# Molecular Geochemistry: Atomistic Simulations of Mineral Interfaces

SAND2015-8848PE

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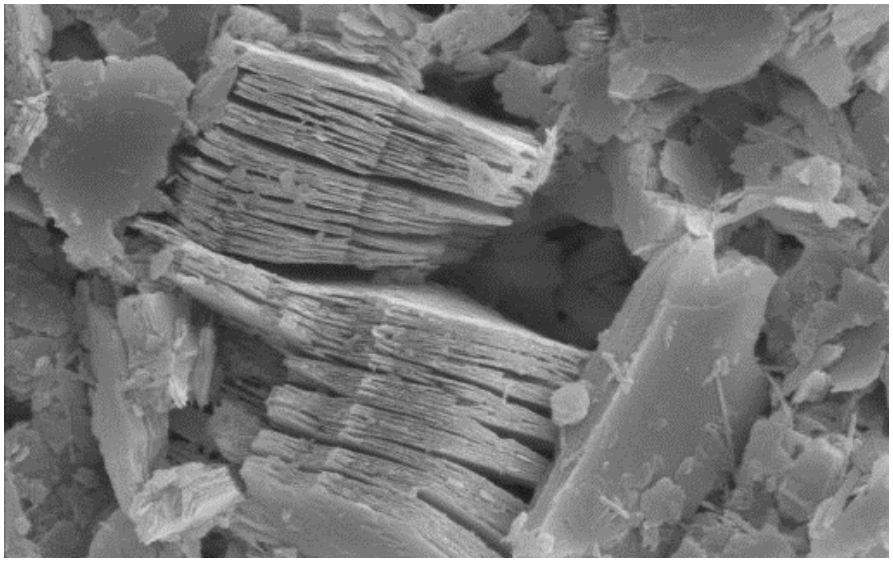
***Geochemistry Department***
***Sandia National Laboratories***
***Albuquerque, New Mexico, USA***

Sandia National Laboratories

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

# Outline

- Overview of Sandia National Laboratories
- Molecular simulations and applications to repository science
- Interlayer structure and dynamics of swelling clays
- Clay edge sites

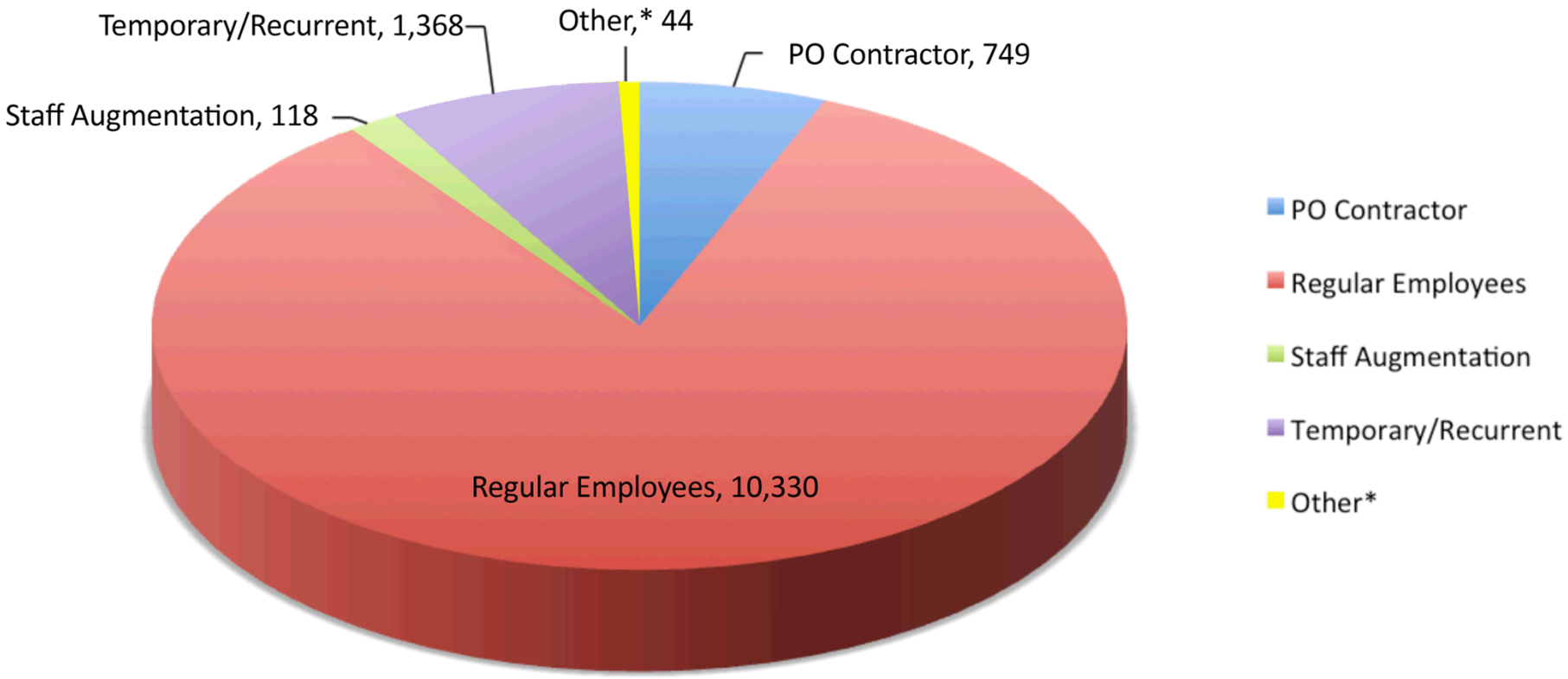


# Our Workforce

- Total Sandia workforce: 12,609
- Regular employees: 10,330
- Advanced degrees: 5,790 (56%)

*Data as of July 20, 2015*

Engineering (mechanical, electrical, other)
Computing
Science (physics, chemistry, other)
Mathematics




** Other badged personnel*

# Technical Staff Disciplines

Sandia National Laboratories

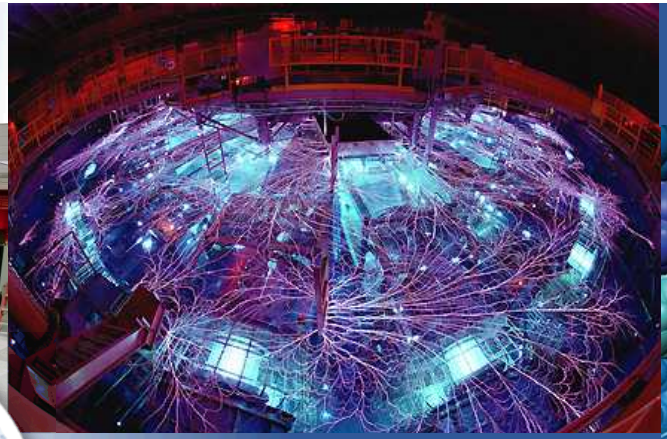
Mechcanical engineering
Computing
Electrical engineering
Other engineering
Other fields
Other science
Physics
Chemistry
Mathematics

# Our Research Framework

*Strong research foundations play a differentiating role in our mission delivery*

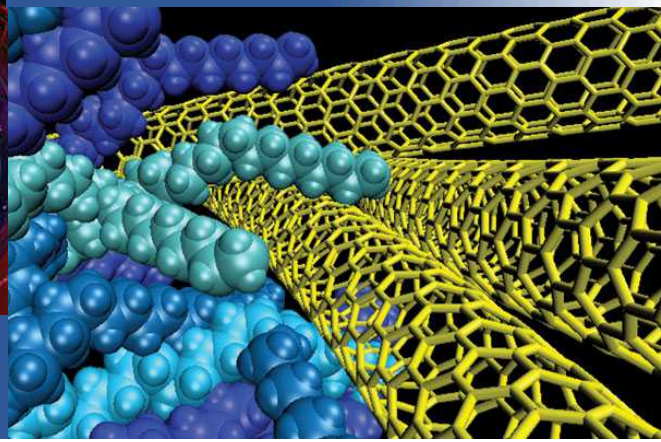
## Computing & Information Sciences



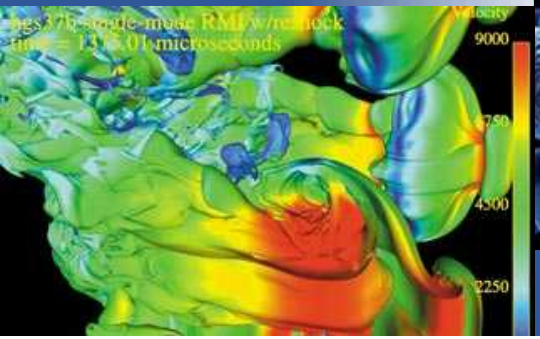


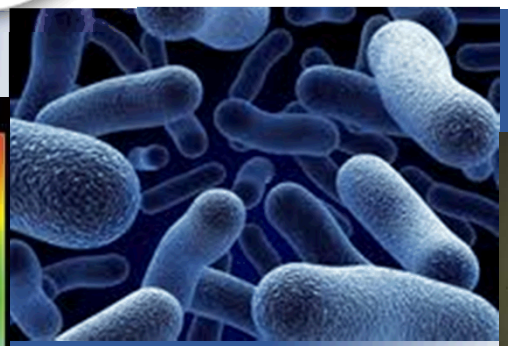
## Radiation Effects & High Energy Density Science

## Materials Sciences



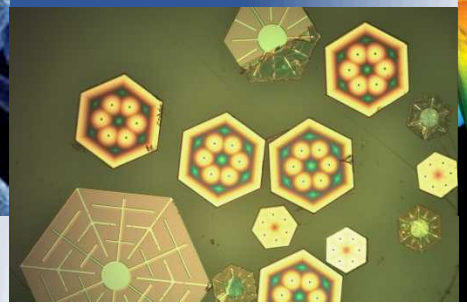
## Engineering Sciences

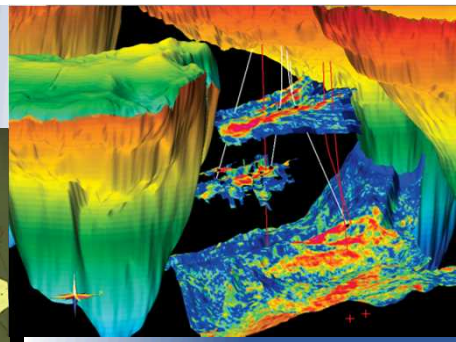




## Bioscience

## Nanodevices & Microsystems



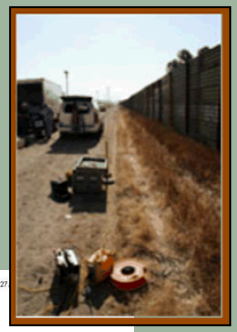


## Geoscience

# Geoscience Research & Applications Group

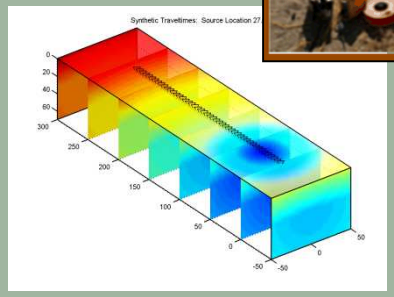
## Overview

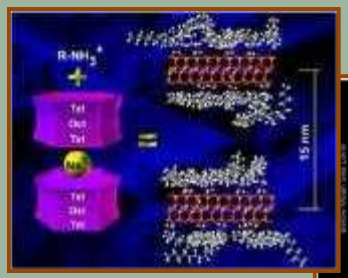
- Geotechnologies and Engineering
- Geophysics and Atmospheric Sciences
- Geomechanics
- Geochemistry
- Geothermal Research

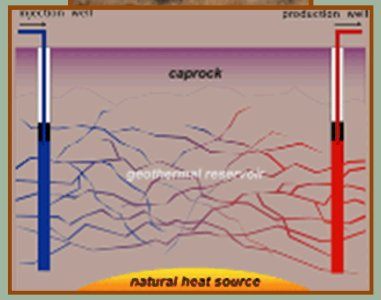


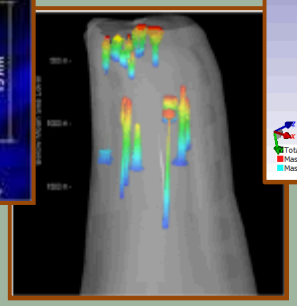
**Technical foundation for Sandia missions connected with the Earth and atmosphere**

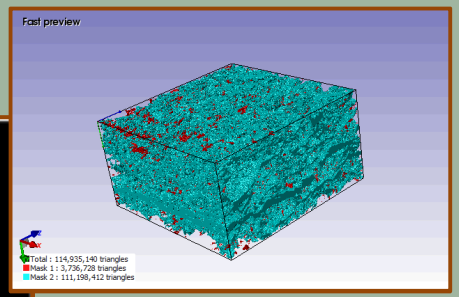
- *Theory*
- *Model development*
- *Analysis*
- *Laboratory expertise*
- *Field activities*

