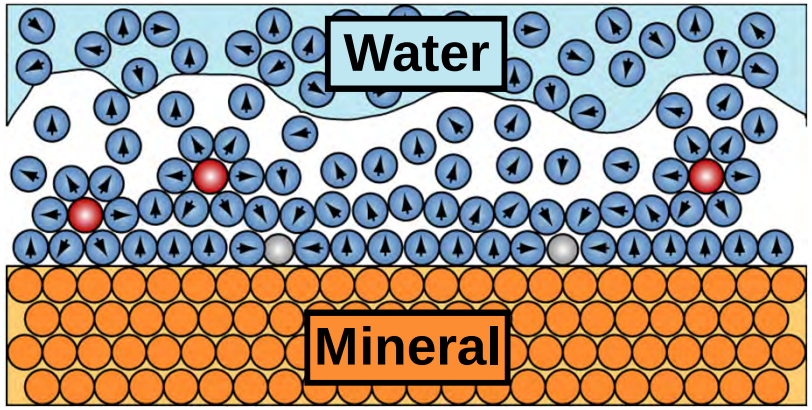
Geochemical Applications of Interfacial X-ray Scattering



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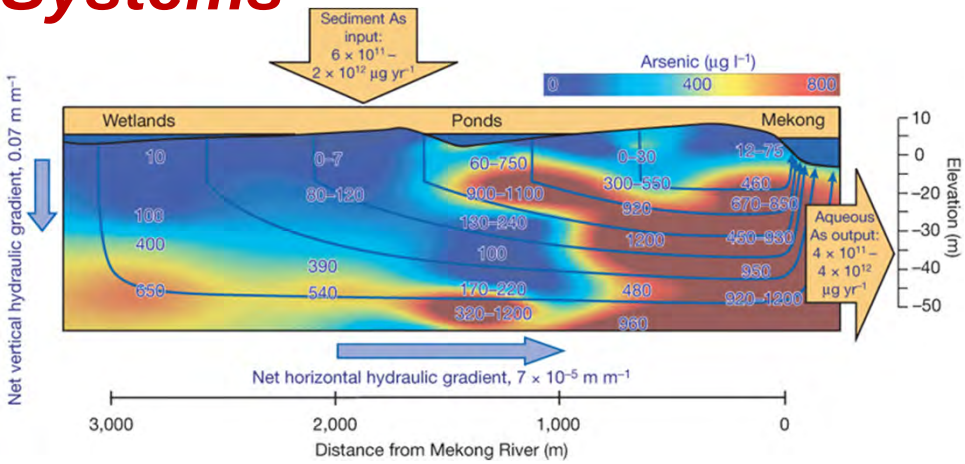
Importance of Interfacial Reactions to Geochemical Systems

Nutrient Availability in Soils and Aquatic Systems

Microbial Metabolic Activity

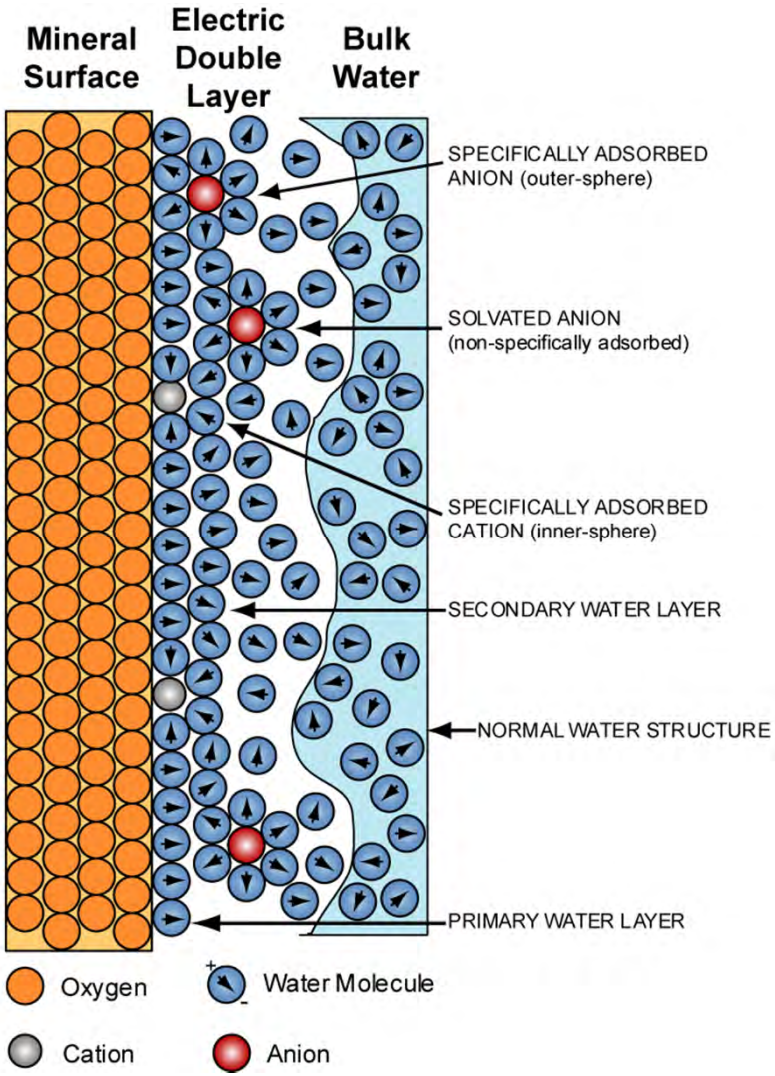


Occurrence, Fate, and Transport of Water Contaminants

- Reactions at the interface between mineral solids and natural waters affect:
  - The behavior of natural and anthropogenic water contaminants, including radionuclides
  - Nutrient bioavailability
  - Electron transfer processes associated with microbial metabolism
  - CO_2 sequestration
  - The composition of natural water

