Molecular-Level Investigations of Nucleation Mechanisms and Kinetics of Formation of Environmental Nanoparticles

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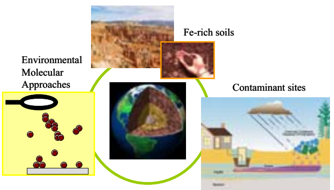
Introduction

Formation of nanoparticles on mineral surfaces controls the reactivity of mineral surfaces and soils and the fate and transport of contaminants

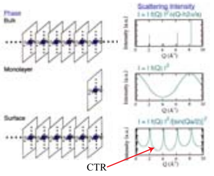


Environmental nanoparticles are often poorly-crystalline or meta-stable structures, whose kinetics of formation and growth are poorly understood. Further, the sorption or growth of nanoparticles on mineral surfaces may control the mineral surface's reactivity and modify its ability to influence contaminant transport. Due to the characteristic length scale, a holistic understanding of the nucleation mechanisms and kinetics of nanoparticle formation on mineral surfaces is difficult to achieve with traditional methodology. In this work, our intent is to determine the molecular nature of nucleation on surfaces, the kinetics of surface nucleation and growth, and the effect of crystal surface topology using new synchrotron-based techniques.

We have approached these objectives by: (1) combining state-of-the-art crystal-truncation rod diffraction (CTR) and grazing incidence x-ray absorption fine structure spectroscopy (GIXAS) techniques to investigate the three-dimensional molecular-scale geometry of silicate monomer sorption on the r-plane of hematite; and (2) developing a new grazing-incidence small angle x-ray scattering (GISAXS) setup at SSRL ($0.08\ \mathrm{nm}^{-1} < q < 8\ \mathrm{nm}^{-1}$) to explore the initial development of environmental nanoparticles on various mineral surfaces. This study also includes complementary techniques such as atomic force microscopy (AFM), bulk SAXS, dynamic light scattering (DLS), XRD, and TEM.

Experimental Techniques

Crystal Truncation Rods (CTRs: Surface Diffraction)

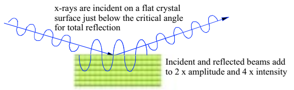


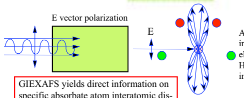
CTR allows detailed atomic structural analysis of the upper several layers of a crystal and overlaying water or sorbate layers.

CTR attributes
-Sensitive to few % of ML.
-Sensitive to 0.01-0.001 Å.
-Can use anomalous effects.
-Probe ordered surface sorbate.
-Probe ordered surface water.
-Can refine atoms of low Z.

from Fenter, P. A. 2002

Grazing Incidence Extended X-ray Absorption Fine Structure

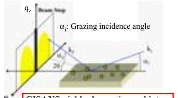


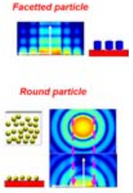


Adsorbers eject photoelectrons in a $\cos^2\theta$ distribution about electric vector.
Hence particular neighbor atoms in the surface may be probed.

GIEXAFS yields direct information on specific absorbate atom interatomic distances to atoms on the surface.

Grazing Incidence Small Angle X-ray Scattering (GISAXS)





GISAXS yields shape, size and inter-particle distance of small clusters at the interfaces.

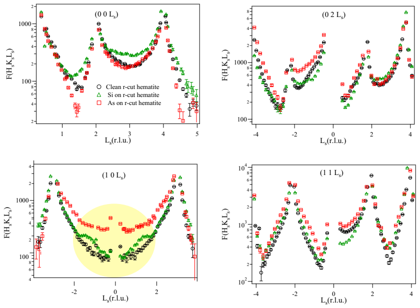
Research Goal: Develop in-situ grazing incidence small angle x-ray scattering (GISAXS) system to allow real-time geochemical kinetics analysis of nanoparticle reactions at environmental surfaces in aqueous systems

