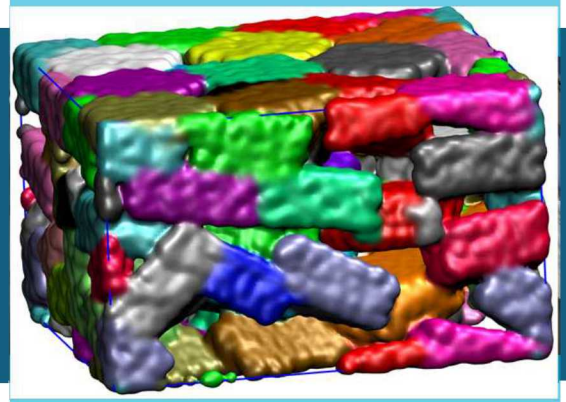
SAND2019-4401C

Interfacial Geochemistry of Nanopores: Molecular Behavior in Subsurface Environments



PRESENTED BY

BES Geochemistry Team

Jeffery A. Greathouse, Louise J. Criscenti, Anastasia G. Ilgen, Kevin Leung, Andrew W. Knight, Tuan Ho, and Jacob Harvey

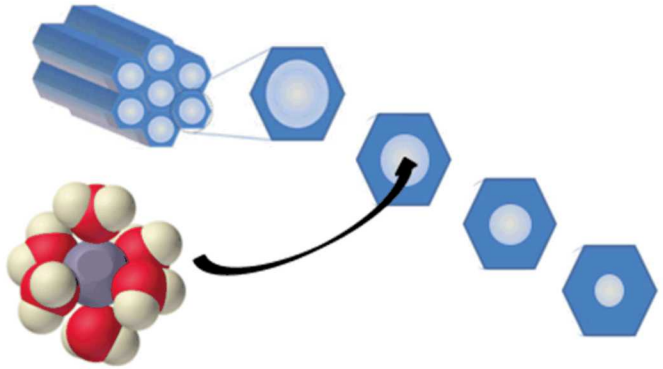
Funding: DOE Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Overview of Sandia BES Geochemistry Project (FY17 – FY19)

Objective

Molecular-level understanding of nanopore geochemistry in the subsurface through modeling and experiment



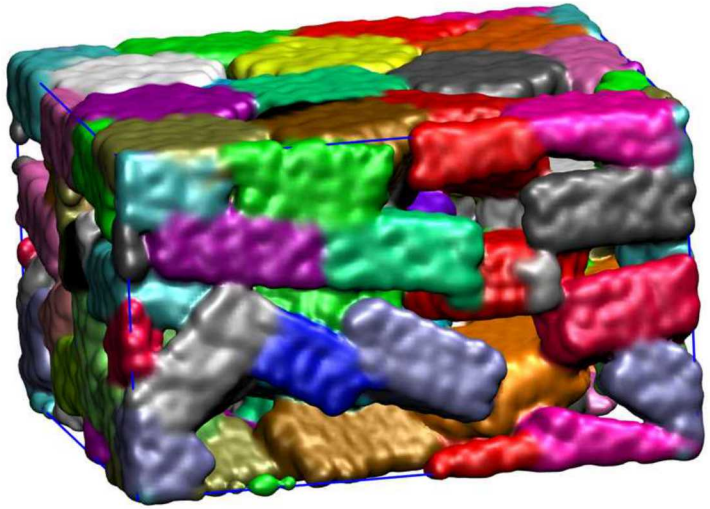
Size of a hydrated cation compared with pore sizes of mesoporous silica materials

Task 1: Chemistry Under Nano-scale Confinement

- Pore Size Effects on Adsorption and Solute Coordination
- Adsorption and Redox Reactions Under Nano-Scale Confinement

Task 2: Upscaling Mineral-Solution Properties from the Nano- to the Meso Scale

- Structure and Dynamics at Hydroxylated Edge Surfaces of Layered Minerals
- Molecular Simulations of Mesoporous Materials
- Large-scale Molecular Modeling of Mineral-Fluid Interactions in Clay Pores