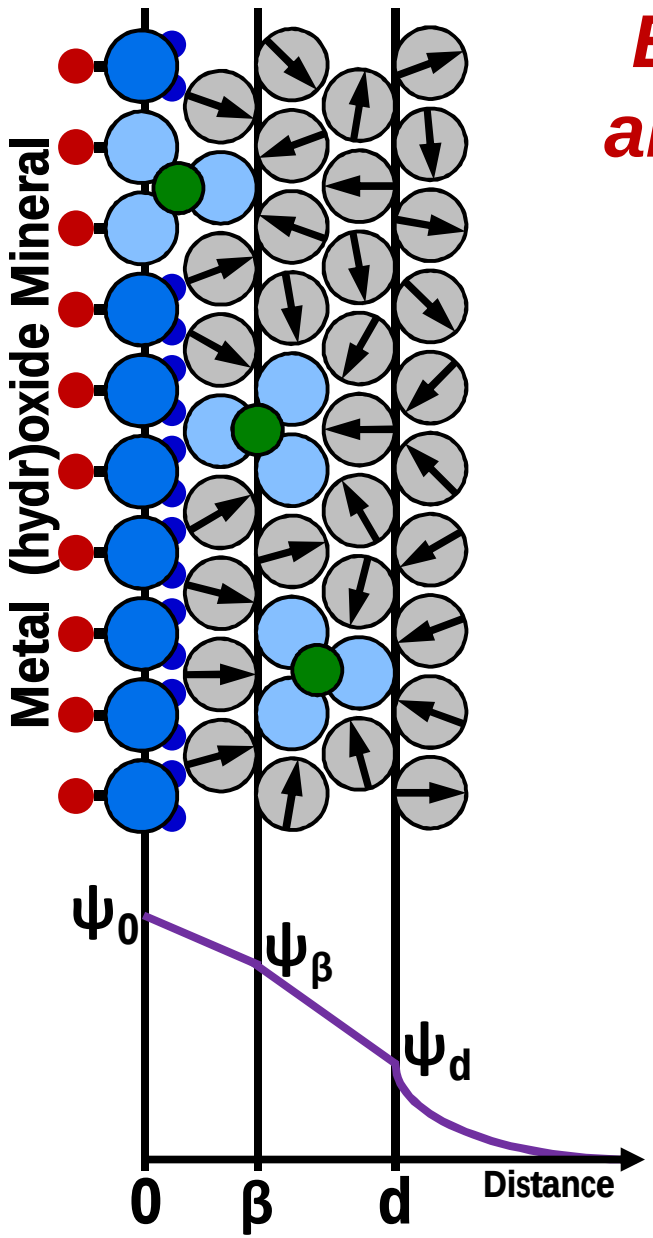
Figure from: USDA-NRCS; PNNL; Polizzotto et al. (2008) *Nature*

Need to Obtain a Fundamental Understanding of the Mineral-Water Interface



- Reactions at mineral-water interfaces affect many important environmental and geological processes
- We must understand mineral-water interfaces at a basic level in order to predict the effect of interfacial reactions on natural and engineered systems
- Essential fundamental questions:
  - ***What is the structure of a mineral-water interface and how does it vary?***
  - ***How do reactive sites and interfacial properties control contaminant adsorption and precipitation?***
  - ***How are mineral-water interfaces involved in and affected by biogeochemical processes?***