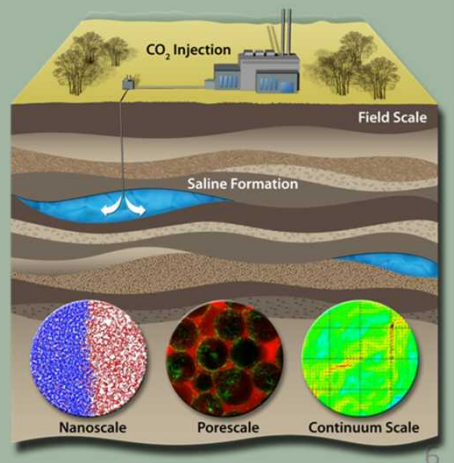


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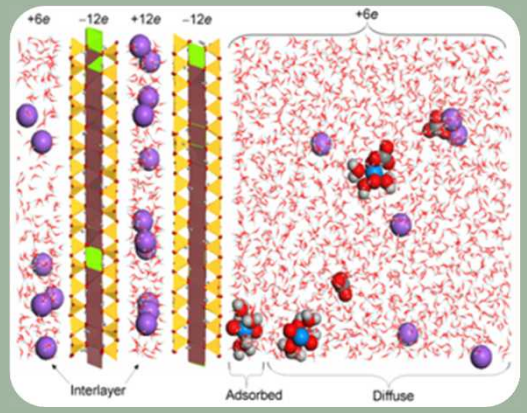
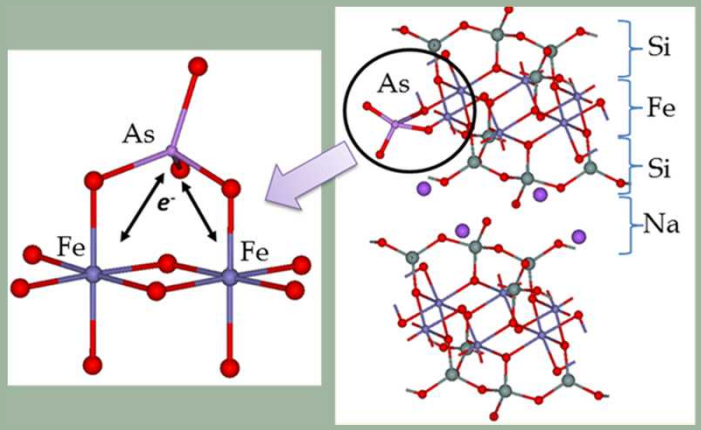
# Geochemistry Department

**We engage and solve challenging technical problems in geochemistry, environmental science and applied materials science with a focus on both basic and applied research that is supported by our computational modeling and experimental capabilities.**

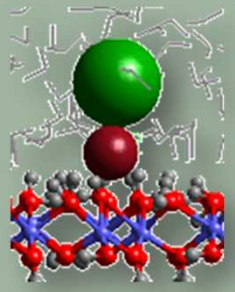
Large-scale MD of $CO_2$ bubble in saturated $H_2O$ on clay (EFRC)




Large-scale models of $UO_2^{2+}$ adsorption on clay (BES)

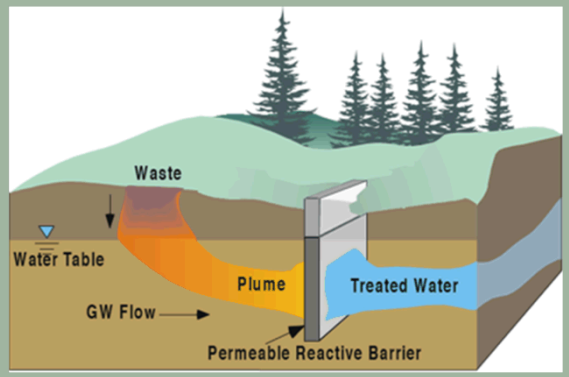



Redox reactions on clay mineral surfaces (BES)



$SrCl^+$ ion-pair Adsorption on Goethite (BES)

Permeable reactive barriers



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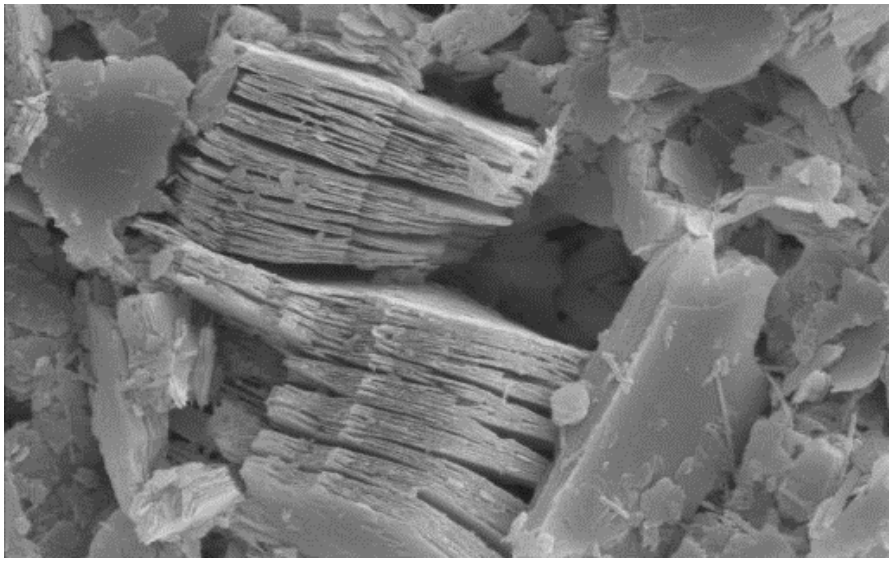
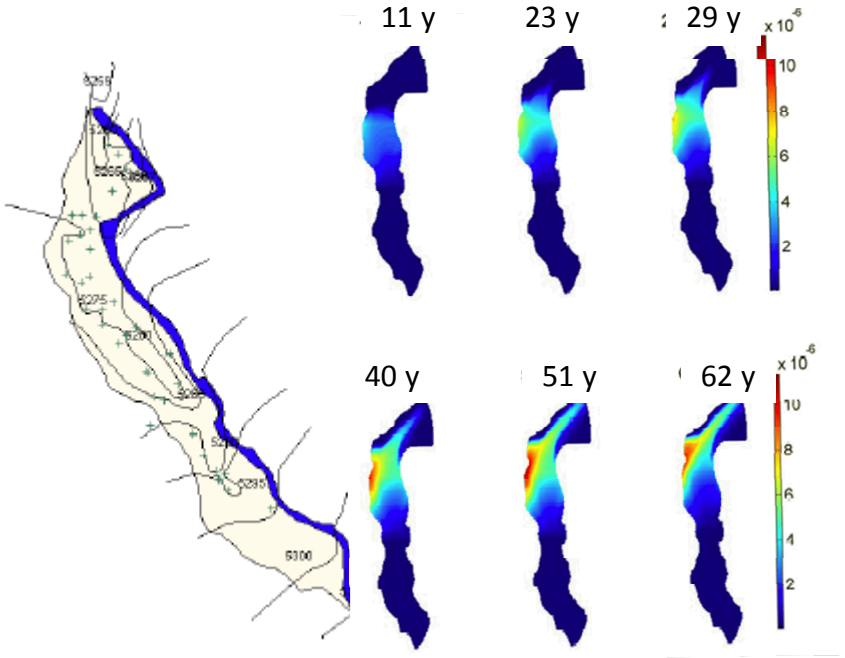
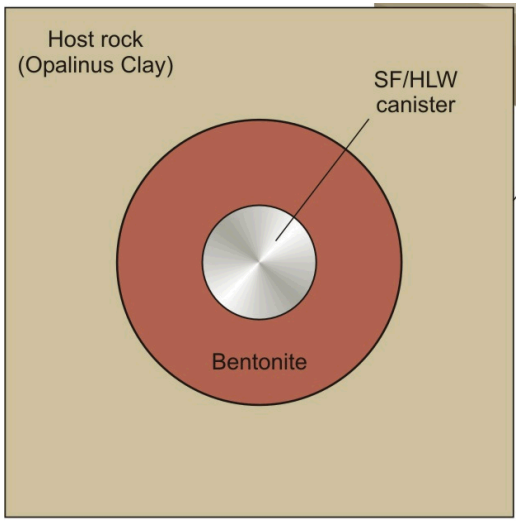


# Background – Repository Science

- **Fate of radionuclides in the environment**
- **Sequestration of radionuclides**
- **Atomistic understanding of the solution-mineral interface**
- **Simulations complement both micro- and macro-experiments**




Uranium migration, Naturita, Colorado, USA
NRC NUREG/CR-6870




Emplacement tunnel SF/HLW

www.nagra.ch



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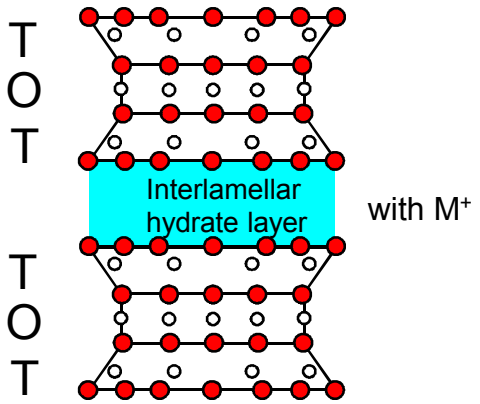
# Molecular Simulation of Clay Minerals

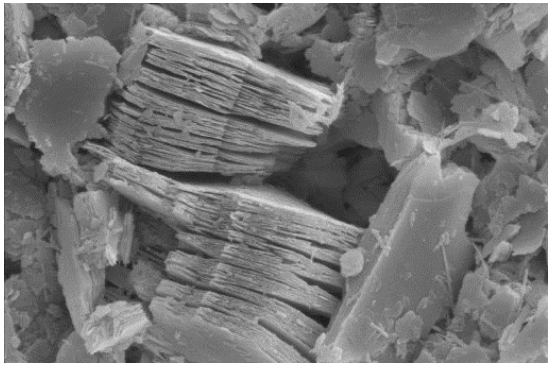
## Crystal structure models of clay minerals are typically unknown

- Nanocrystalline materials (less than 1 μm grain size)
- No large single crystals for X-ray diffraction refinements
- Hydrogens positions are often unknown (require neutron diffraction analysis)
- Complex chemistry with multicomponent systems, cation disorder, and vacancies
- Low symmetry (monoclinic or triclinic)
- Stacking disorder complicates structural analysis

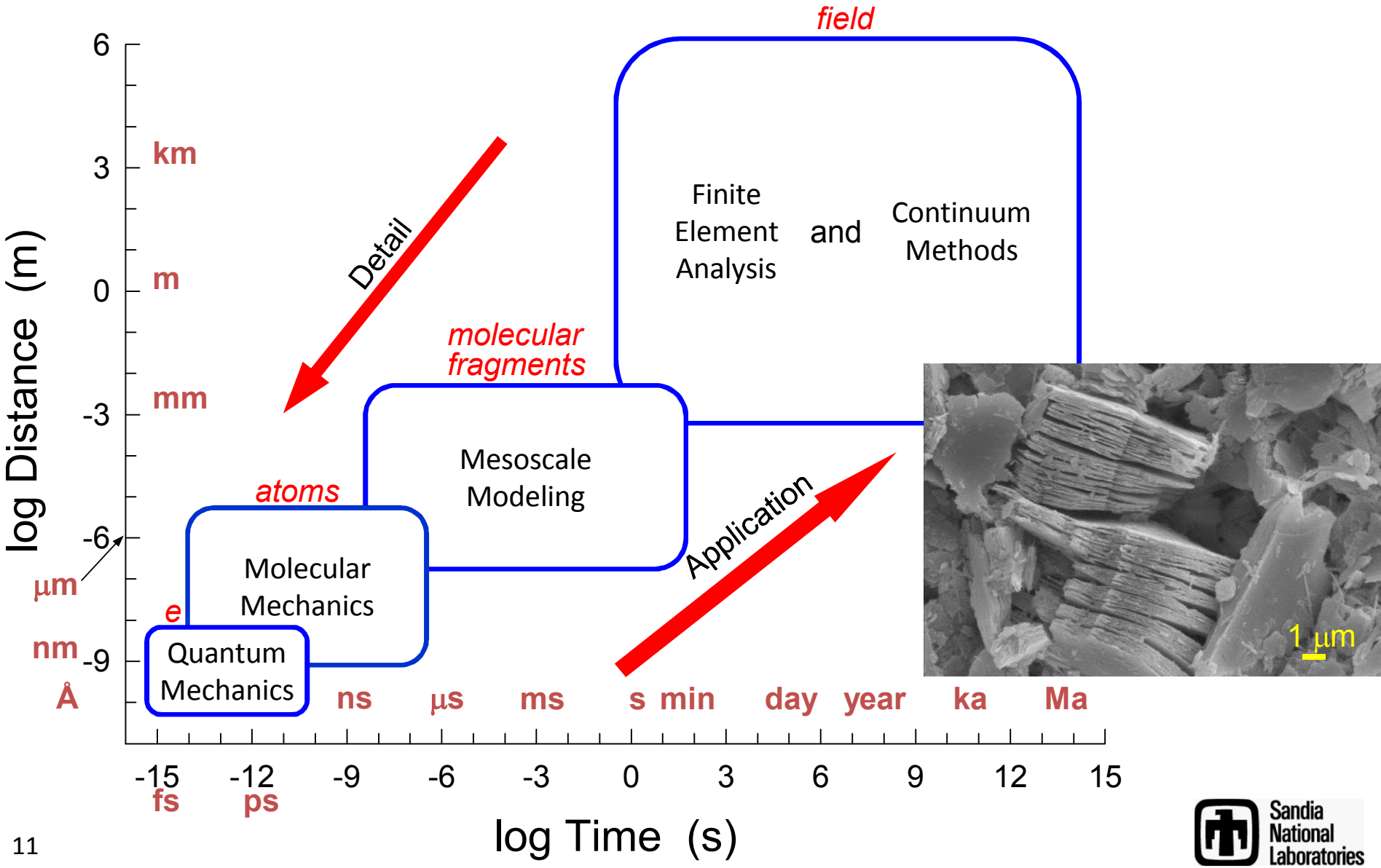



## Atomistic simulations of clay minerals are non-trivial

- Require accurate empirical energy forcefield; quantum methods are typically too costly
- Large unit cells or simulation supercells are required (100s to $10^6$ atoms)
- Significant electrostatic fields associated with layer structure
- Validation of models is difficult