Nanopore structure created from gibbsite nanoparticles

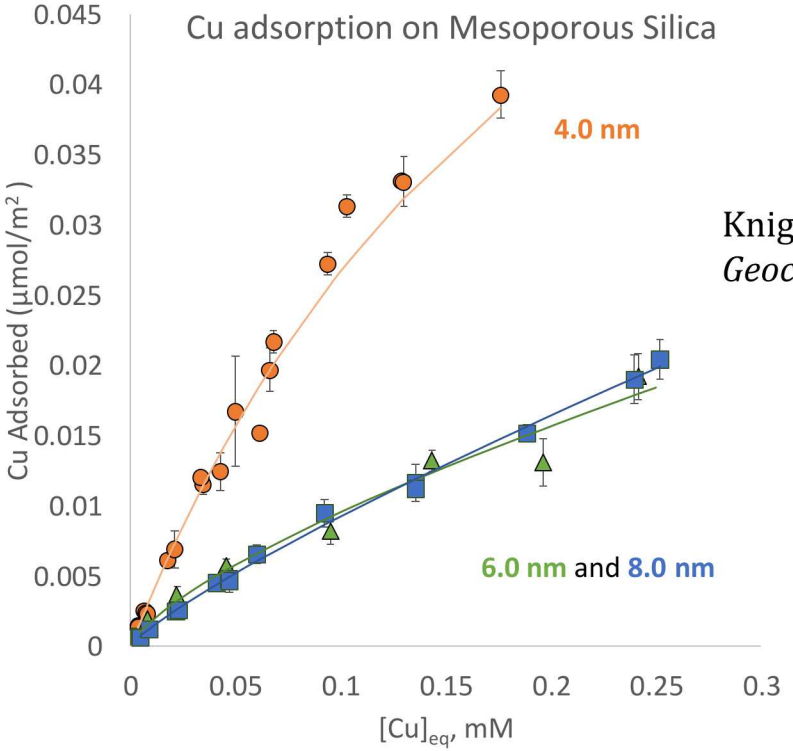
Ho et al. *Sci. Reports* **2017**

Continuous funding from BES since the 1990s

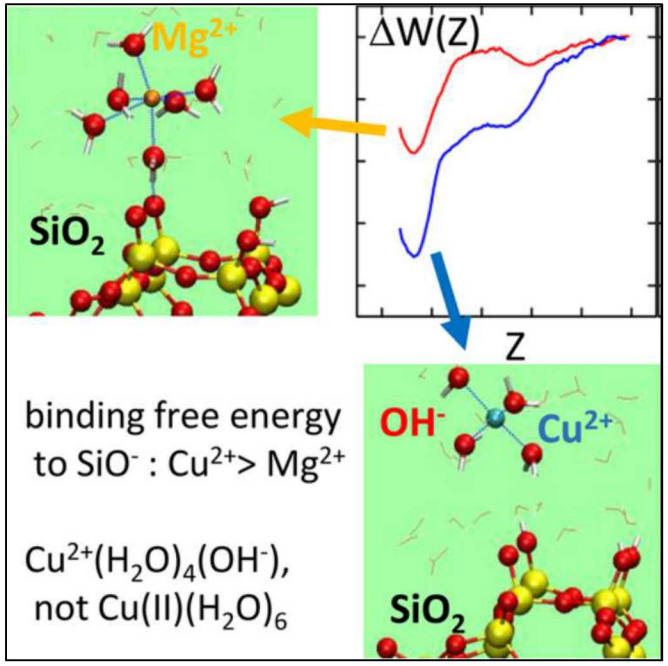
Copper Adsorption in Silica Nanopores

Nano-scale Confinement Effects on Ion Adsorption

Measured Cu^{2+} adsorption on silica materials (8 nm, 6 nm, and 4 nm pore diameter). Adsorption in the 4 nm pore is significantly great than 6 nm or 8 nm, indicating nano-scale confinement effects.



Knight, Tigges, and Ilgen. *Geochem. Trans.* **2018**



Leung, Criscenti, Knight, Ilgen, Ho, and Greathouse. *J. Phys. Chem. Lett.* **2018**