Courtesy of Byeongdu Lee

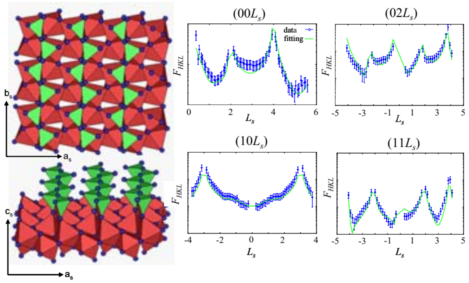
Silicate Sorption on Hematite

CTR Analysis: Comparison between arsenate and silicate sorption on the ($1\bar{1}02$) surface of hematite

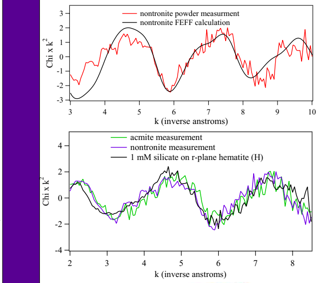
Although both silicate and arsenate are the tetrahedral anions, silicate sorption geometry to the hematite surfaces is different from that of arsenate

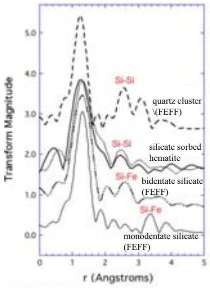


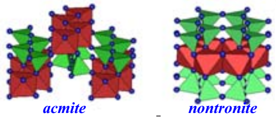
Silicate sorbs to hematite surface with a monodentate goemetry rather than other sorption geometries



First Si K-edge GIEXAFS measurements: Silicate sorption on the ($1\bar{1}02$) surface of hematite







acmite ***nontronite***

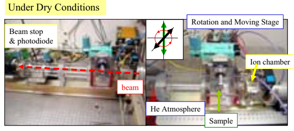
The complexed silicate on the hematite ($1\bar{1}02$) surface is linked by a single oxygen to surface Fe, i.e. a monodentate connection, with an interatomic Si-Fe distance close to those observed in the nontronite and acmite structures. This is the first evidence that identifies silicate as a well-defined sorption complex rather than only as an amorphous surface precipitate.

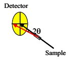
Iron Oxide Nanoparticles on Quartz

First Environmental Application of GISAXS:

New GISAXS setup developments for kinetic analysis of nucleation and growth of environmental nanoparticles

Under Dry Conditions





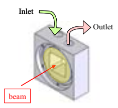
$$q = \frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{\lambda}\frac{d}{D}$$

d = pixel size

Sample to detector distance (D) defines q range for given λ

Beamline 1-4 at SSRL
Flux: ~10^{10} photons
Wavelength: fixed at 0.1488 nm
Detector: 1 inch x 1 inch;
1300 x 1340 pixels

In Situ Time-Resolved GISAXS in Aqueous Systems

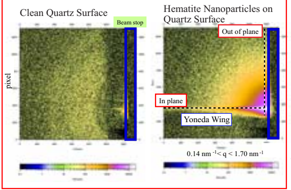


Beamline 4-2 at SSRL
Flux: ~10^{11} photons, Energy: 11 keV
Detector: 512 x 512 pixels

1 cm beam path in water
(2.2% transmission at 11 keV)

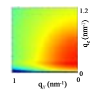
Nanoparticles on mineral surfaces under dry conditions

Measured with GISAXS



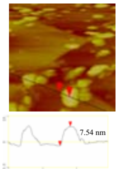
Simulated GISAXS

Input particle diameter: 7.5 nm
Randomly distributed particles



using IsGISAXS program

Measured with AFM

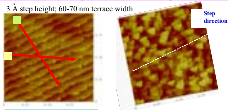


Using Local Monodisperse Approximation, Mean particle diameter of hematite nanoparticles: 7.86 nm (Stdev: 0.32 in log-normal distribution)
This result is consistent with measurements using other techniques. D_{DLS} = 7.18 nm and D_{SAXS} = 7.54 nm

Heterogeneous nucleation and growth of nanoparticles at water-mineral interfaces

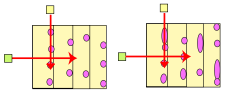
Surface steps direct the iron oxide nucleation and affect the kinetics of nucleation and growth of iron oxide nanoparticles at water-quartz interfaces

3 Å step height; 60-70 nm terrace width



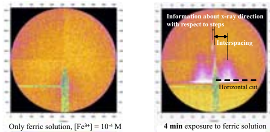
Clean m-plane quartz surface (1 μm x 1 μm)