# Simulations Cover a Wide Ranges of Length and Time Scales



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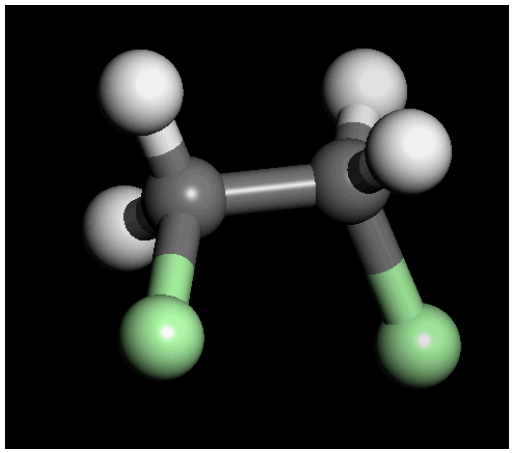
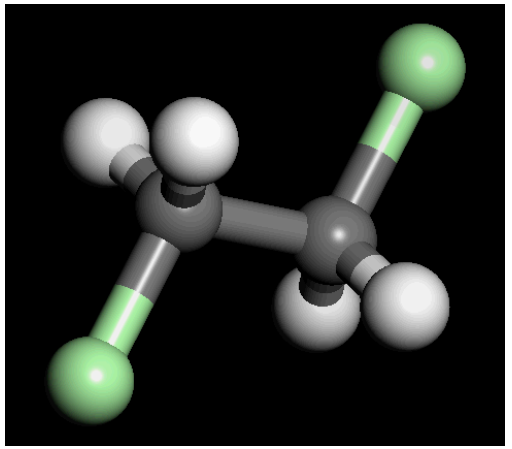
# Energy Minimization

***Molecule***

**Dichloroethane**

$C_2H_4Cl_2$





Potential Energy Surface (rotation about the C-C bond)

1.63 kcal/mol

Local Minimum

Transition State

-1.28 kcal/mol

Global Minimum



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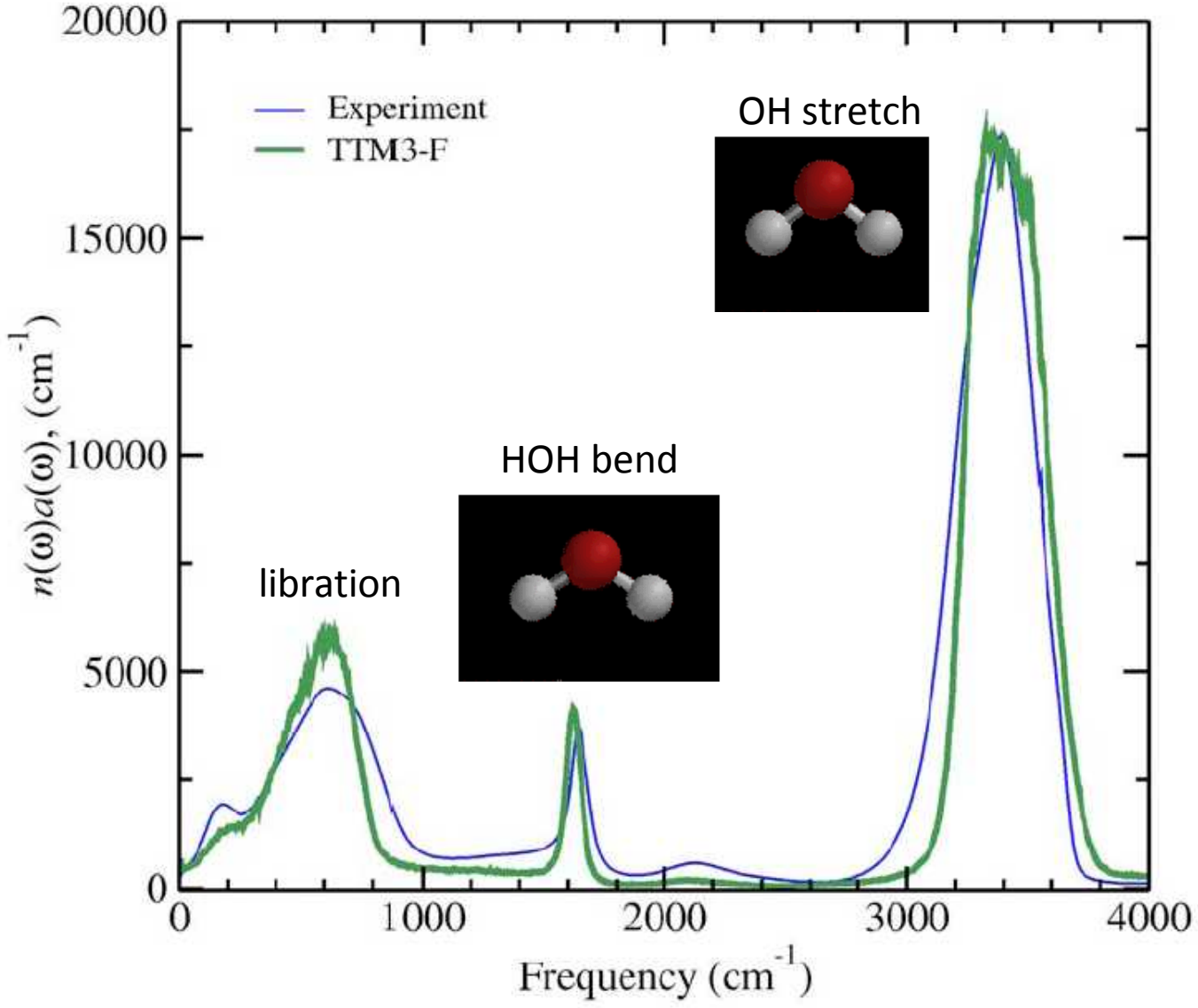
# Intramolecular Properties – Vibrational Spectrum

Vibrational spectrum of liquid water

Fanourgakis and Xantheas, *J. Chem. Phys.* **2008**



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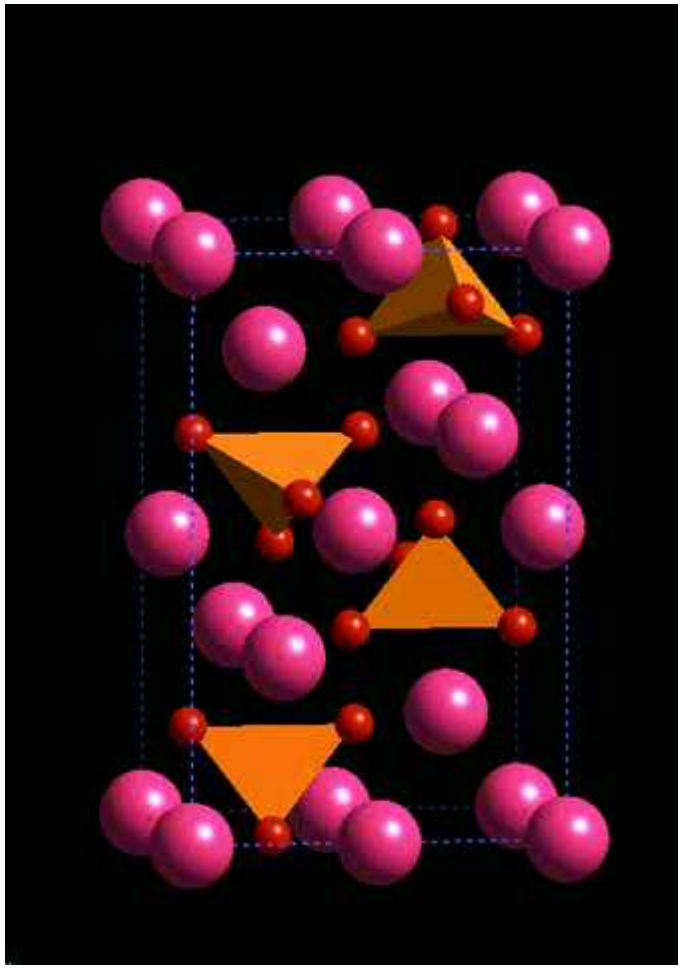
# Energy Minimization

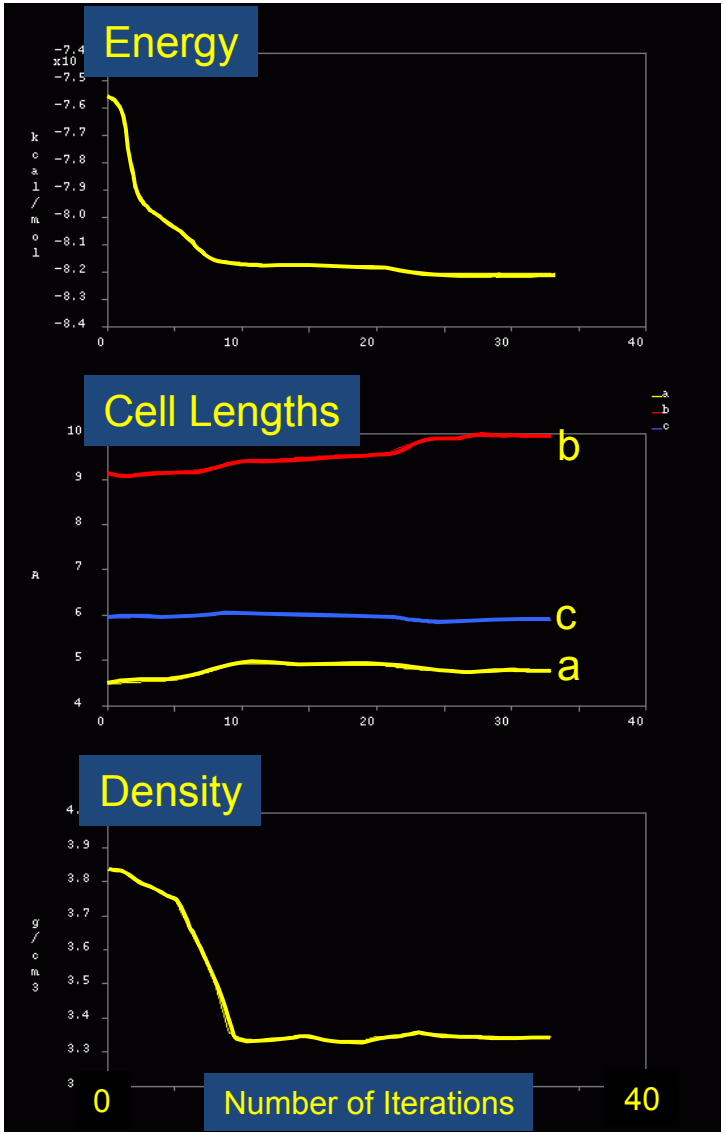
## *Periodic Structure*

**Forsterite**

$Mg_2SiO_4$



(100) view




Structural optimization with periodic boundary conditions



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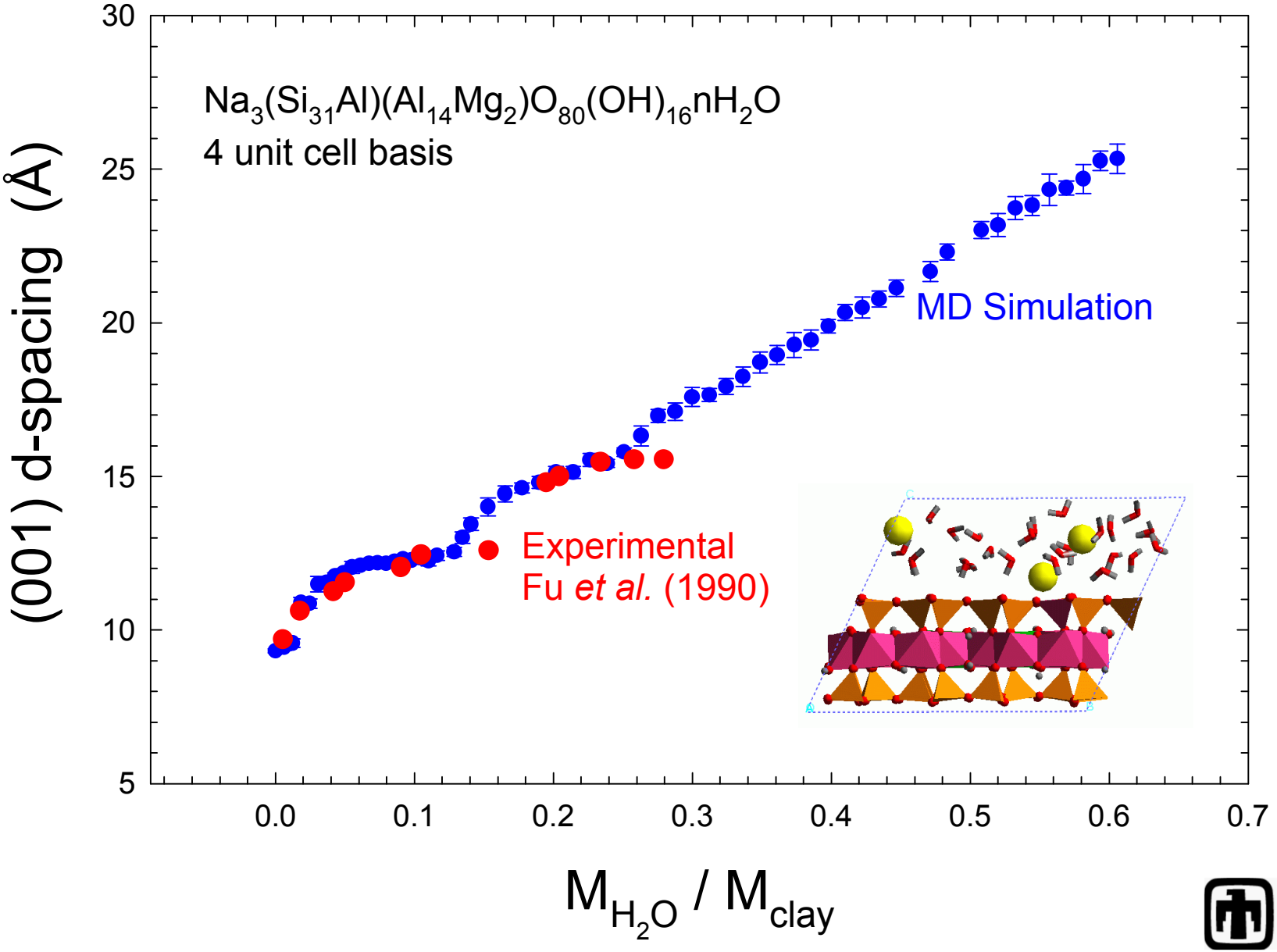
# Swelling Behavior of Montmorillonite