Figure after: Brown and Parks (2001) *Int. Geol. Rev.* **43**, 963-1073

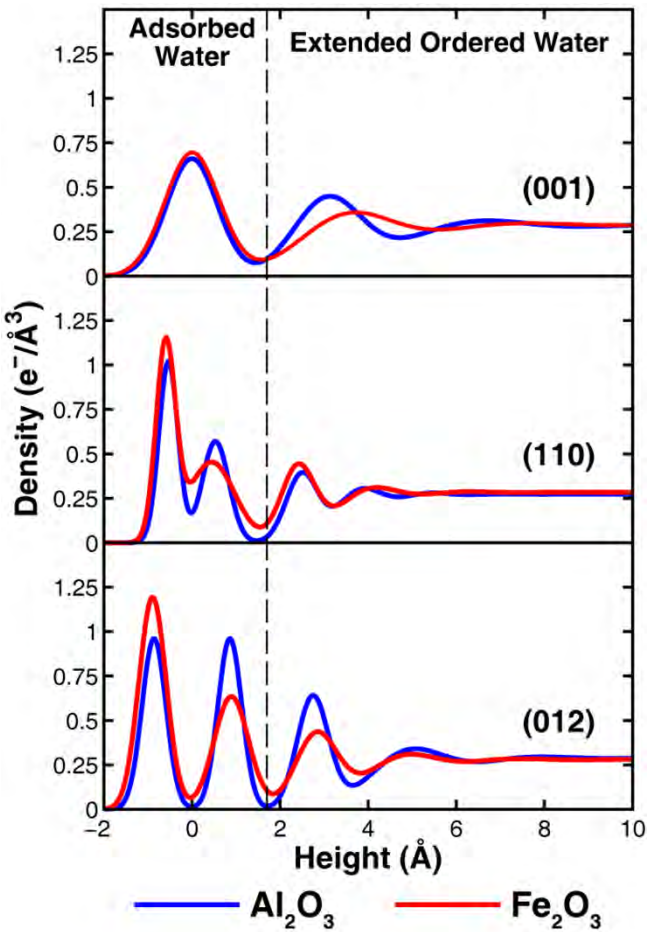


Effects of Interfacial Structure and Properties on Geochemical Processes

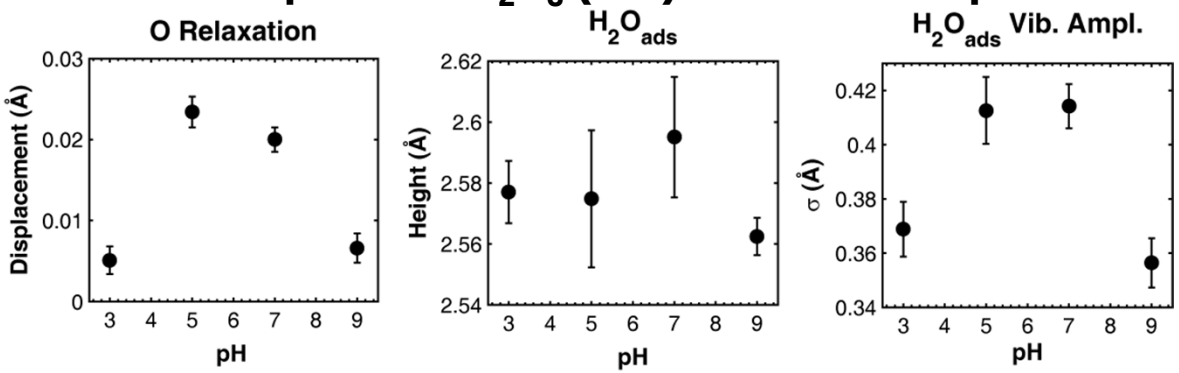
- Reactive sites on mineral surfaces control the chemical interactions with aqueous species
- Charging at the surface generates a local electric potential that substantial alters the favorability of interfacial reactions
- Mineral surfaces induce ordering of interfacial water that in turn affects the stability of surface complexes
- Feedbacks may exist between surface charging, ion adsorption, and water ordering

Water Variation on Iron and Aluminum Oxides

Water Profile Variability



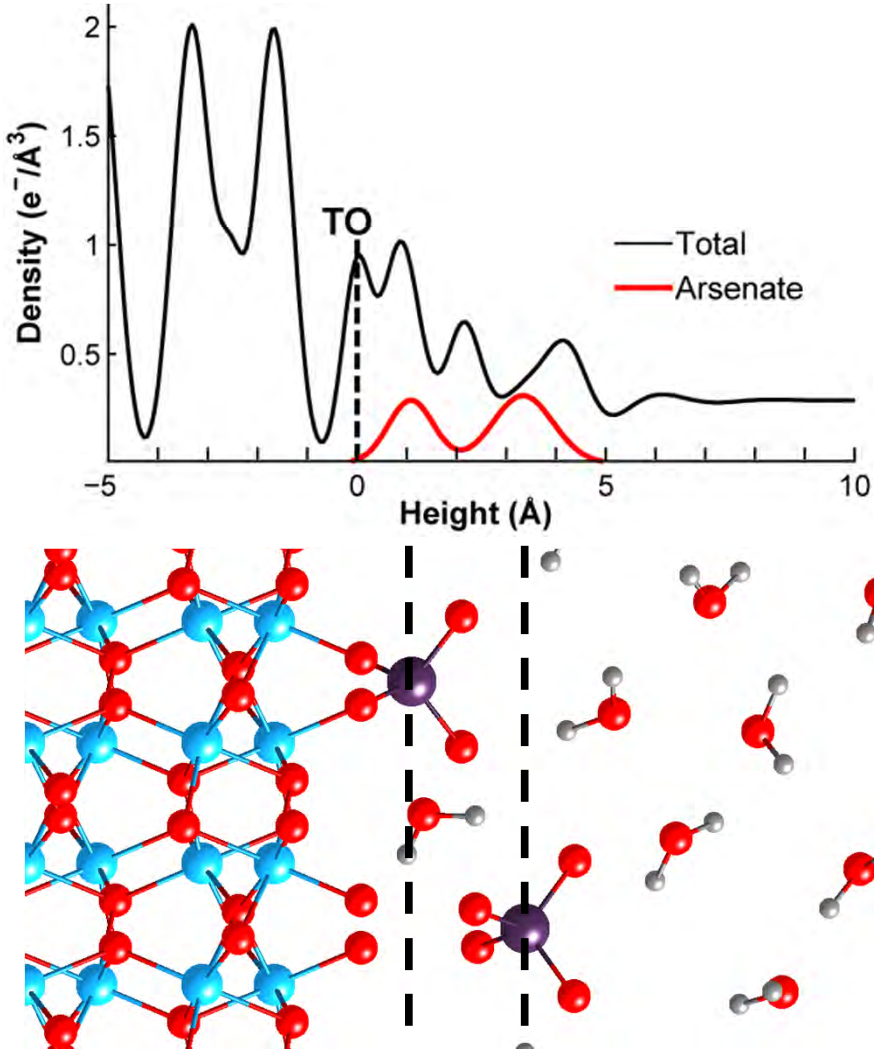
Effects of pH on α-Al_2O_3 (001) Interfacial Properties



- The arrangement and ordering of interfacial water varies among different crystallographic surfaces
  - Water shows substantially weaker ordering on (001) surfaces
- (001) surfaces and adjacent interfacial water show weak structural responses to pH changes

Catalano et al. (2006) *Langmuir*
Catalano et al. (2007) *GCA*
Catalano et al. (2009) *GCA*
Catalano (2010) *J Phys Chem C*
Catalano (2011) *GCA*
Catalano (2012) *in preparation*

