous nucleation of precipitate nanoparticles of

iron-aluminum has also proceeded with two data collection runs on beamline 11-2 at SSRL, though complete results for these systems has not yet been fully analyzed.

Preliminary indications of the GISAXS work is that we should be able to perform experiments under aqueous solution given sufficient flux in real time for all the systems of interest. This will require use of a microfocussed beam line with insertion device, such as at the APS. For the silicate sorption work we note that significant passivation will result from the mode of attachment that we observe with monomers. Polymer work. Which may show quite different results, is continuing at the present time.



3rd generation GISAXS apparatus (SSRL beamline 1-4). Sample enclosure has door with red outline connected to He beam path. 2D detector system is at left along with beam stop and photodiode beam detector. Sample is aligned both vertically and to the proper grazing-incidence angles with computer controlled stepper drives. He path can be extended at will by adding other sections.

Planned Activities

In the next year we will be extending the GISAXS work to real systems under aqueous solution with additional optimization of our apparatus and work at insertion device beamlines at SSRL and at the APS. We hope to perform several experiments at two temperatures and in this way capture activation energies for growth and aggregation. The silicate sorption work will proceed to polymeric cases and to GIEXAFS work at the APS using an elliptically polarized undulator beamline. This line allows EXAFS to be collected with both in-plane and normal to plane electric vector geometry, providing more information on silicate topology. At the completion of this work we should be able to combine both GIEXAFS and CTR data for a definitive statement on silicate passivation. The nanoparticle nucleation work will be continuing at SSRL, and including clean test sample substrates (quartz) buried at field sites to determine the nature of nucleation on those surfaces. Numerous presentations have been given on these projects, and two papers are presently in preparation.

Information Access

The following presentations have been given on the research described above:

K Bazilevskaya, G Waychunas, C E Martinez “What surface analyses/techniques tell us about mixed Al-Fe coatings formed on quartz surfaces.” ACS National Meeting, Washington DC Aug 28, 2005. LBNL-61154

G A Waychunas, Y.-S. Jun, P. J. Eng, S. Ghose and T. P. Trainor “Anion sorption topology on hematite: Comparison of arsenate and silicate.” ACS National Meeting, Atlanta GA March 27, 2006. (invited) LBNL-61150

G A Waychunas, Y.-S. Jun, M. Toney, P. J. Eng, S. Ghose and T.P. Trainor “Kinetics and morphology of nanoparticle nucleation and growth on mineral surfaces.” DOE BER ERSP meeting, Airlie House VA April 4, 2006. LBNL-61149

YS Jun, G A Waychunas, P J Eng, T P Trainor, S K Ghose “Silicate adsorption on the r-plane (1-102) surface: A crystal truncation rod study.” 2006 ACS meeting, San Francisco CA LBNL-61144

YS Jun, G A Waychunas, M F Toney “Nucleation and growth of nanoparticles on mineral surfaces: First environmental applications of grazing incidence small angle x-ray scattering.” 2006 ACS meeting, San Francisco CA

Submitted publication

Benning, L. and Waychunas, G.A. (2006) Kinetics of precipitation on mineral surfaces. LBNL-61155 (Book Chapter for Elsevier text on kinetics)

Papers in preparation

G A Waychunas, Y.-S. Jun, P. J. Eng, S. Ghose and T. P. Trainor Anion sorption topology on hematite: Comparison of arsenate and silicate. Book Chapter (to be submitted-Elsevier) LBNL-61150

YS Jun, G A Waychunas, M F Toney Nucleation and growth of nanoparticles on mineral surfaces: First environmental applications of grazing incidence small angle x-ray scattering.