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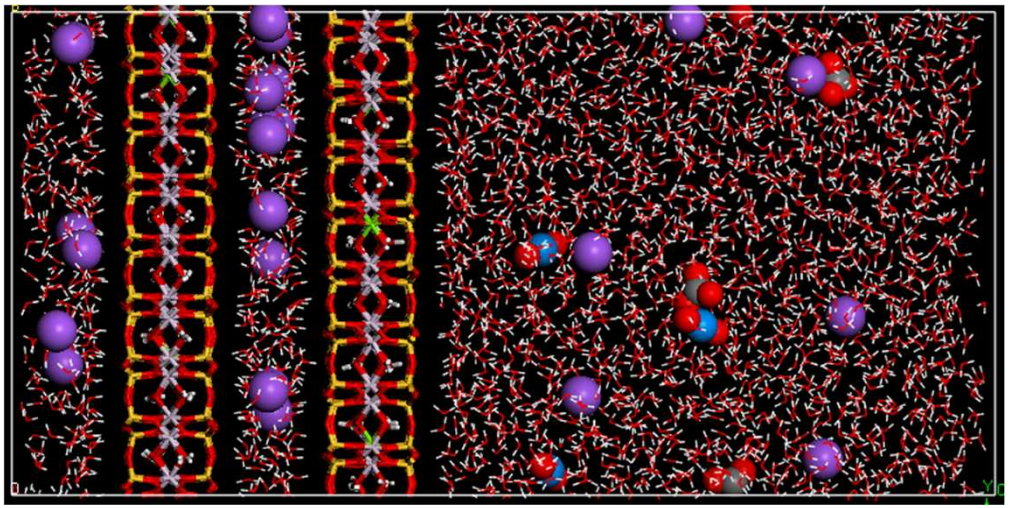
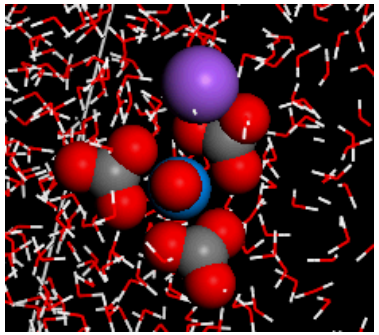
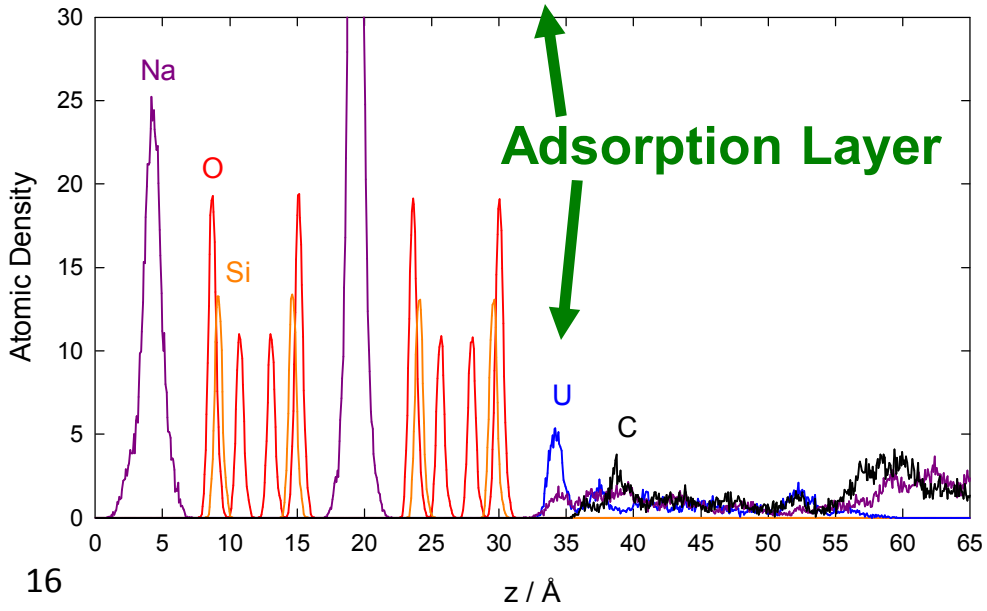
# Large-scale Simulations of Uranyl-Clay Interfaces

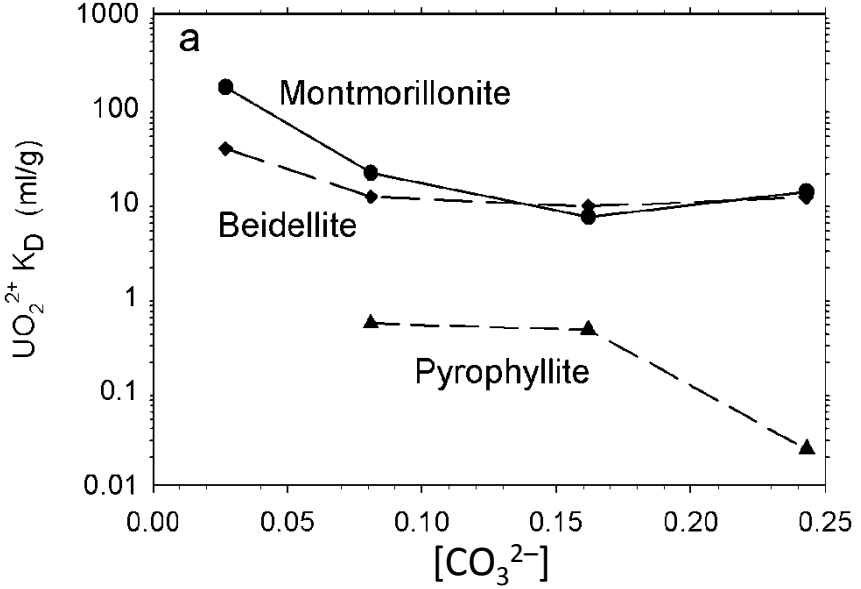


Carbonate concentration influences uranyl adsorption



$[UO_2(CO_3)_3]^{4-}$




Greathouse, J. A.; Cygan, R. T. (**2005**) *Phys. Chem. Chem. Phys.*



Sandia National Laboratories

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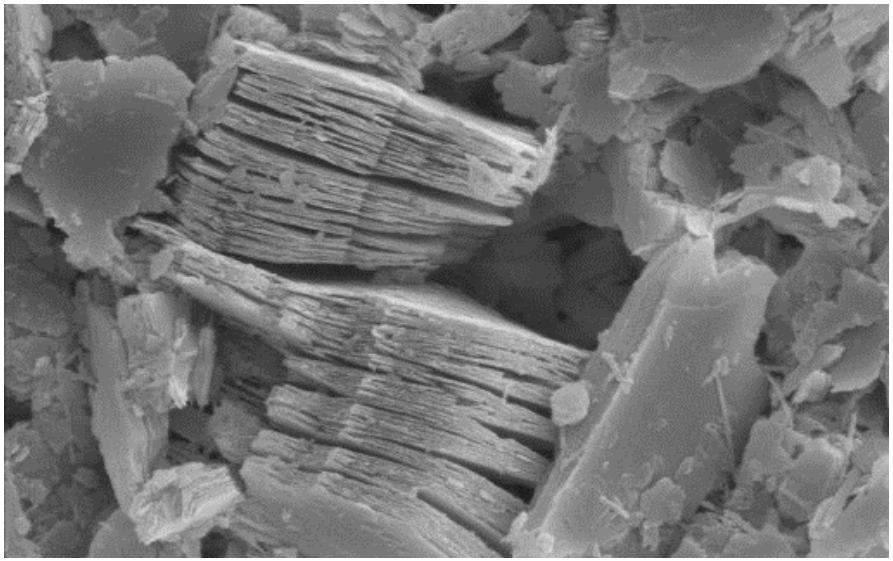
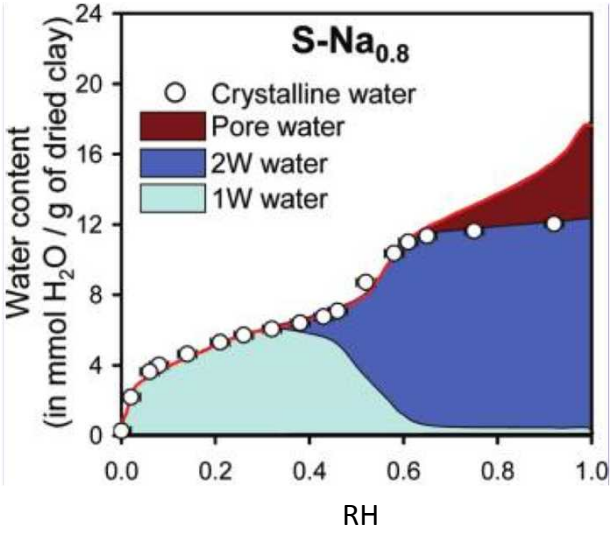
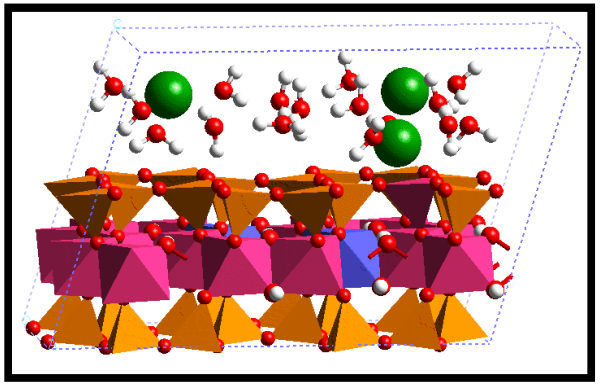


# Using Molecular Simulation to Understand Clay Hydration

- Predict properties of clay barriers considered for use in nuclear waste repositories.
- Aid in interpretation of experimental diffraction studies.
- Explain trends in structural (swelling) and thermodynamic (hydration energies) properties as functions of:
  - Interlayer water content (relative humidity, RH)
  - Interlayer cation (e.g., $Na^+$ vs $Cs^+$)
  - Temperature
- Upscale results to thermodynamic models
  - Hydration energies
  - Ion exchange energies
  - Water loading at a given RH and temperature