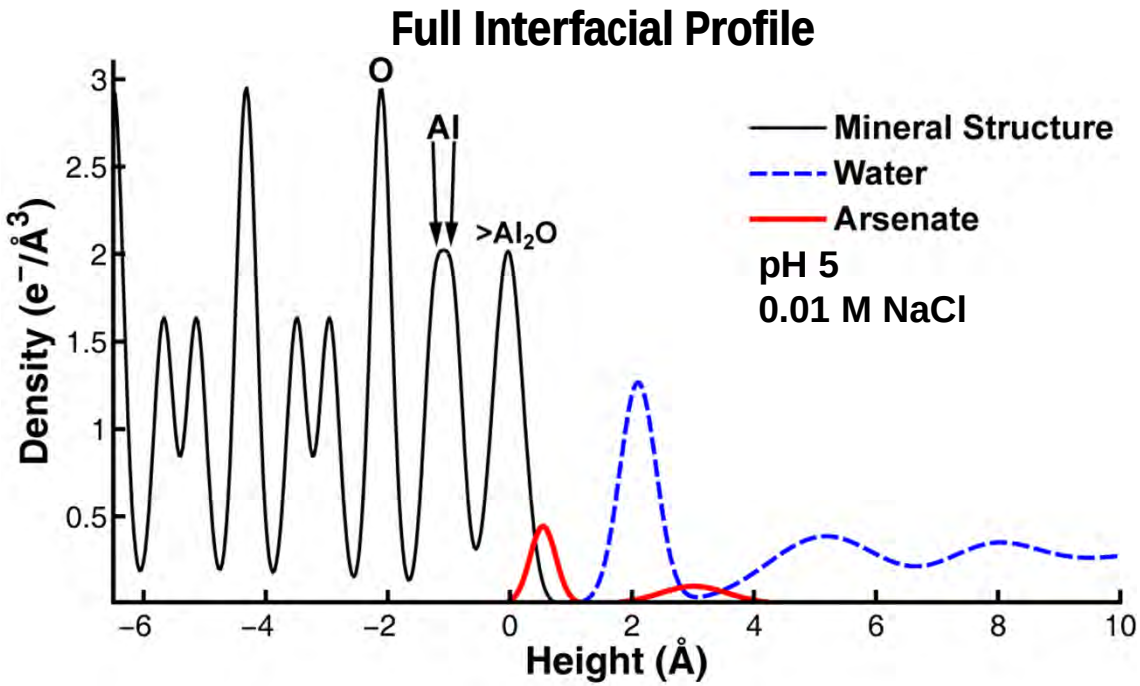
Complex Contaminant Adsorption



- RAXR measurements demonstrate that arsenic adsorbs through two mechanisms
  - The more distant, outer-sphere arsenate was previously unknown
- The ratio of arsenic adsorption through the two mechanisms is insensitive to coverage and ionic strength but is strongly pH dependent
- Arsenic adsorption shows greater complexity than has been assumed for last 40 years

Catalano et al. (2008) *GCA* **72**, 1986-2004

Site Reactivity and Water Restructuring

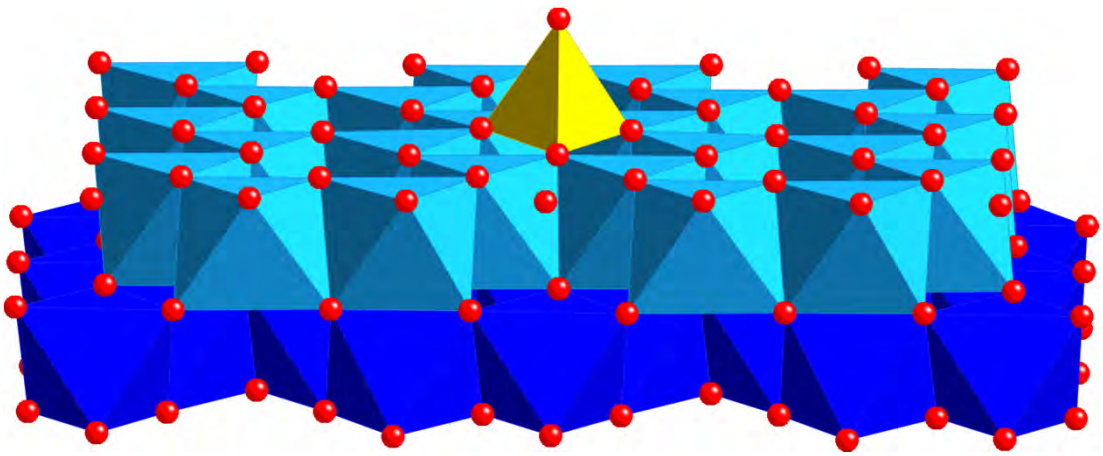


- Al_2O_3/Fe_2O_3 (001) surfaces show unique reactive sites that are widely assumed to be unreactive towards adsobates
- Arsenate unexpectedly binds to these sites through a ligand exchange mechanism
- Arsenate adsorption induces the structuring of interfacial water with a substantial increase in positional ordering

