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Molecular Modeling of Clays and Clay-Water Interfaces

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Acknowledgements

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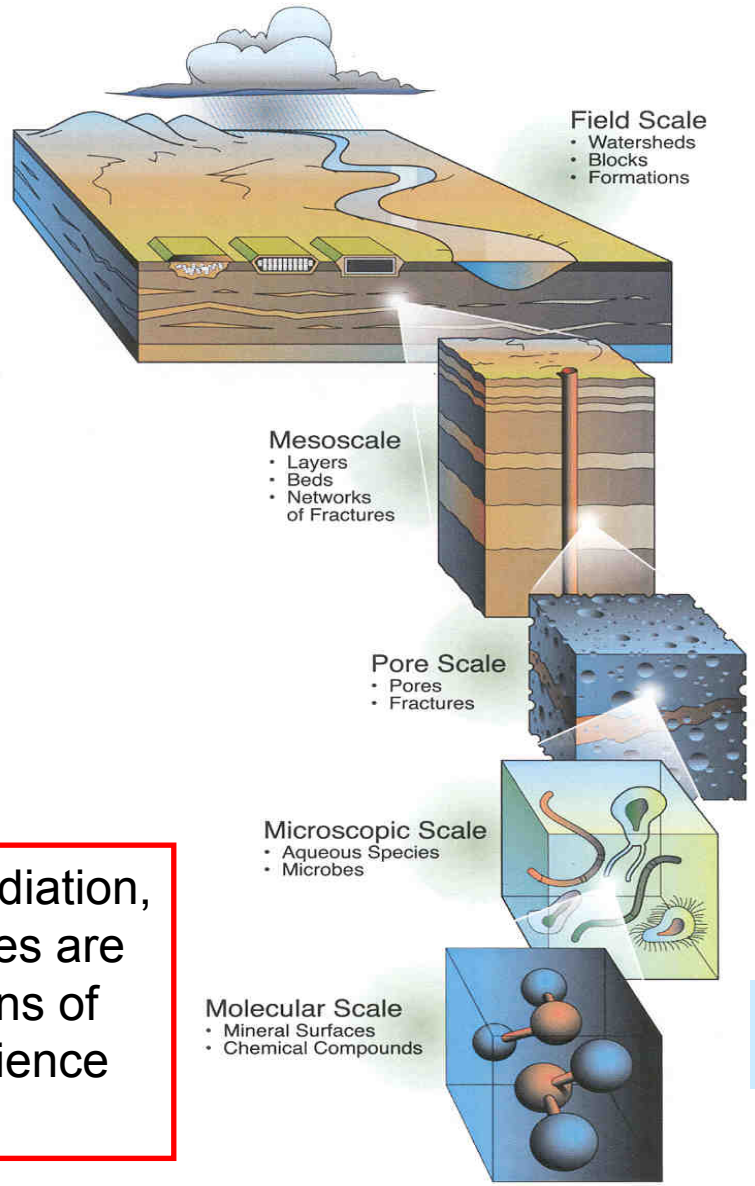
Investigating Multi-Scale Contamination

- DOE legacy of the Cold War
- 5000 surplus facilities
- 144 sites located in 31 states
- 380,000 m^3 of high-level radioactive waste
- 1.8 billion m^3 contaminated soil, groundwater, and sediment
- Contaminants include complex mixtures of radionuclides, metals, and organics



>10^3 m

Mesoscale $10^{1.5}$-10^3 m

Pore scale 10^{-3}-$10^{1.5}$ m

Microscopic 10^{-7}-10^{-3} m

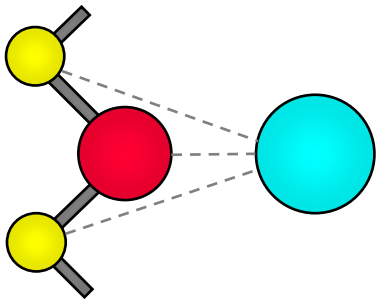
Molecular/nano 10^{-10}-10^{-8} m

Waste treatment, environmental remediation, and long-term stewardship of DOE sites are estimated to require hundreds of billions of dollars and major breakthroughs in science and technology