Ferrage et al (2010) *J. Phys. Chem. C*





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# Clay-Water-Ion Behavior

$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$

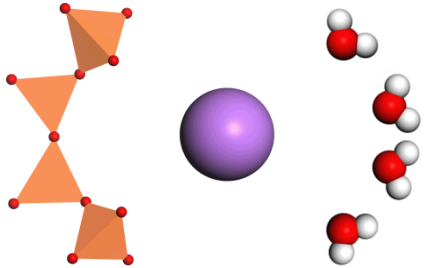
Lowest Hydration Energy

Highest Hydration Energy

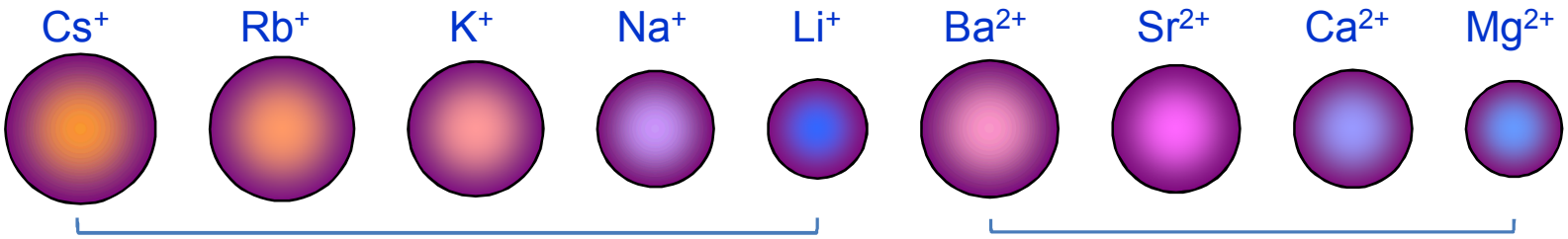
Weakly Hydrated

Strongly Hydrated

Clay-Ion Interactions Dominate



Water-Ion Interactions Dominate




Larger ionic radius
Lower charge density

Smaller ionic radius
Higher charge density



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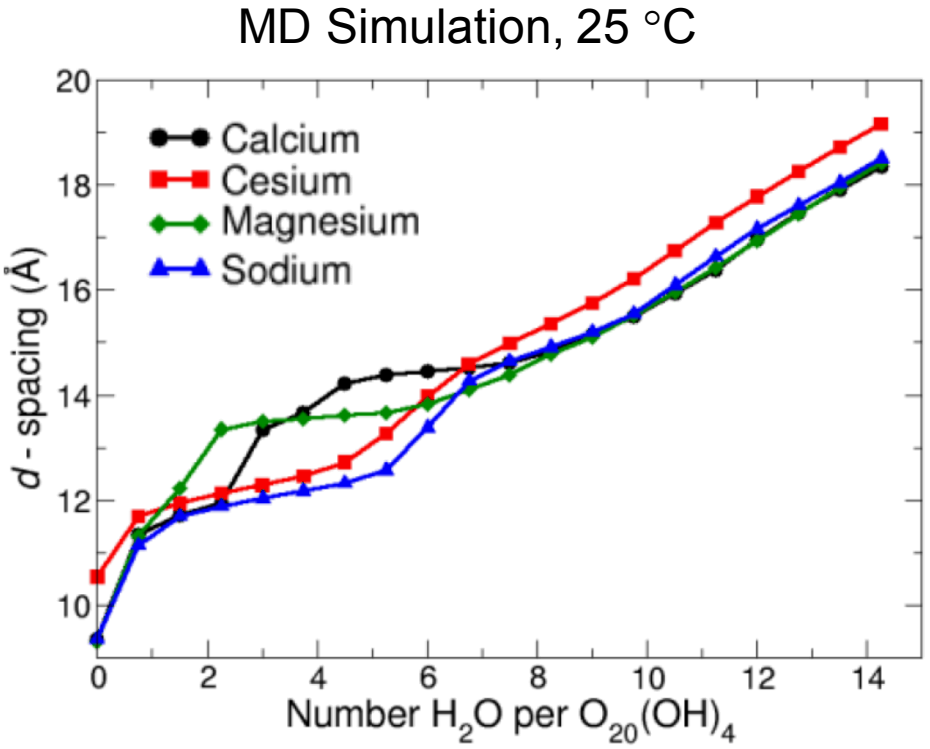
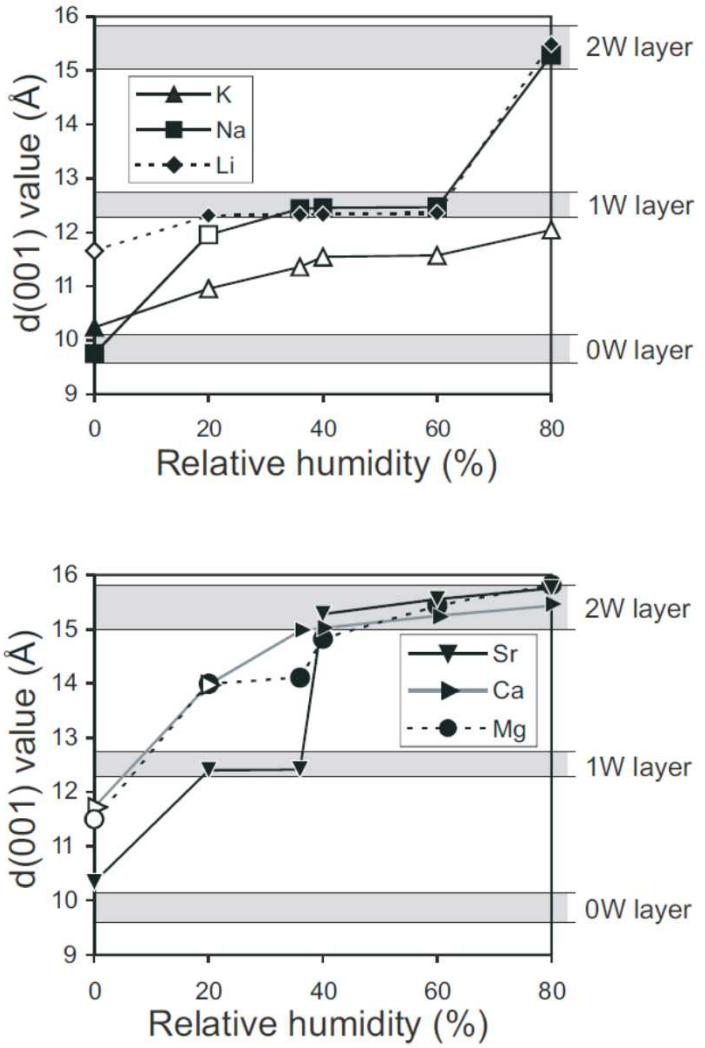
# Comparison of Simulation and Experiment (SWy1)




Ferrage et al (**2005**) *Am. Min.*

- Pronounced 1-layer hydrate (1W) phases for monovalent cations.
- Onset of swelling at low water content to form 2-layer hydrate (2W) phases for divalent ions.
- Simulation results are consistent with experiment

Teich-McGoldrick et al (**2015**) *J. Phys. Chem. C*



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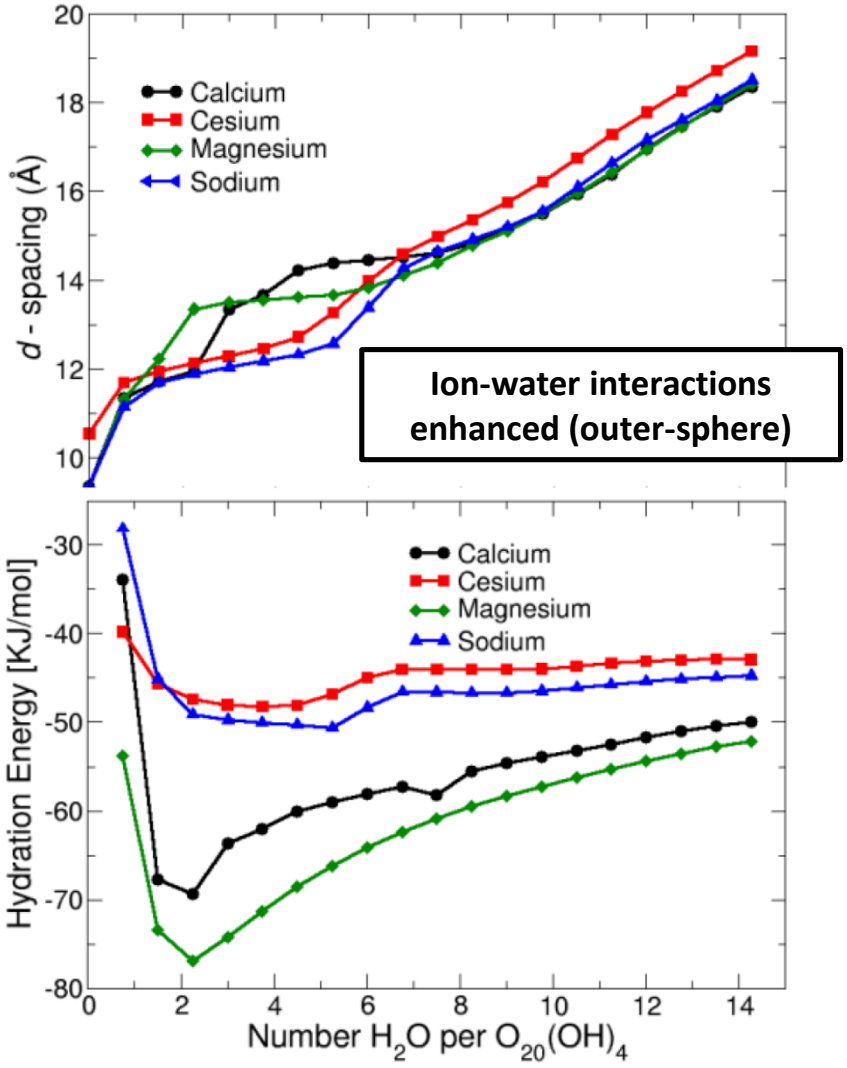
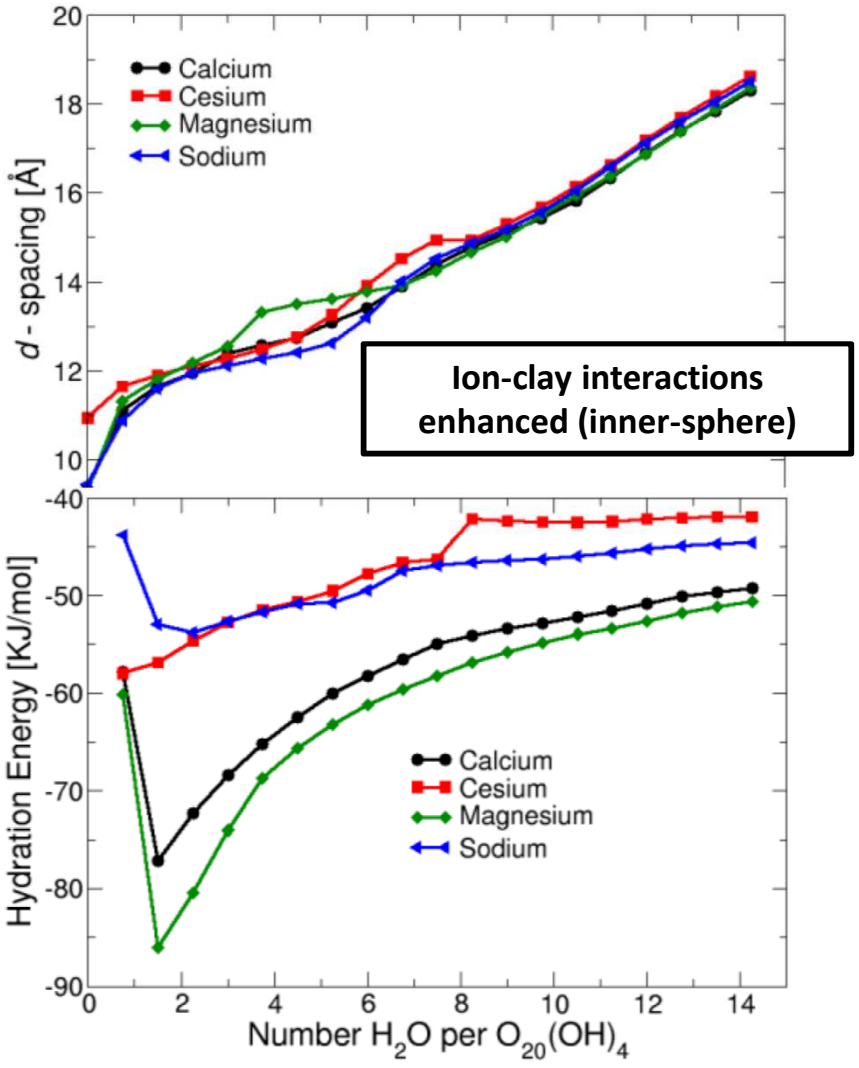
# Effect of Cation Hydration and Layer Charge Location




Montmorillonite, 25 °C




Beidellite, 25 °C



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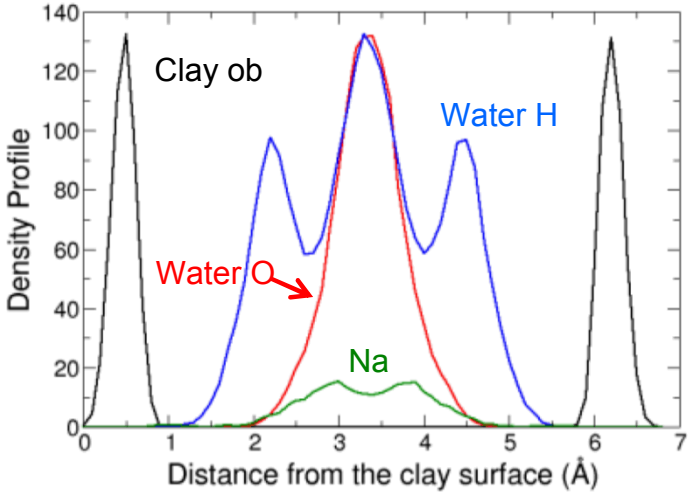
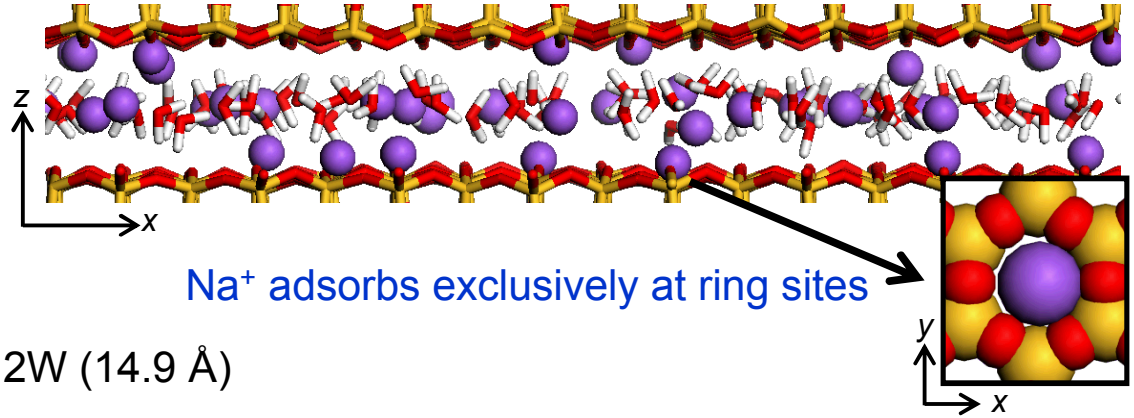
# Interlayer Structure, Na-montmorillonite

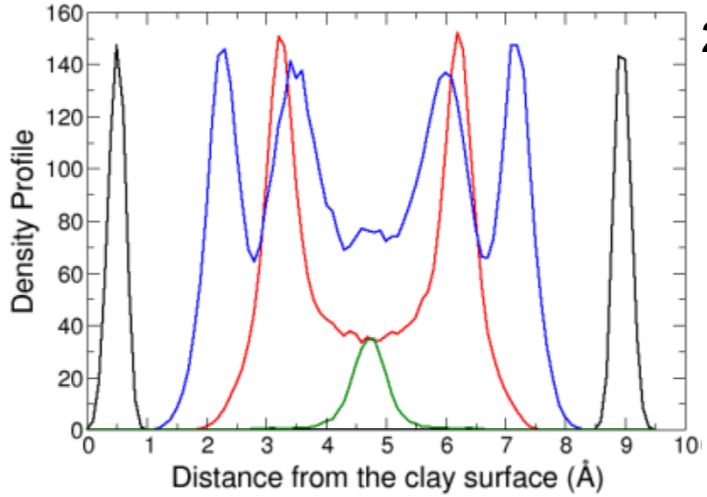



1W (12.2 Å)

Na⁺ aligned with hexagonal rings or at mid-plane

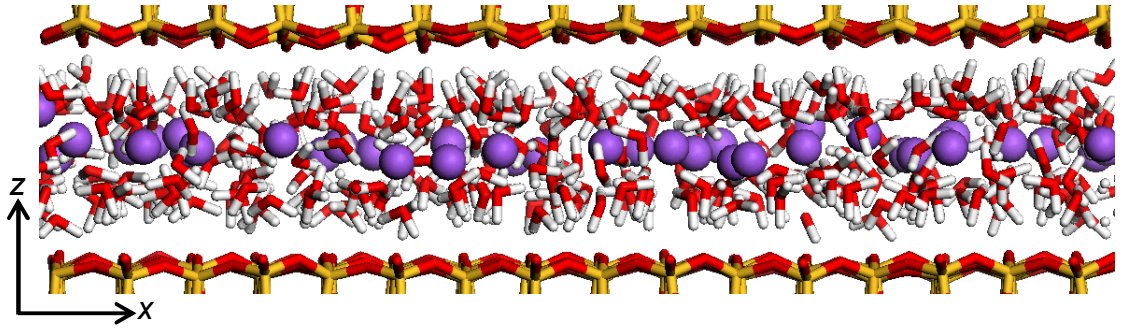



Na⁺ adsorbs exclusively at ring sites




2W (14.9 Å)