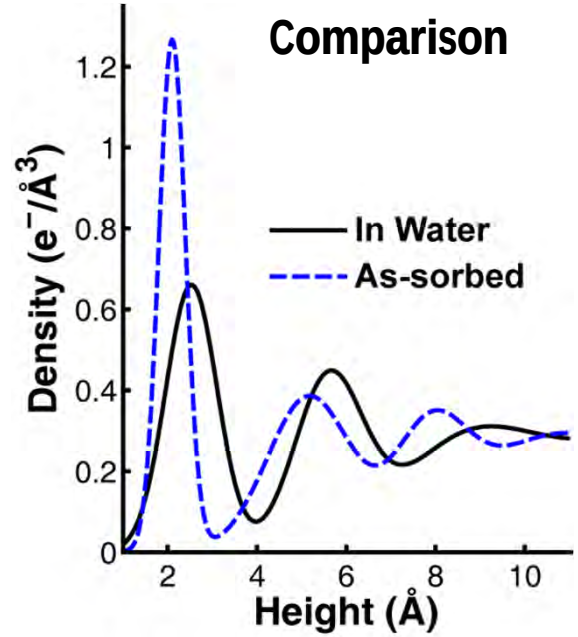
Catalano, *in preparation*

Site Reactivity and Water Restructuring

AsO_4^{3-} Binding Geometry



Interfacial Water Comparison



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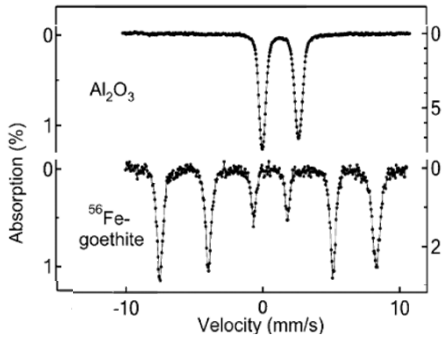
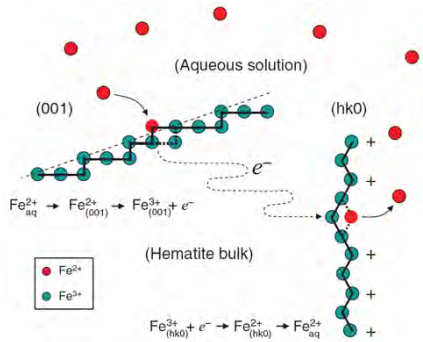
Catalano, *in preparation*

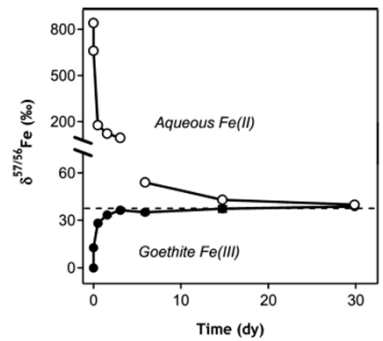
Processes Involved in or Resulting from Interfacial Fe(II)-Fe(III) Self-Exchange



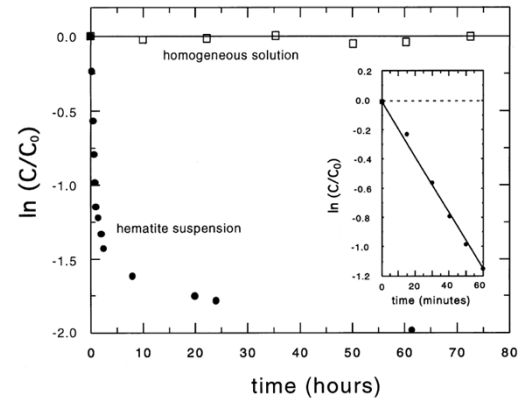
Oxidative Fe(II) Adsorption
Williams et al. (2004)



Electron Conduction
Yanina and Rosso (2008)



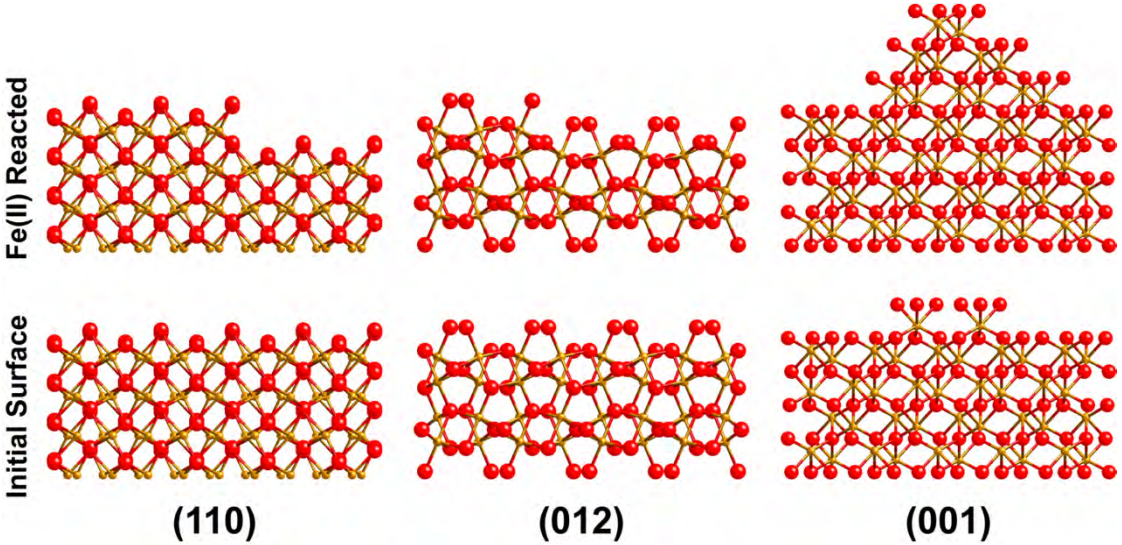
Isotope Equilibration
Handler et al. (2009)

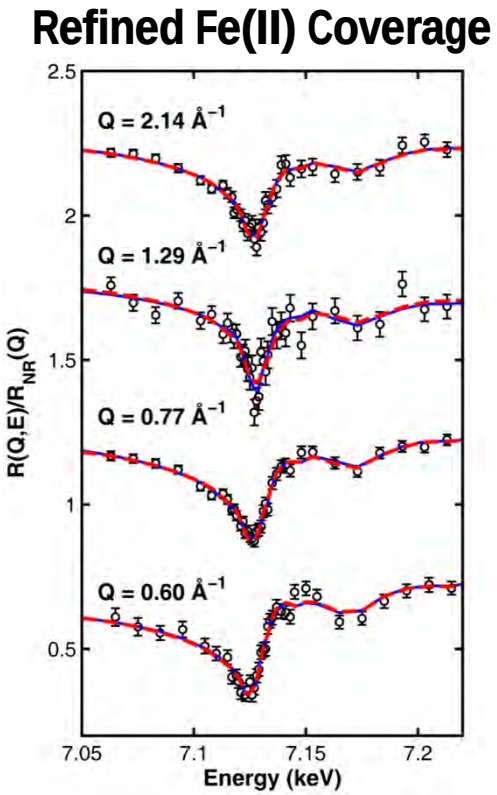


Contaminant Reduction
Liger et al. (1999)