DOE Basic Energy Sciences

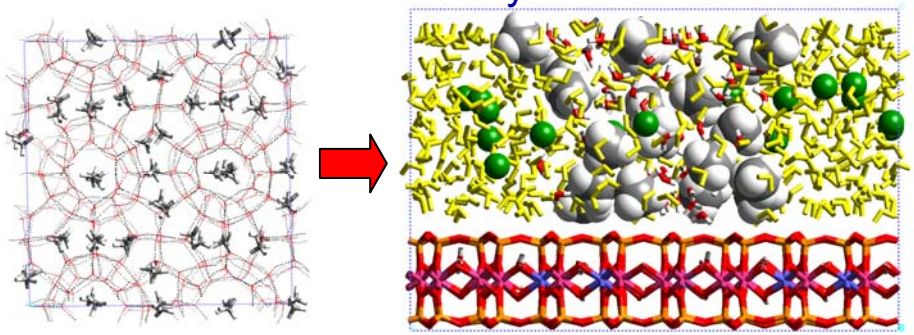
Models of Environmental Materials: Adsorption, Intercalation, and Interfacial Behavior of Layered Minerals

ClayFF flexible force field



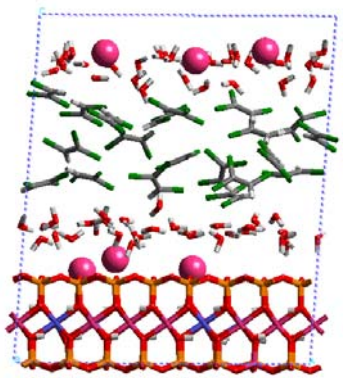
Cygan et al., *J. Phys. Chem. B* 2004

Intercalation of methane hydrates in smectite



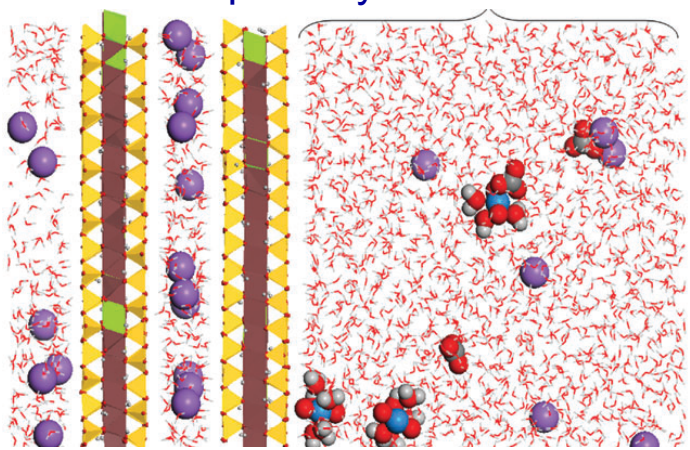
Cygan et al., *J. Phys. Chem. B* 2004

Intercalation of TCE in clay



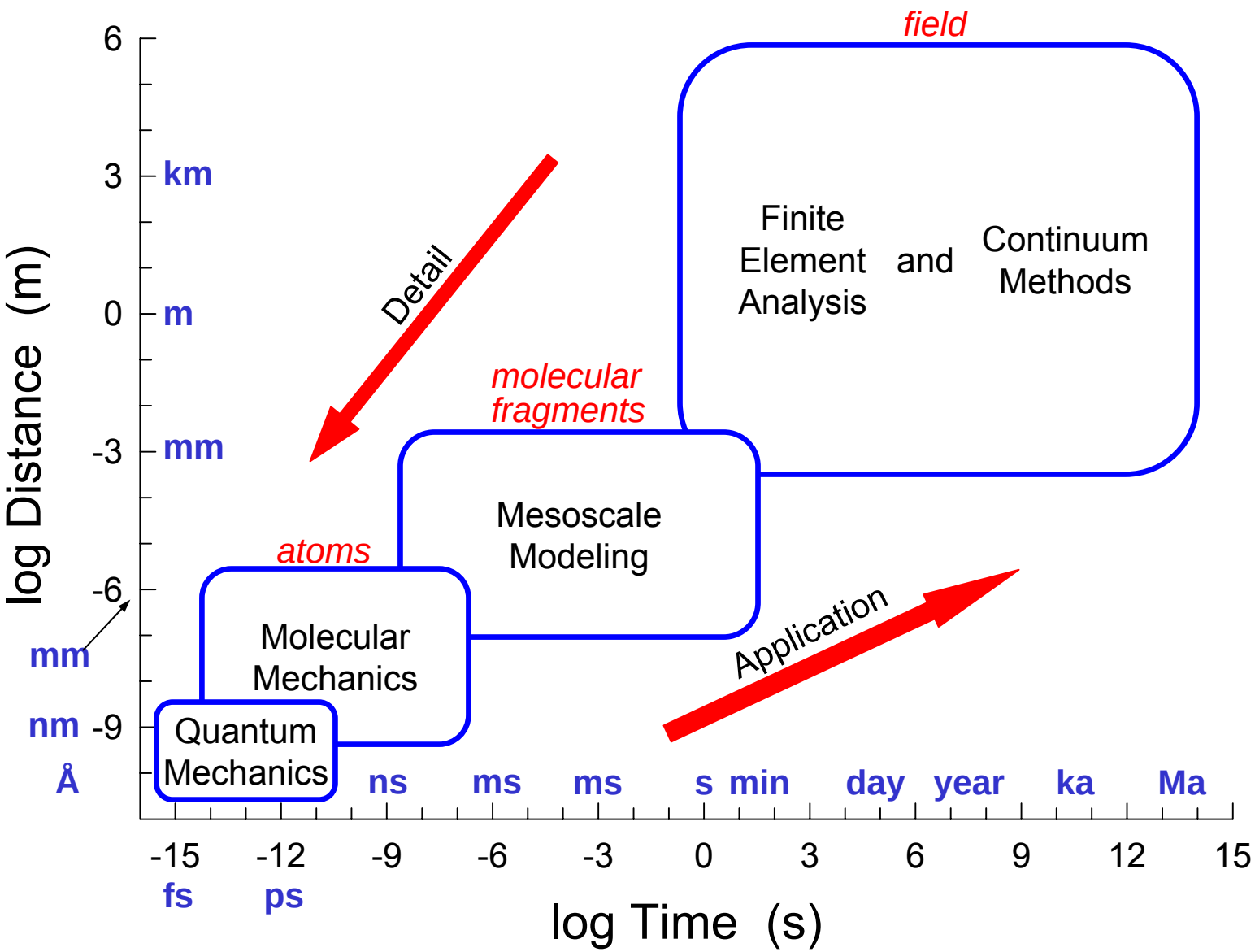
Criscenti and Cygan 2003

Uranium adsorption by Na-montmorillonite



Greathouse and Cygan, *Phys. Chem. Chem. Phys.* 2005

Computer Simulation x-t Array



Simulation vs Experiment

Property	Simulation	Experiment
Unit cell data	Lattice constants (constant P simulation)	Diffraction