Outer sphere coordination (similar for $Mg^{2+}$, $Ca^{2+}$)



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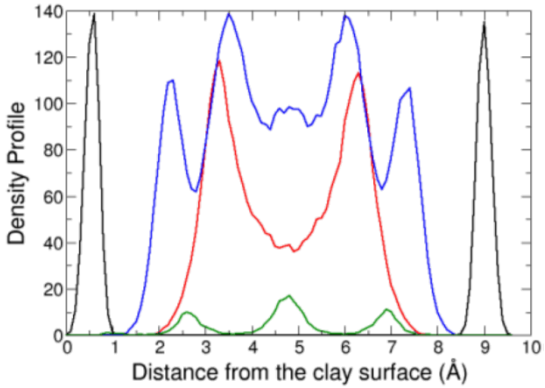
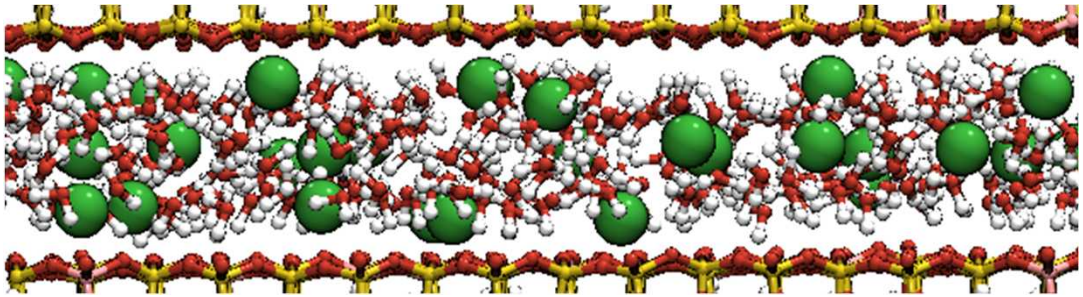
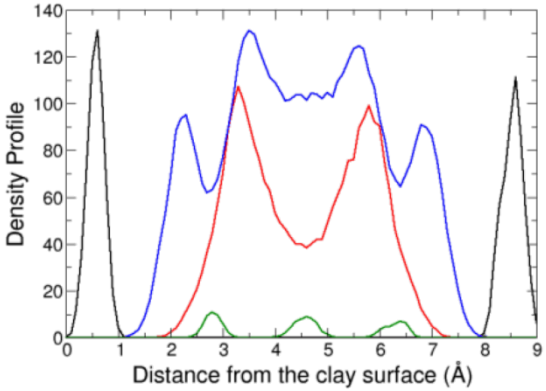
# Interlayer Structure, Beidellite (2W, 15 Å)

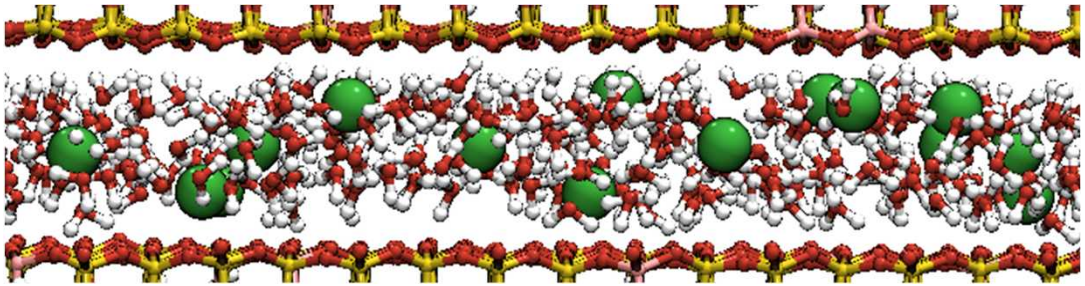


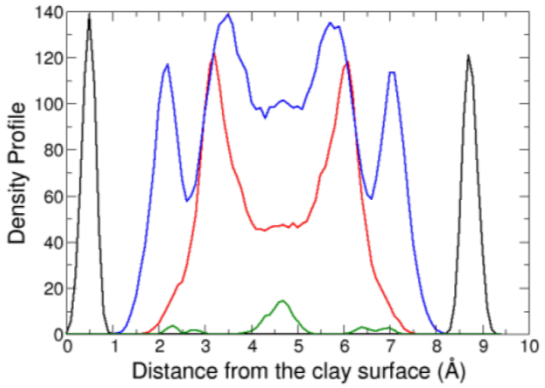

$Na^+$



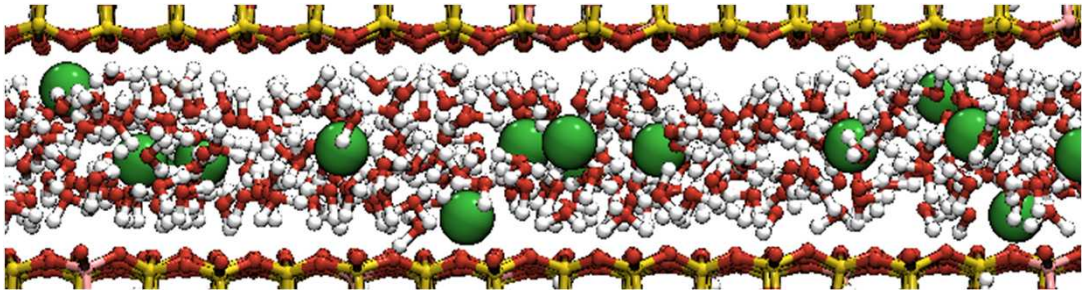



$Ca^{2+}$






$Mg^{2+}$



Inner-sphere complexes due to tetrahedral charge sites.



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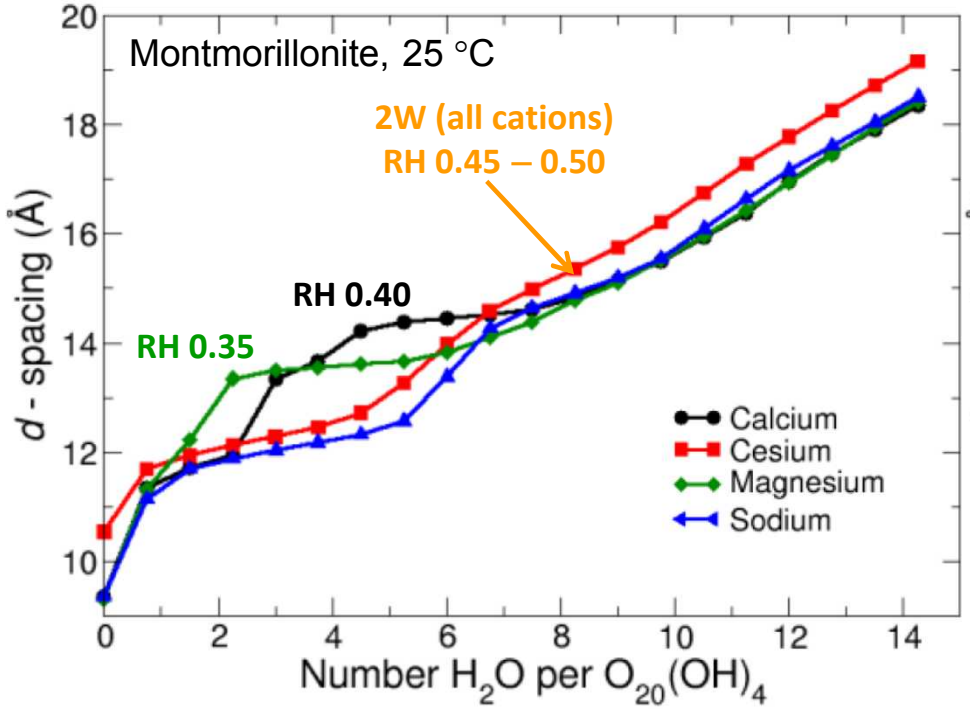
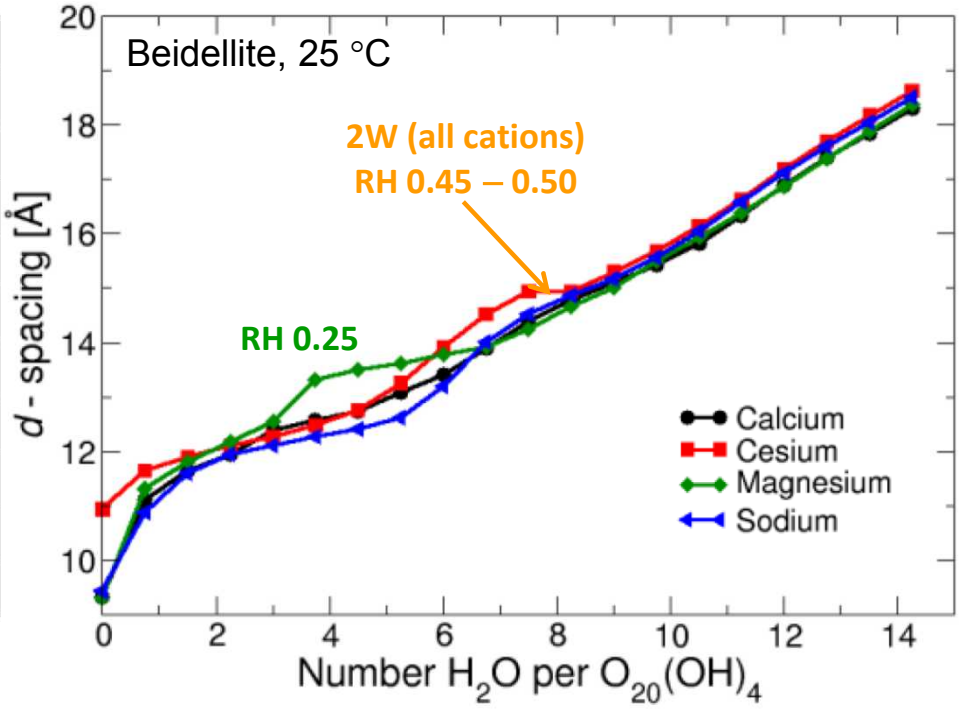
# Correlating RH Values With Water Content

RH values at onset of stable swelling states can be obtained by comparing adsorption isotherms (RH–$H_2O$/u.c.) with swelling curves ($d$–$H_2O$/u.c.).




RH values from experiment

- **0.5 – 0.6** (2W, Na-saponite and Na-montmorillonite)
- **0.2 – 0.4** (1W-2W intermediate states, Mg- and Ca-montmorillonite)

Ferrage et al: (**2005**) *Am. Min.*, (**2010**) *J. Phys. Chem. C*



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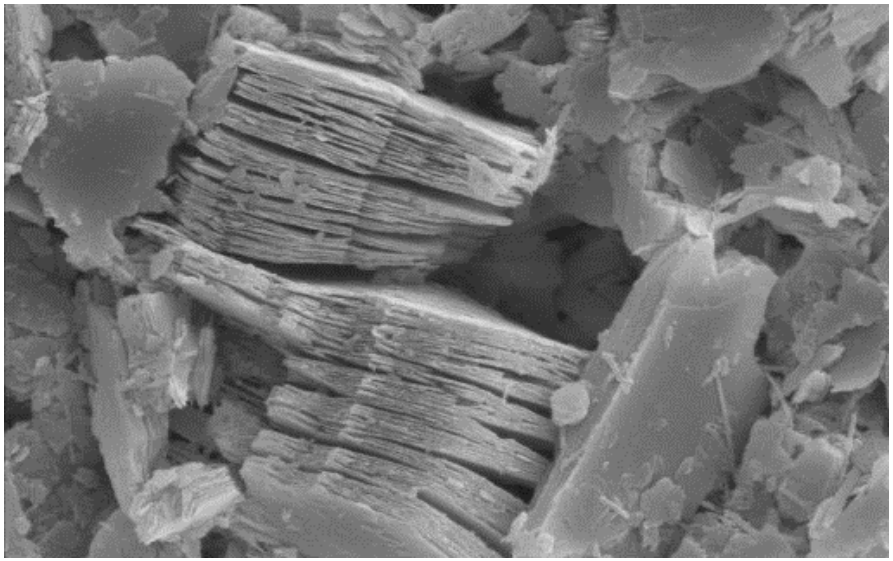
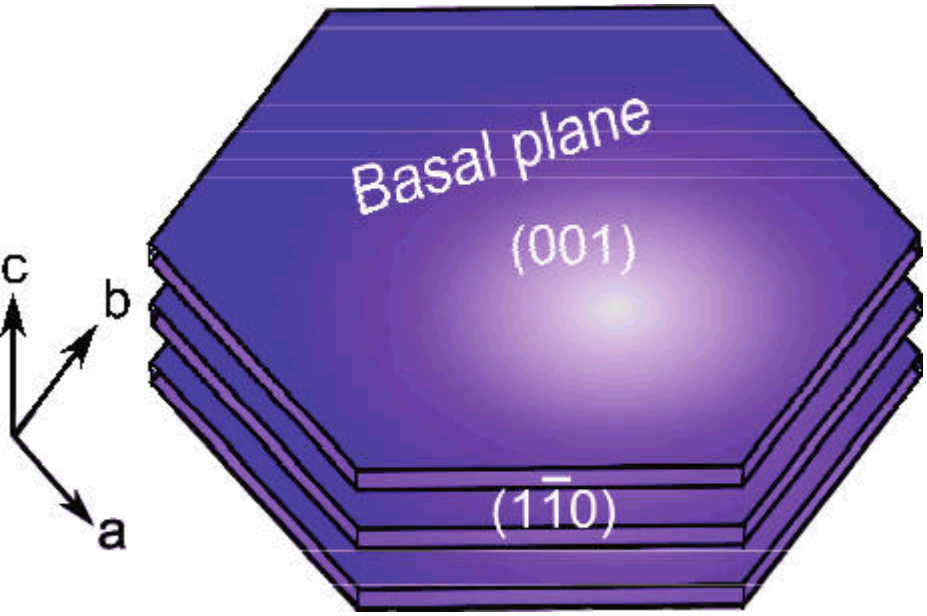
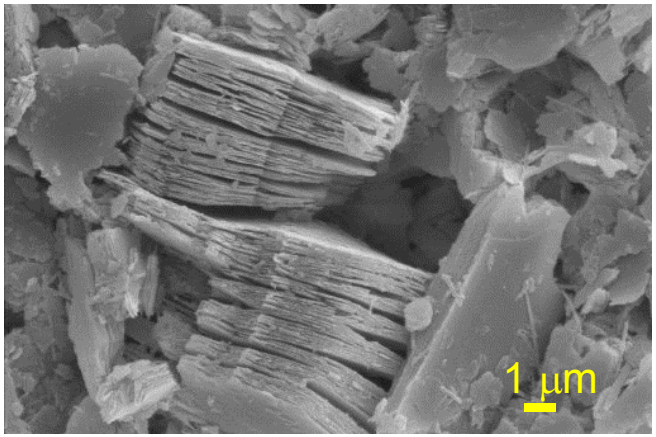
# Outline