- Many complex abiotic reactions occur in systems containing aqueous Fe(II) and Fe(III) oxides:
  - Oxidative Fe(II) adsorption
  - Electron conduction
  - Isotope exchange and equilibration
  - Contaminant redox changes
- Current uncertainties include:
  - How these processes alter mineral surfaces
  - How common aqueous species affect these processes
  - The effect of these reactions on redox-inactive contaminant and trace element fate

Mineral Surface Transformations during Biogeochemical Cycling



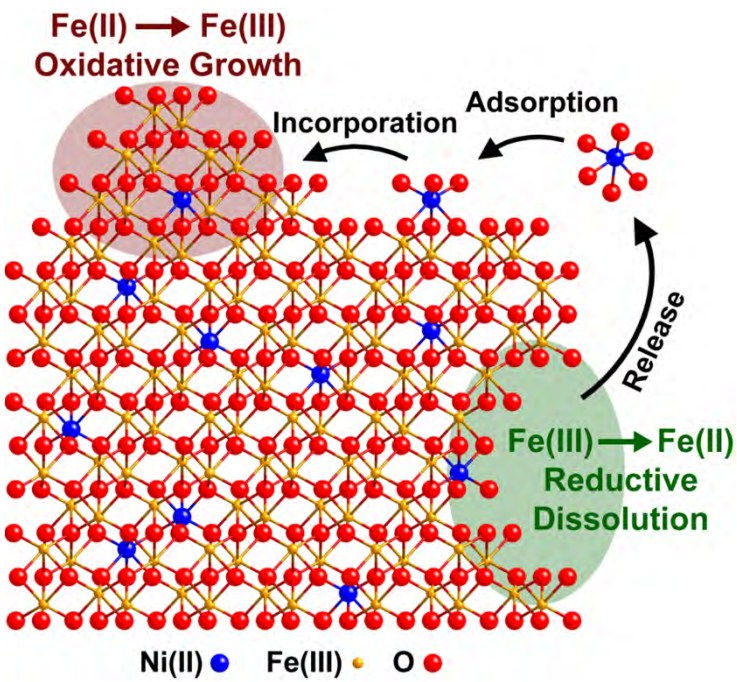


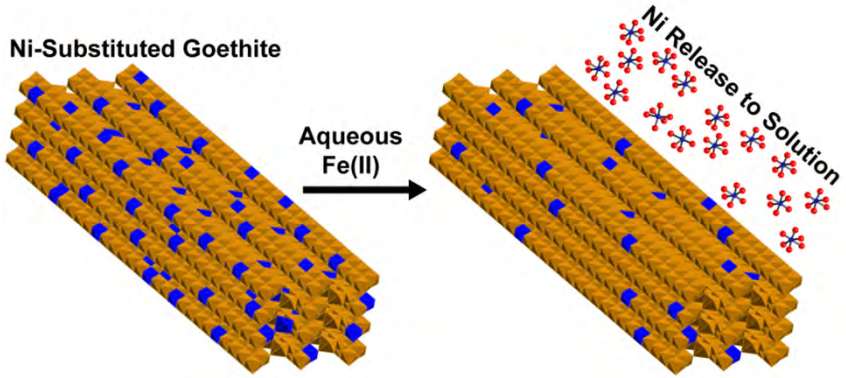
- XR shows that Fe(II), a product of microbial metabolic activity, causes localized growth and dissolution of iron oxide surfaces
- This process leaves behind no Fe(II) on the surface as verified by RAXR, confirming that oxidative adsorption has occurred

Catalano et al. (2010) *GCA* **74**,1498-1412

Impact of Surface Transformations on Contaminant Fate

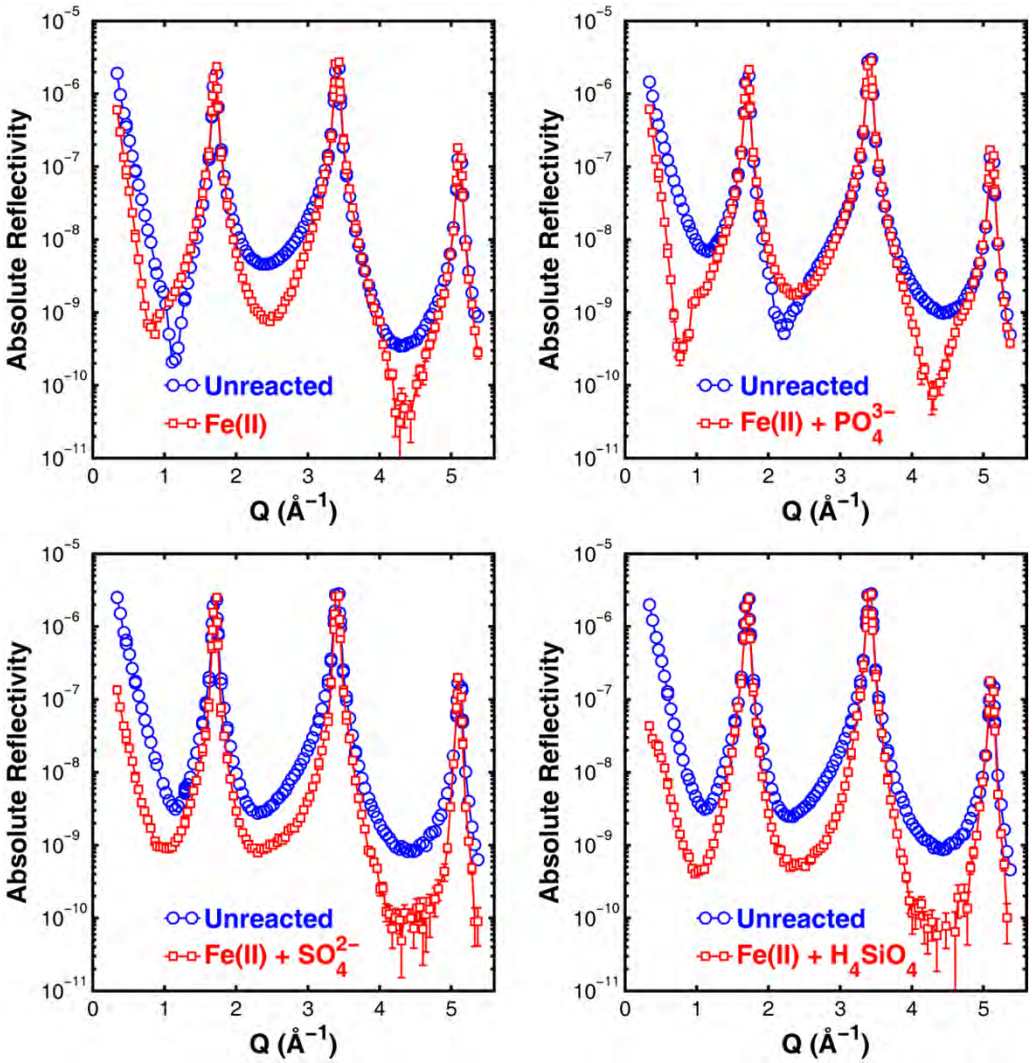
- Iron oxide surface transformations during biogeochemical cycling affect contaminants:
  - Adsorbed contaminants are overgrown and incorporated
  - Existing incorporated contaminants are released back into water
- Represent previously unknown dynamic surface processes that substantially affect how contaminants behave in the environment