Local atomic coordination	Radial distribution functions	EXAFS
Interfacial structure	Atomic density profiles	X-ray scattering
Solute adsorption	Atomic density profiles	Batch adsorption isotherms
Vibrational motion	Power spectra	IR/Raman
Mechanical properties	Stress-strain, moduli	Elastic constants

Molecular Modeling Methods

Experiment
Ab initio

Forcefield + Structure

Structure

Molecular Mechanics

$F = ma$

Energy Minimization

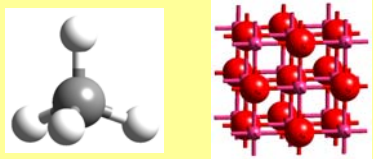
Conformational Analysis

Lattice Dynamics

Molecular Dynamics

Monte Carlo

Molecular Model



Cluster Periodic

Quantum Mechanics

$H\psi = E\psi$

Hartree-Fock and DFT

EM, CA, AIMD

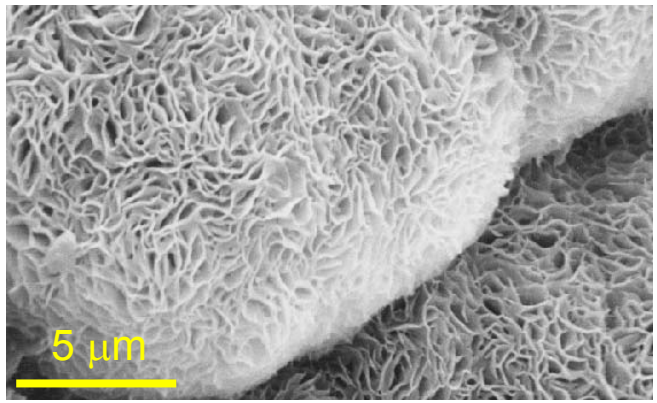
Structure
Physical properties
Thermodynamics
Kinetics
Spectroscopy
:
:

Validation

Atomistic Simulation of Clays and Clay Processes

Crystal structure models of clay minerals are typically unknown

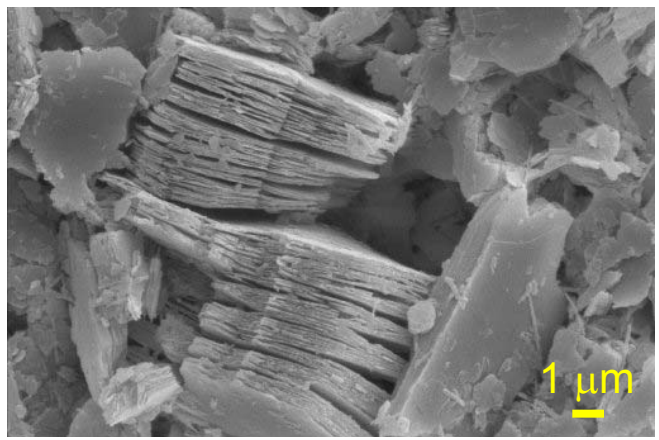
- Nanocrystalline (cryptocrystalline) materials (less than 1 μm grain size)
- No large single crystals for X-ray diffraction refinements
- Hydrogens positions are often unknown (require neutron diffraction analysis) and control sorption process
- Complex chemistry with multicomponent systems, cation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



montmorillonite

Atomistic simulations of clay minerals are non-trivial

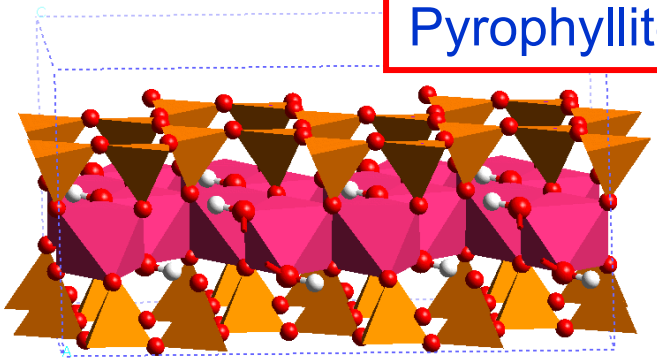
- Require accurate empirical energy force field or **quantum methods**
- Large unit cells or simulation supercells are required (>100 atoms)
- Significant electrostatic fields associated with layer structure
- Validation of models is difficult



kaolinite

Structure and Composition of Complex Clays

Pyrophyllite

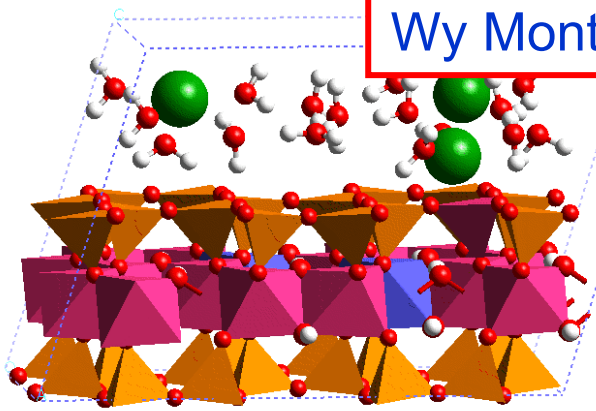


$Si_{32}Al_{16}O_{80}(OH)_{16}$
No substitutions
No interlayer cations or water
Non-swelling

Dioctahedral Smectites

$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$
Some tetrahedral Al sub
Mostly octahedral Mg sub
Swelling