- Overview of Sandia National Laboratories
- Molecular simulations and applications to repository science
- Interlayer structure and dynamics of swelling clays
- Clay edge sites

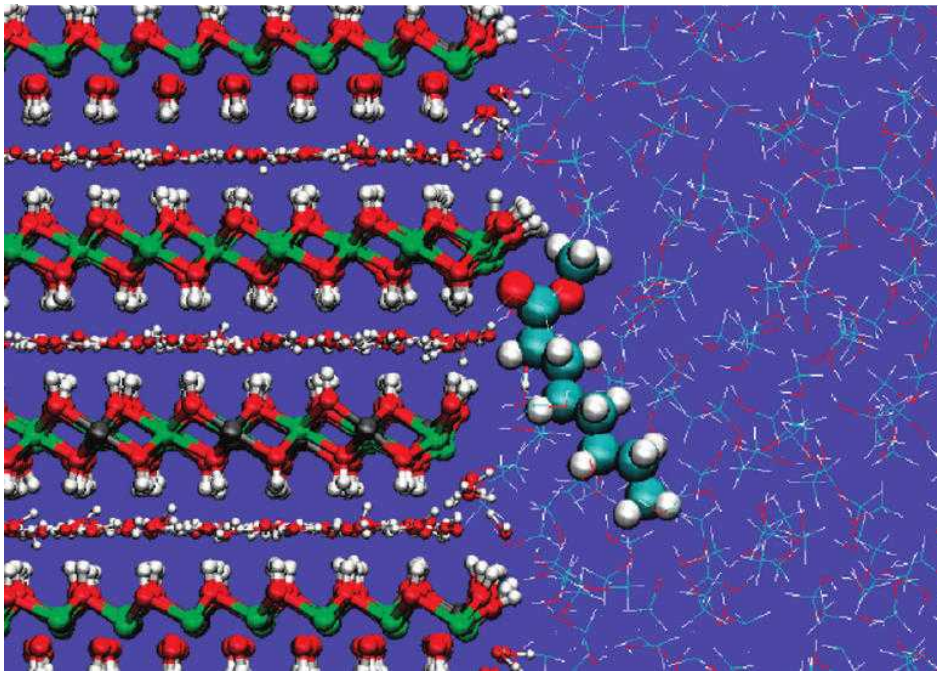


# Sorption at Clay Edge Sites




hydrotalcite (1$\bar{1}$0)



Yu and Schmidt (**2011**) *J. Phys. Chem. C*

Adsorption on edges can be fundamentally different from that on basal surfaces



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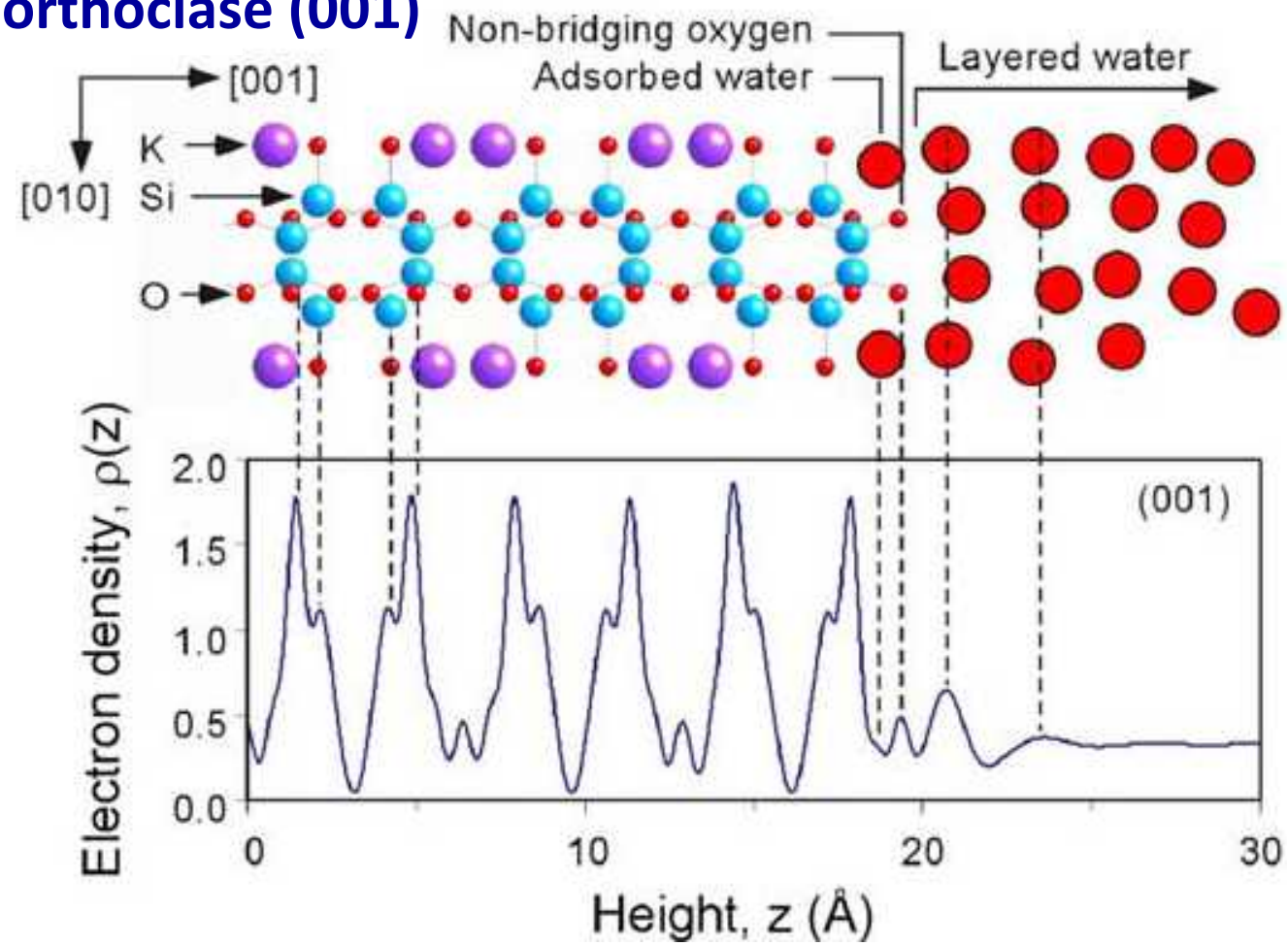
# Mineral-Water Interfacial Structure: Experiment

**orthoclase (001)**




**X-ray reflectivity experiment**

Fenter, P. et al (**2003**) *Geochim. Cosmochim. Acta*



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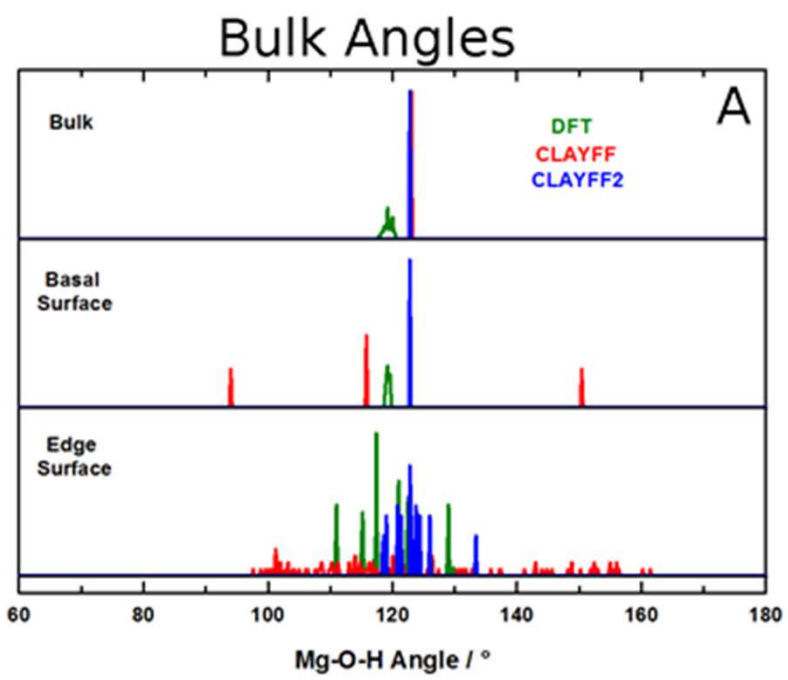
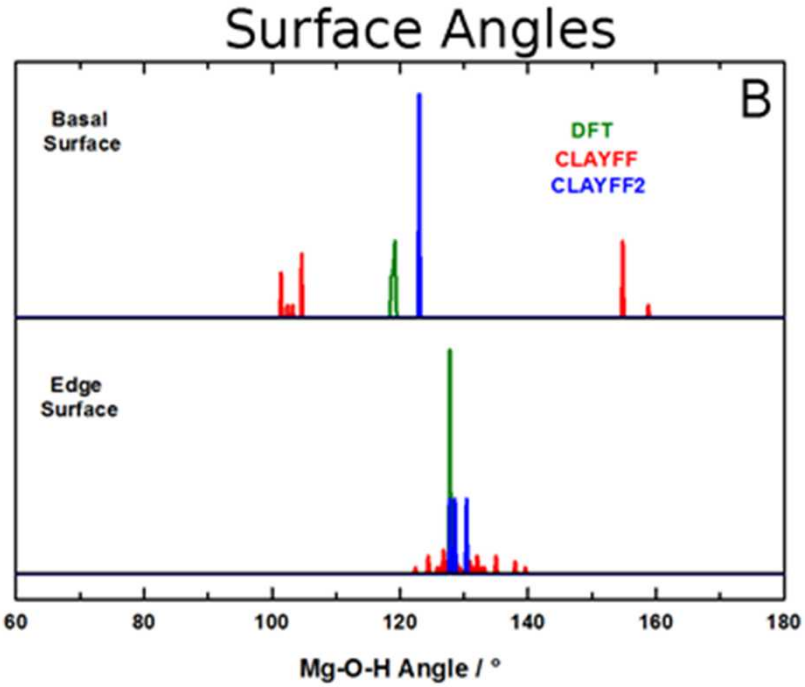
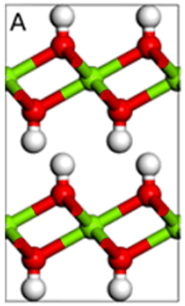
# Structural Comparisons: Mg-O-H Angle

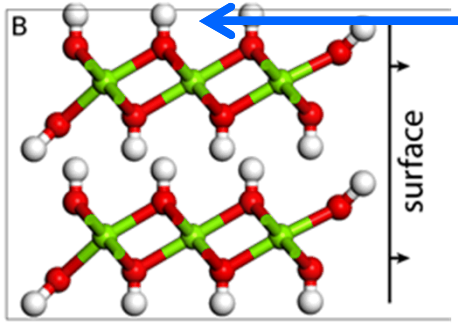
- Comparison of classical static calculations (GULP) with DFT (VASP) for models of bulk brucite, basal surface, and edge surface.
- Equilibrium angle parameter ($\theta_0$ = 120°) matches with DFT optimization for bulk brucite.