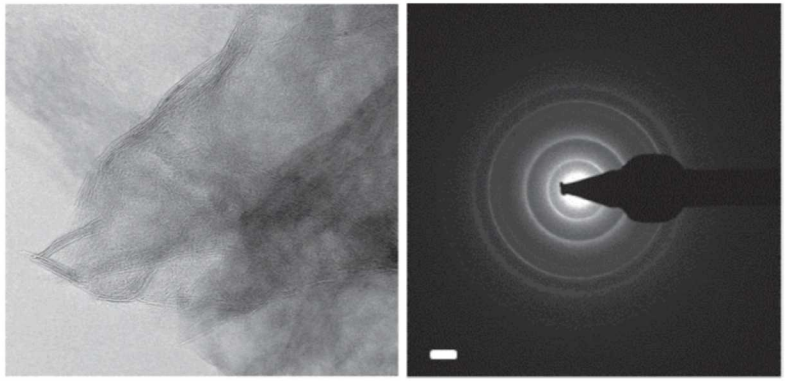
Cation Desorption and Proton Transfer on Silica Surfaces

Trends in cation adsorption on silica surfaces combining classical and quantum modeling and experiment. This marks, to our knowledge, the first time concerted cation desorption and SiOH protonation state changes is modeled.

Iron-Rich Minerals: Redox Properties

Synthesis and characterization of redox-active ferric nontronite

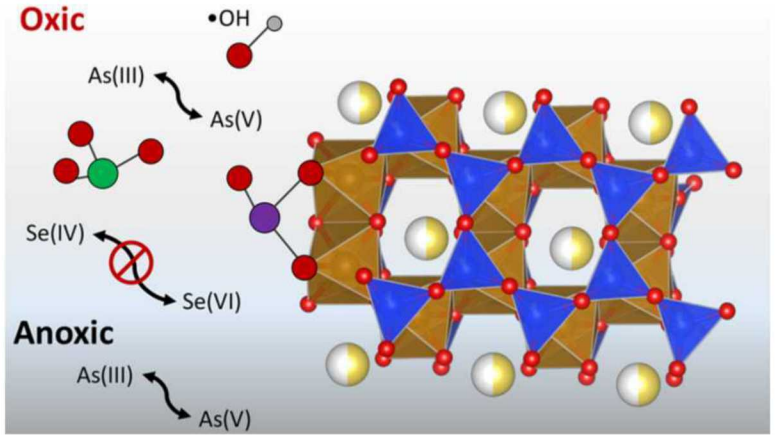
We developed a novel synthesis procedure for iron-rich smectite (nontronite). The reactivity of this synthetic nontronite is similar to the natural nontronite. This synthetic analog is necessary to understand the reactivity of iron in clay mineral structures.



Ilgen et al. *Chem. Geol.* **2017**

Redox Transformations at Nontronite Surfaces

EXAFS experiments (Advanced Photon Source, Argonne) contribute to fundamental understanding of the dynamic redox behavior of iron-containing clay minerals and chemical controls on their redox reactivity.