Frierdich et al. (2011) *Geology* **39**, 1083-1086
Frierdich and Catalano (2012) *ES&T*, in press

Common Ions Alter Biogeochemical Transformations of Surfaces

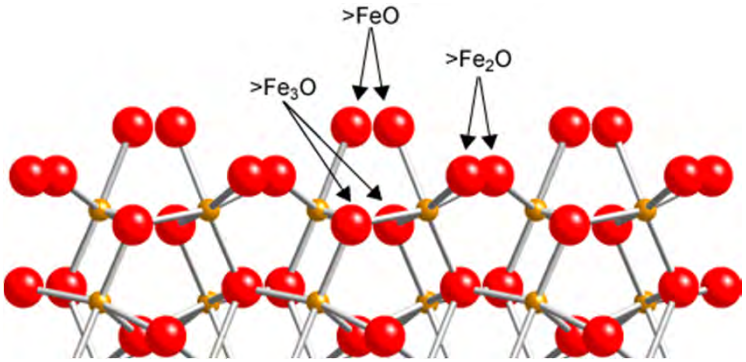


- Oxoanions are common in natural waters and adsorb to oxide surfaces
  - These may interfere with Fe(II) surface reactions
- Surface transformations unaffected by phosphate
  - Termination change without substantial increase in step density
- Sulfate and silicate alter surface processes
  - No change in termination
  - Large increase in step density
  - Suggests that dissolution and growth is now localized on terraces and not at steps