Bulk brucite




Basal surface

$(1\bar{1}0)$ edge



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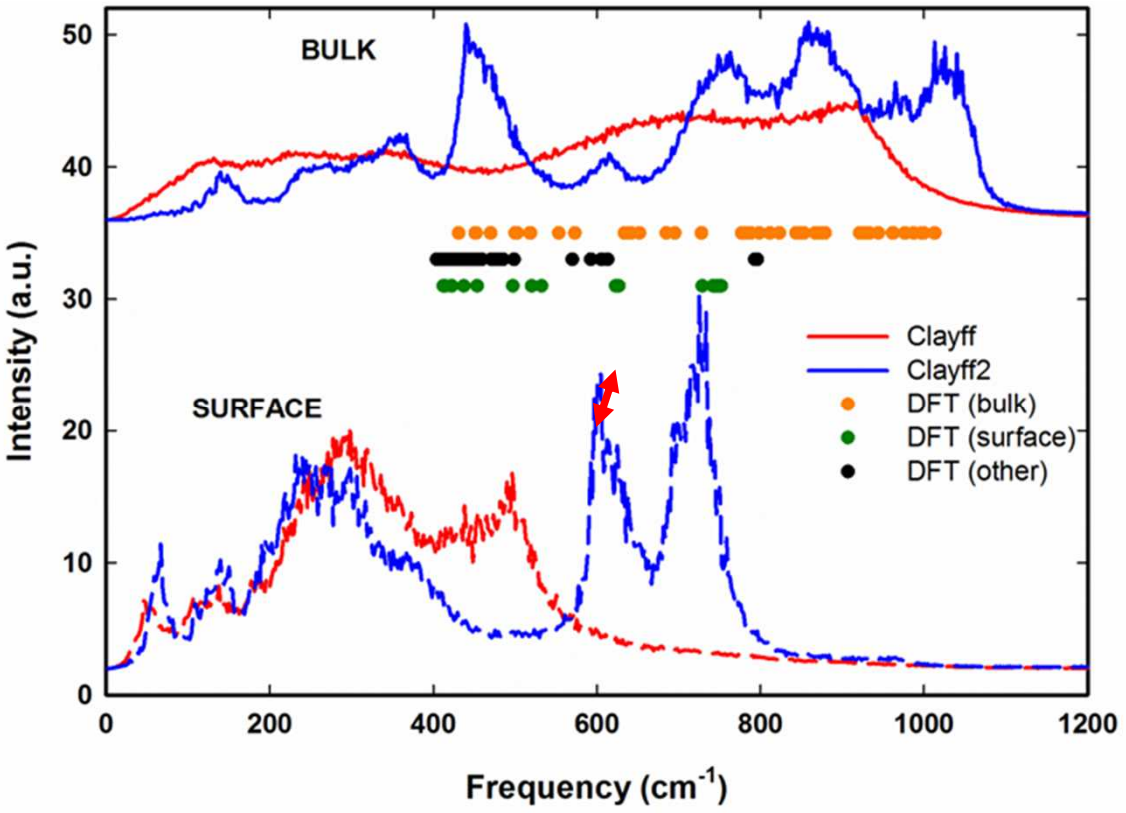
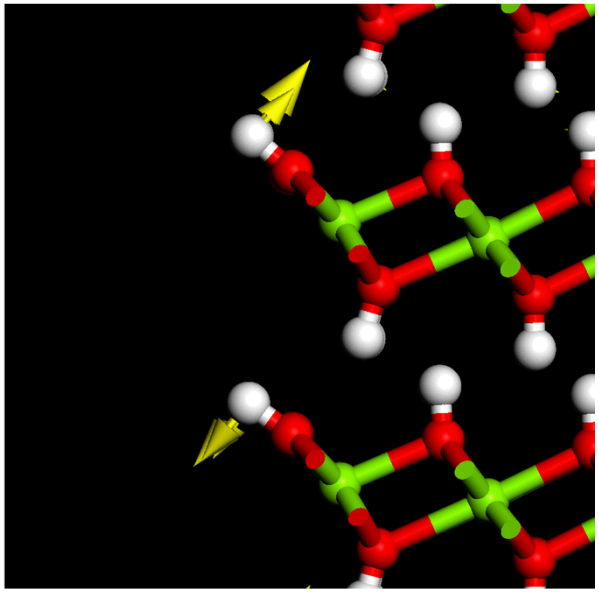
# Vibrational Comparisons: Edge Surface

- Validation: vibrational power spectra from MD simulation using ClayFF (vacuum interface) compared with DFT normal modes.
- Good agreement between MD and DFT frequencies for Mg-O-H bend modes.




$(1\bar{1}0)$ edge



Zeitler et al (**2015**) *J. Phys. Chem. C*



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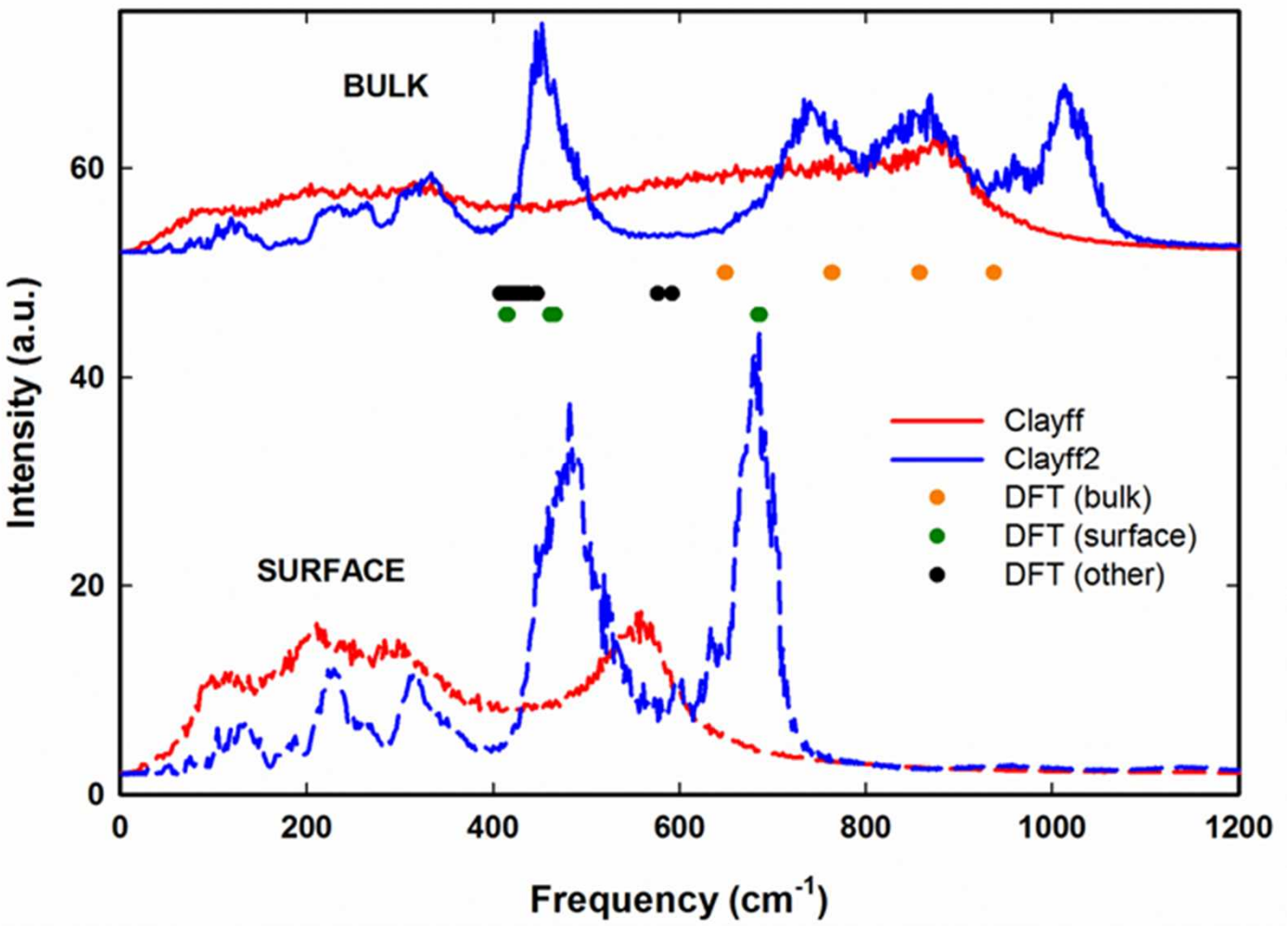
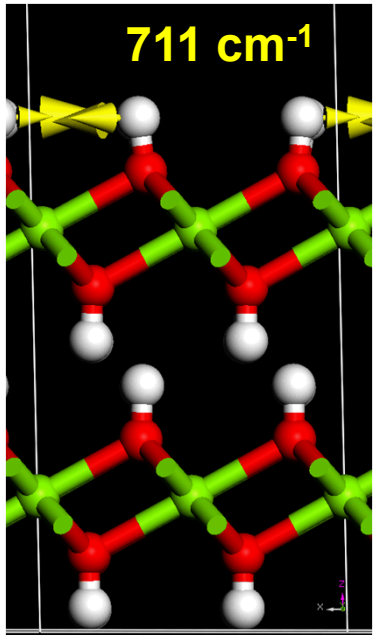
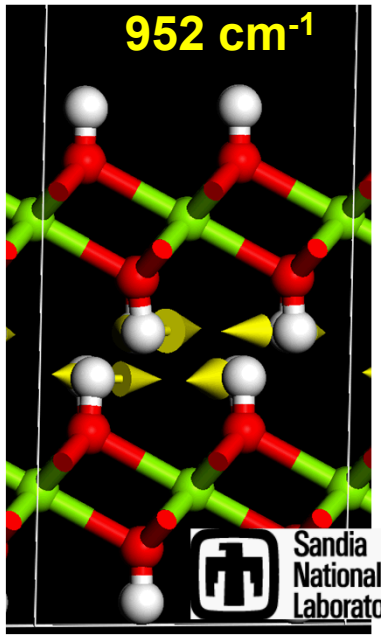
# Vibrational Comparisons: Basal Surface

Brucite (001)




Surface modes are blue-shifted in the bulk.



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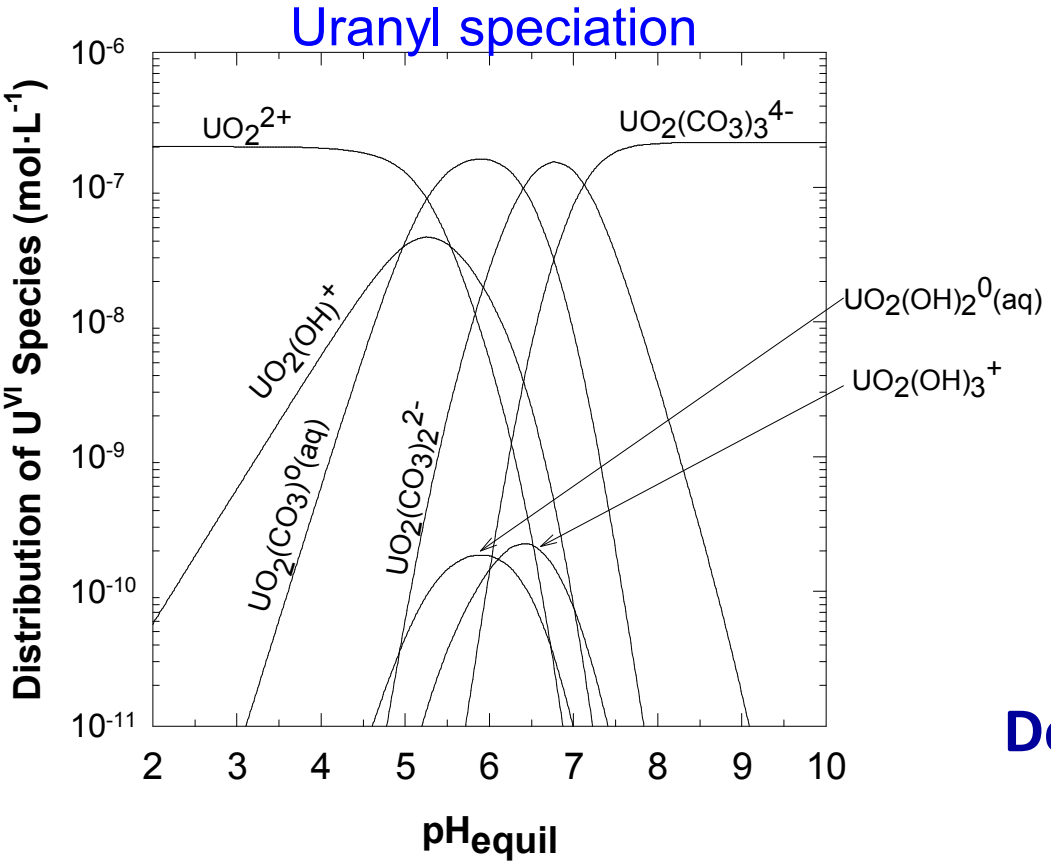
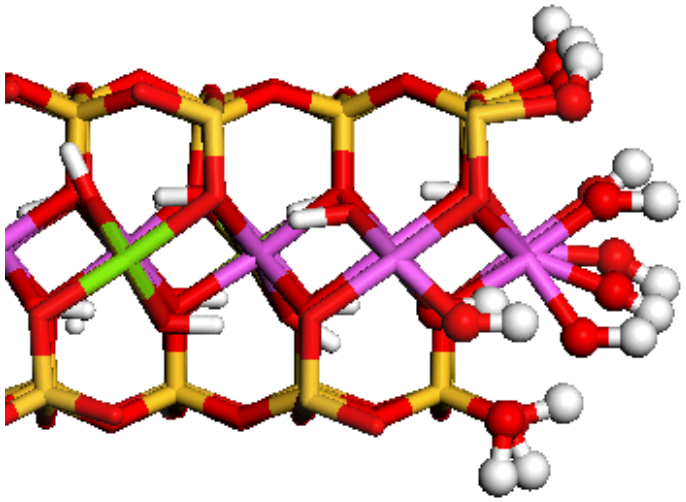
# Application of Edge Site Models



Montmorillonite (100)

**Deprotonation of edge surface**

**pH-dependent adsorption**

Pabalan and Turner, *Aquatic Geochem.* **1997**



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# Acknowledgements


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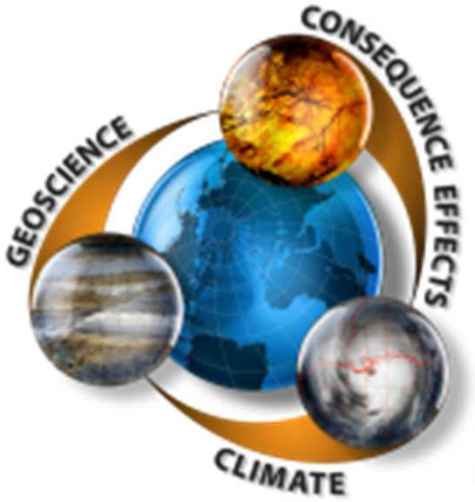


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# Summer Internships at Sandia

***Department of Homeland Security Internships***

- Look for projects at Sandia (New Mexico or California)
- (e.g. Molecular Modeling of Chemical Threat Agent Interactions with Concrete)
- Application deadline Dec 22
- http://www.orau.gov/dhseducation/internships/index.html

***Sandia Internships Website***

http://www.sandia.gov/careers/students_postdocs/internships/index.html

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