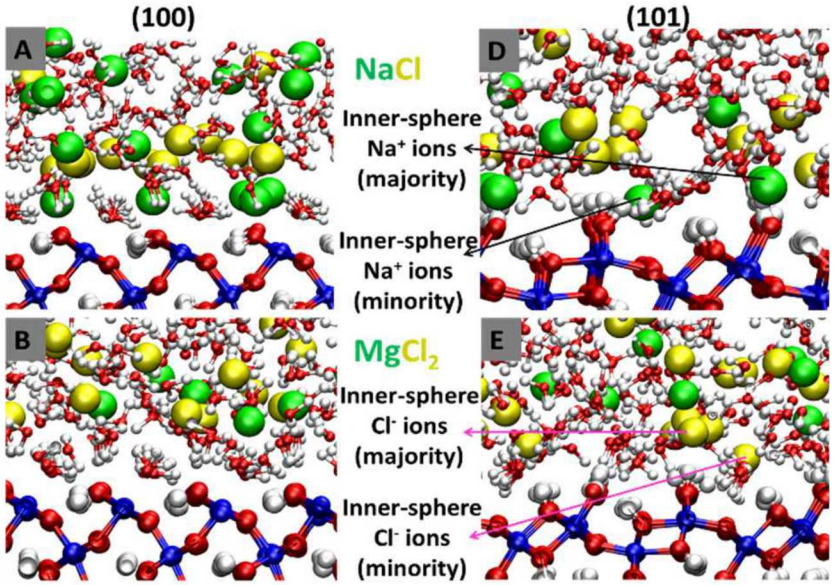


Ilgen et al. *Environ. Sci. & Technol.* **2017**

Iron-Rich Minerals: Molecular Modeling

Structural Properties of Aqueous Solutions at Goethite Surfaces

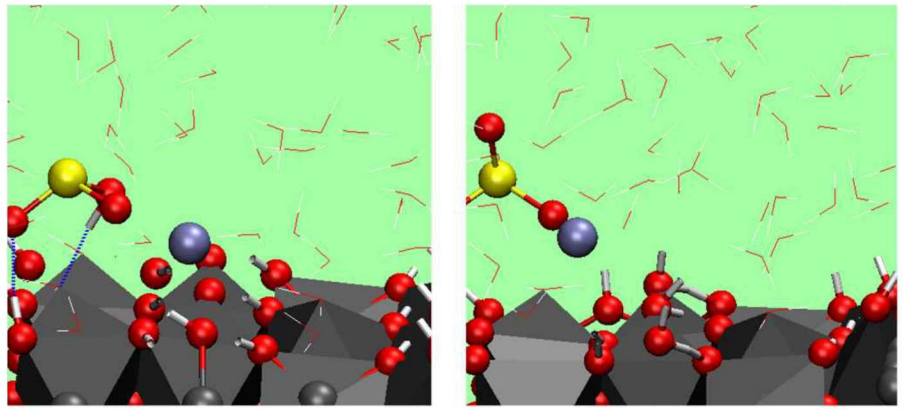
The fundamental differences in interfacial properties for these surfaces suggest that the adsorption properties of one goethite surface cannot be averaged to represent goethite interfaces present in soils and sediments.



Criscenti, Ho, and Hart. *Langmuir* **2018**

Adsorption of Ion Pairs at Iron (Oxy)hydroxide Surfaces

Ab initio molecular dynamics simulations of transition metal cation and ion-pairs at water-goethite interfaces. Demonstrated that real-time dynamics and fluctuations in ion coordination environments are useful indicators of surface binding site stability.

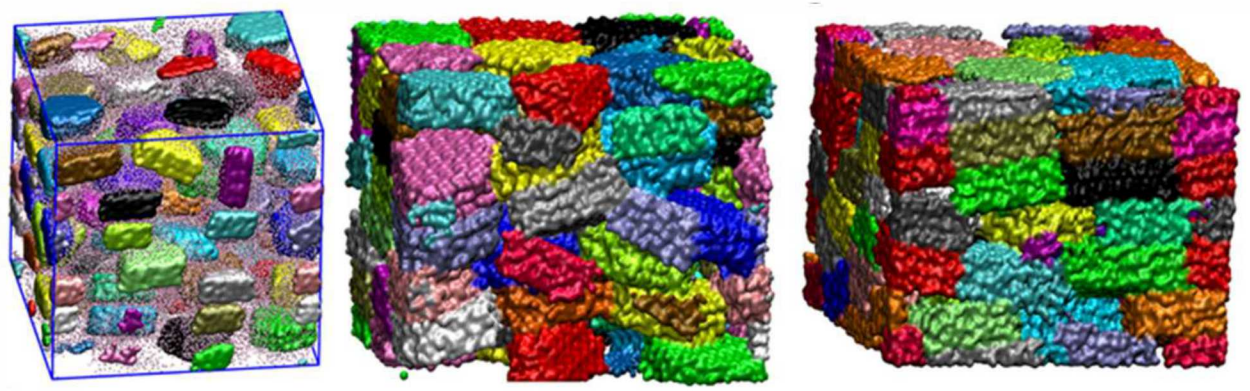


Leung and Criscenti. *J. Phys. Condens. Matter* **2017** **FRONT COVER**

Molecular Simulations of Mesoporous Materials

Compaction and Dewatering of Mineral Nanoparticle Aggregates

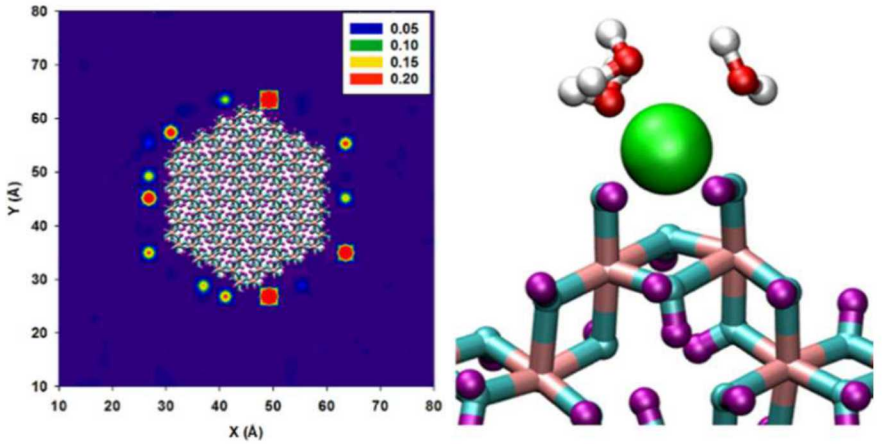
We have developed the first method of its kind for creating complex and realistic clay-like nanoparticle aggregates with interparticle pores and grain boundaries.