170 min exposure to $[\mathrm{Fe}^{3+}] = 10^{-4}$ M (1 μm x 1 μm)



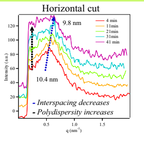
early stage later

When the beam path is perpendicular to step direction



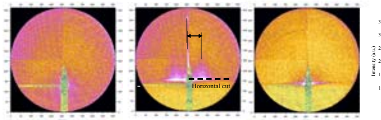
Only ferric solution, $[\mathrm{Fe}^{3+}] = 10^{-4}$ M

4 min exposure to ferric solution acquisition time (3 min)

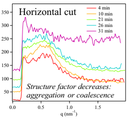


At 4 min reaction time, iron oxide nanoparticle shape is disc shape (lateral diameter: 5.26 ± 0.50 nm; height: 1.87 ± 0.20 nm). Particle interspacing ($S_{interparticle} = 2\pi/q_m$) is 10.4 ± 0.3 nm.
With time, the particle interspacing decreases and polydispersity of particles increases.

When the beam path is almost along step direction



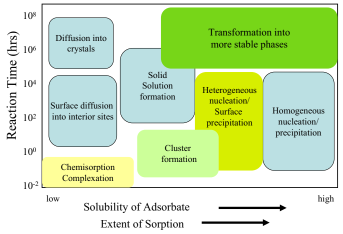
Only ferric solution, $[\mathrm{Fe}^{3+}] = 10^{-4}$ M **4 min** exposure to ferric solution **31 min** exposure to ferric solution



At 4 min reaction time, iron oxide nanoparticle shape is disc shape. Particle interspacing is 10.4 ± 0.3 nm.
At 31 min, the particle interspacing decreases quickly, which means the nuclei begin to coalesce with each other and form larger surface clusters.

Conclusion

The Fates of Sorbed Ions in Soil-Water Environments



The CTR analysis of silicate sorbed on the hematite identifies a significant fraction as being ordered on the surface, and specifically with a monodentate-like geometry. This geometry is similar to that observed in pyroxene and amphibole minerals, and may explain how the beginnings of a silicate surface phase may precipitate. Complementing this work, the first Si K-edge GIEXAFS data were successfully collected and this data indicate that the bulk of silicate appears to precipitate on the surface as a poorly ordered structure with a small Si-O-Si coordination number. This phase is not unlike the colloidal silica used in polishing samples, and may be encouraged to form by the presence of such contaminants on the surface. To our knowledge, this CTR and GIEXAFS work presented here are the first detailed molecular analysis of silicate adsorption geometry on iron oxide surfaces, and perhaps on any mineral surface.

In the other part of our study, we devised the first environmental application of GISAXS in aqueous systems and studied the kinetics of nucleation and growth of iron oxide nanoparticles at water-quartz interfaces using *in situ* time-resolved GISAXS. The changes in the sizes and shapes of nuclei and the interspacing between nuclei on quartz surfaces are determined as a function of exposure time and the direction of x-ray beam with respect to that of steps. The iron oxide nuclei started to grow close to steps rather than on terraces. At 31 min, the nuclei began to coalesce with each other and form larger surface clusters. We found that the surface steps direct the iron oxide nucleation and affect the kinetics of nucleation and growth of iron oxide nanoparticles at water-quartz interfaces. This technique can provide statistically improved morphological information of environmental nanoparticles compared with AFM and SEM, and allow real-time geochemical kinetics analysis of nanoparticle growth and reactions.

Molecular-Level Investigation Tools for Environmental Interfaces

CTR: ordered sorbate atomic structure at the mineral surfaces.
GIEXAFS: sorbate sorption geometry (ordered and disordered) at mineral surfaces.
GISAXS: size, shape, distributions of the early nuclei or nanoparticles at water-mineral surfaces (*In situ* time-resolved mode).
AFM: Imaging of surface reactions in real time.

Future Plans

By using this arsenal of newly developed state-of-the-art techniques, we intend to investigate the mechanisms and kinetics of the nucleation and growth of nanoparticles on surfaces having varying step density (i.e. varied surface topologies), the presence of heavy metal ions or organic compounds, and at different temperatures.

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