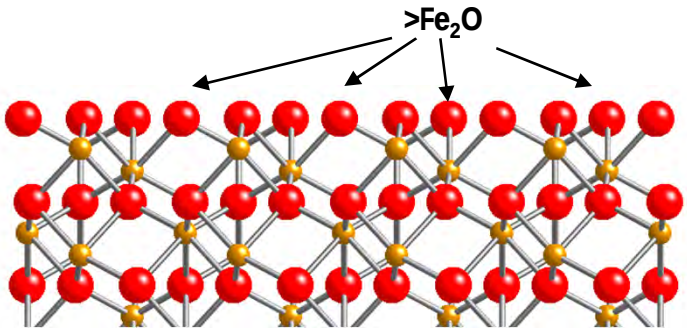
Catalano et al., *in preparation*

Potential Future Applications and Sector Needs

Interfacial Dynamics and Site-Specific Reactivity



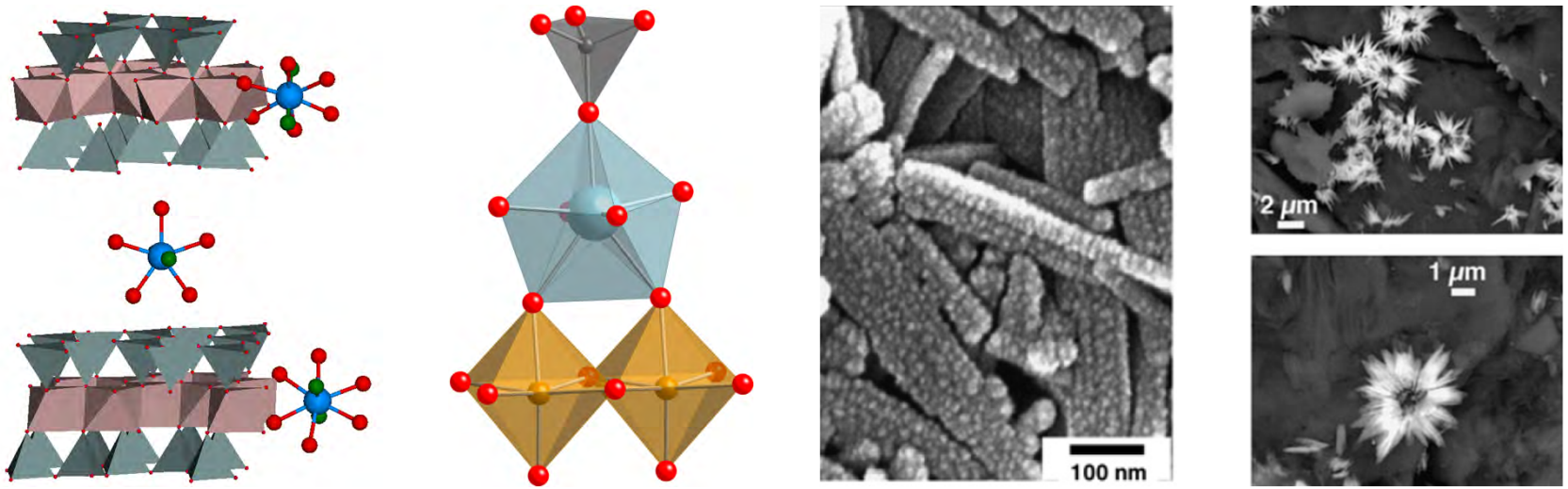
Corundum-type (012) Surfaces



Corundum-type (001) Surfaces

- Mineral surfaces display multiple types of reactive sites that differ in their coordination to the underlying crystal structure
  - These are predicted to have different protonation behavior but only singly coordinated O sites are believed to react with adsorbates as other sites are assumed to be kinetically inert
- Inner-sphere surface complexes bind to surface sites but outer-sphere complexes have strong interactions with interfacial water
  - The rates of formation of these complexes and their effect on interfacial water may differ
- ***These assumptions about fundamental aspects of interfacial reactivity and dynamics have never been tested experimentally***

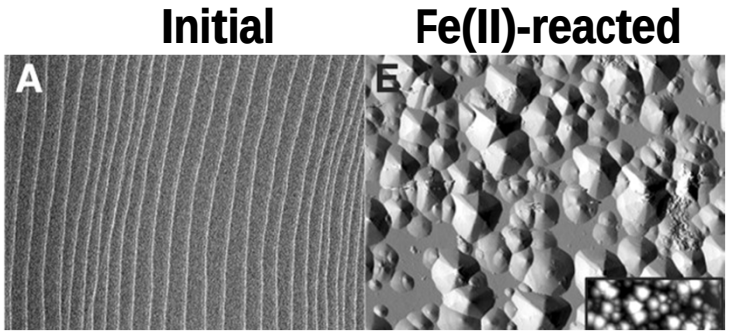
Complex Actinide Adsorption, Nucleation, and Precipitation Behavior on Mineral Surfaces



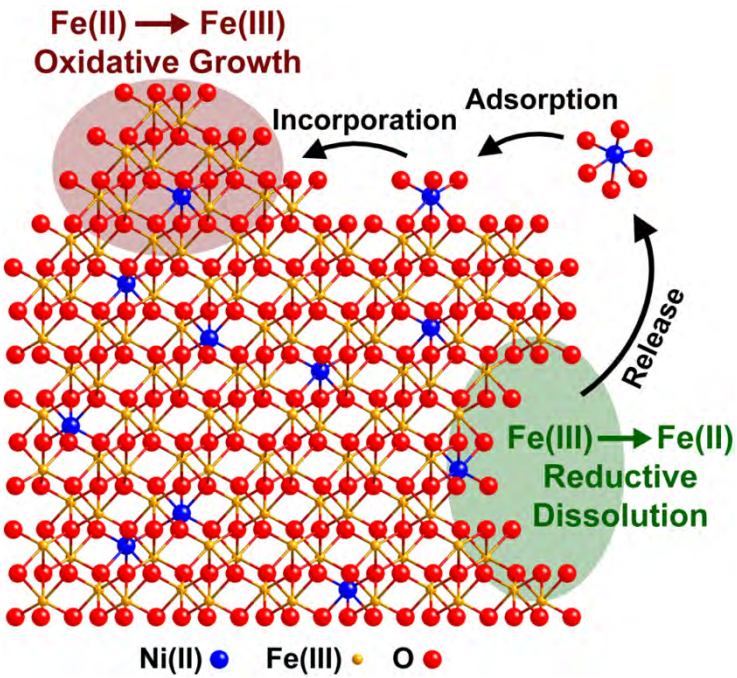
Binary Adsorption **Ternary Adsorption** **Heterogeneous Nucleation & Growth**

- Actinides displays complex modes of adsorption and frequently forms ternary surface complexes with common ligands
- These complexes may be critical precursors to nucleation and could dictate the spatial distribution of precipitates in contaminated sediments
- ***The structure of ternary surface complexes, the transition states and timescales of nucleation, and the crystallographic relationship between nuclei and mineral substrates are currently unknown***

Interfacial Dynamics in Biogeochemical Systems



From: Yanina and Rosso (2008) *Science*



Frierdich et al. (2011) *Geology* **39**, 1083-1086
Frierdich and Catalano (2012) *ES&T*, in press

- Microbial activity alters chemical conditions, activating dynamic mineral recrystallization
- This repartitions nutrients and contaminants among the mineral surface, mineral interior, and aqueous fluid
- ***The mechanisms and timescales of these transformations are still uncertain, as is how common inorganic and organic components of natural systems modify these transformations***

A Geochemist's Wishlist for Components of an XIS Sector

- **Required:** Station on-axis with undulator; monochromator optimized for both scattering and spectroscopy; large vertical and horizontal focusing mirrors; spectroscopic-grade ion chambers; area detector
- **Important:** Vertical focusing to 5-10 μm; area detector with rapid readout, some energy windowing, and pixels <100 μm; integrates XRF detector; XRIM setup optimized at mid- to high-energy (15-30 keV)
- **Dream:** Energy-dispersive reflectivity setup for time-resolved RAXR
- **Desired Techniques:** Specular and non-specular XR, RAXR (minor and major component), time-resolved XR, XRIM, time-resolved RAXR