Ho, Greathouse, Wang, and Criscenti. *Sci. Reports* **2017**

Enhanced Ion Adsorption on Mineral Nanoparticles

Comparison of simulated ion adsorption trends with experiment will be improved when more realistic mineral models containing nanoparticles or nonideal binding sites are included.

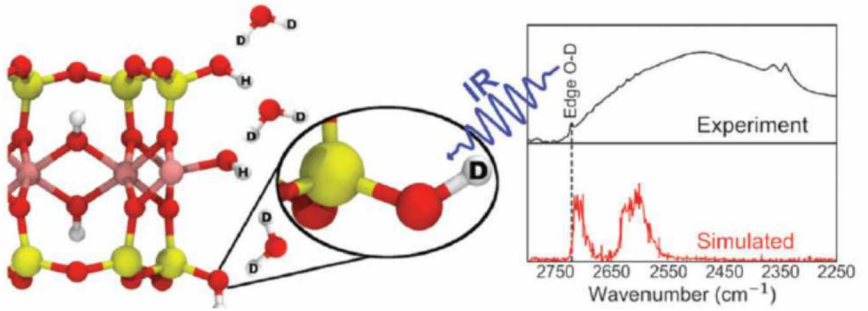


Ho, Greathouse, Lee, and Criscenti. *Langmuir* **2018**

Molecular Modeling of Clays – ClayFF Force Field Development

Direct Observation of Vibrational Properties at Clay Edges

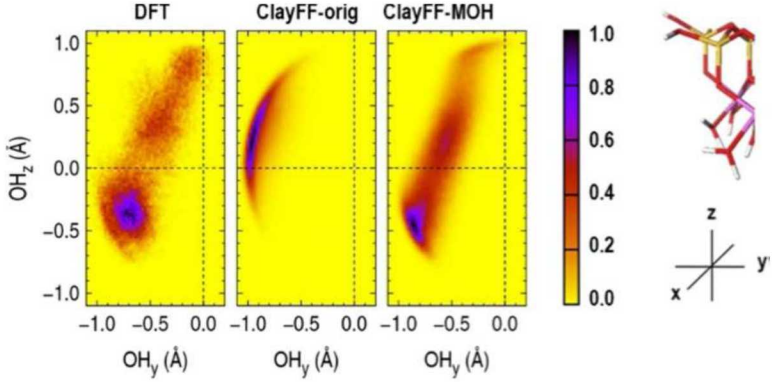
First direct observation of infrared spectral modes associated with clay edges with direct comparisons between computational and experimental results.



Harvey, Johnston, Criscenti, and Greathouse.
Chem. Commun. **2019** **INSIDE BACK COVER**

Force Field Development Enabling Molecular Simulation of Mineral Edges

Combined with earlier efforts to develop similar parameters for hydroxyl groups containing octahedrally coordinated cations (Al^{3+}, Mg^{2+}), these improvements in ClayFF addresses the problem of edge surface instability at fluid interfaces.



Pouvreau, Greathouse, Cygan, and Kalinichev.
J. Phys. Chem. C **2019** **SUPPLEMENTAL COVER**

New Directions

Adsorption and Ion Coordination Under Nano-scale Confinement

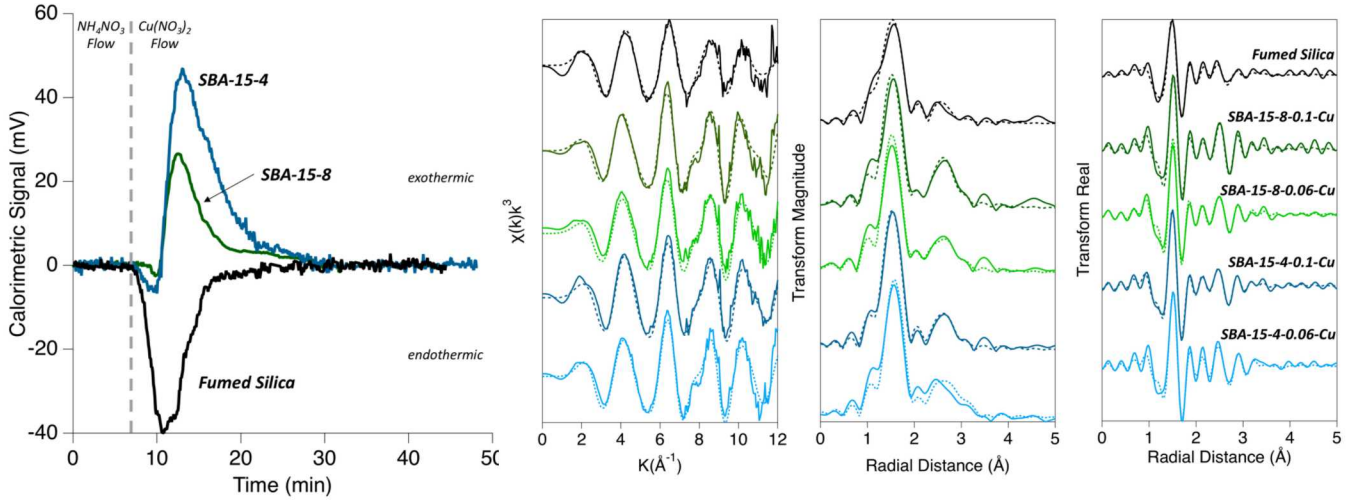
Thermodynamics of Clay Hydration and Swelling

Effects of Surface Hydroxylation on the Confined Mineral-Fluid Interface

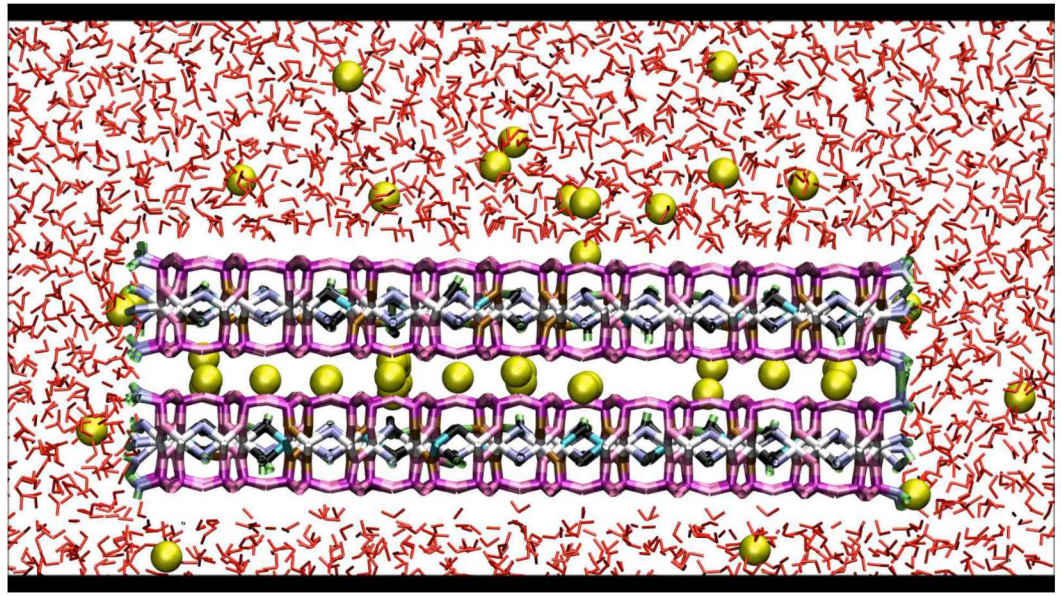
Surface Complexation Modeling

Aggregation and Compaction Impacts on Reactive Nano-scale Transport

Nano-fluidics



Interfacial reactions driven by nano-scale confinement.
Knight, Ilani-Kashkouli, Harvey, Greathouse, Ho, Kabengi, and Ilgen. In preparation



Molecular simulation of stepwise interlayer hydration of clay minerals
Ho, Criscenti, and Greathouse. In preparation