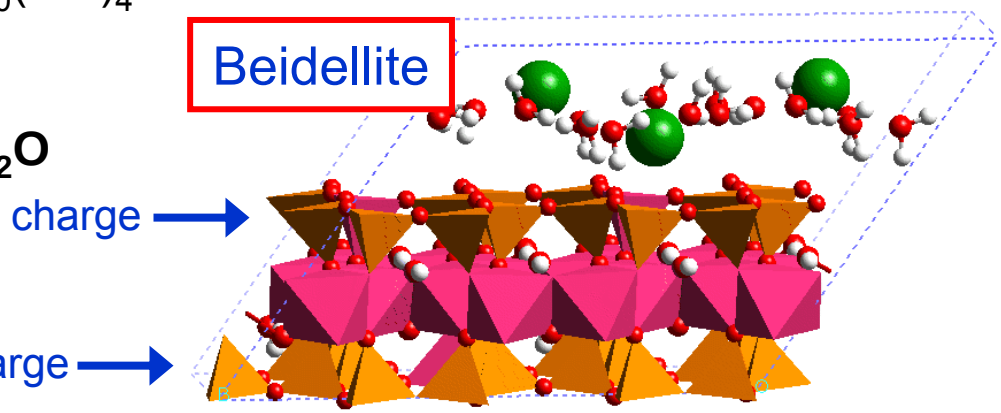
Wy Montmorillonite



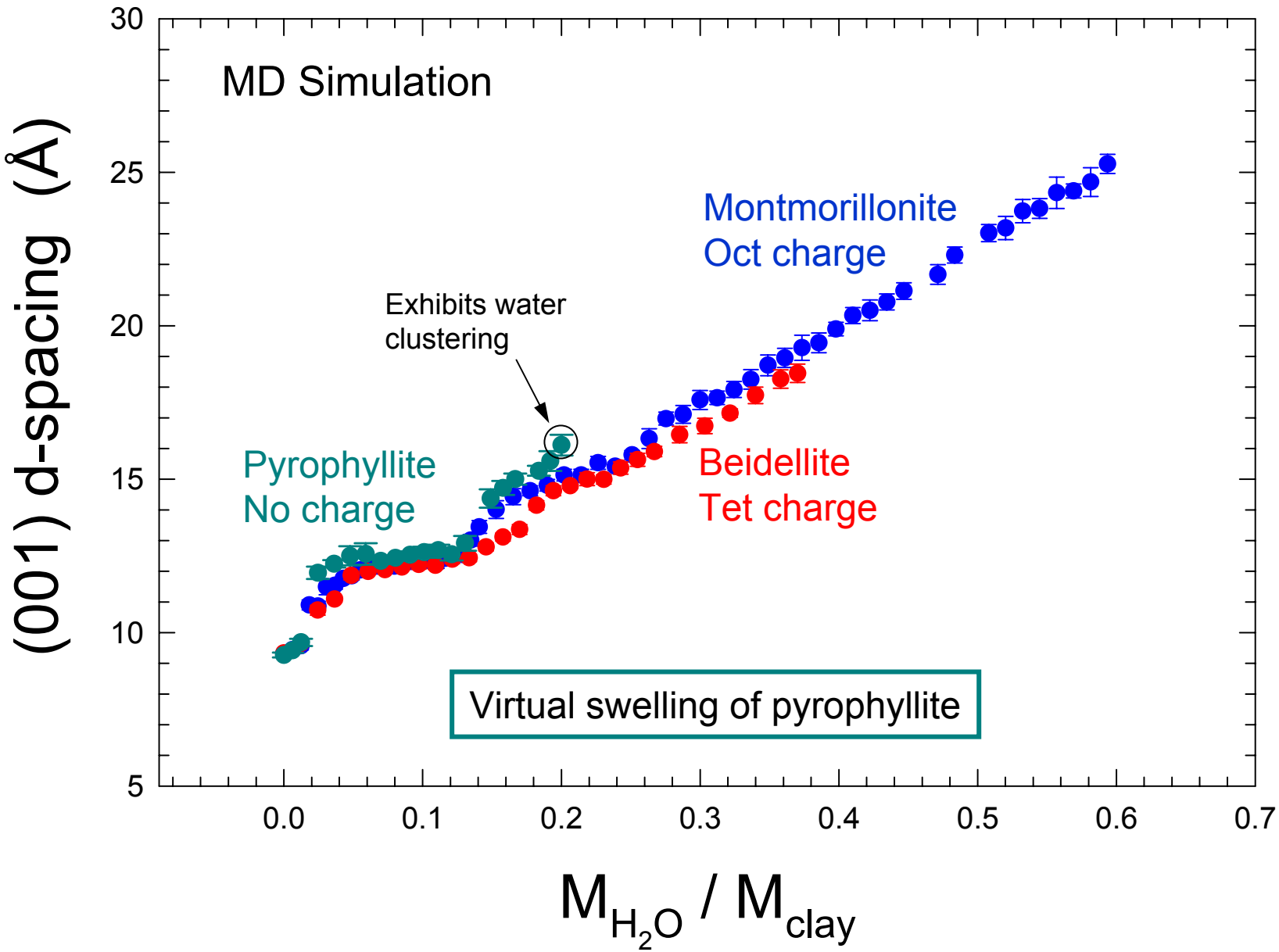
0.75 charge per $O_{20}(OH)_4$

$Na_3(Si_{29}Al_3)Al_{16}O_{80}(OH)_{16}\cdot nH_2O$
Mostly tetrahedral Al sub
Swelling

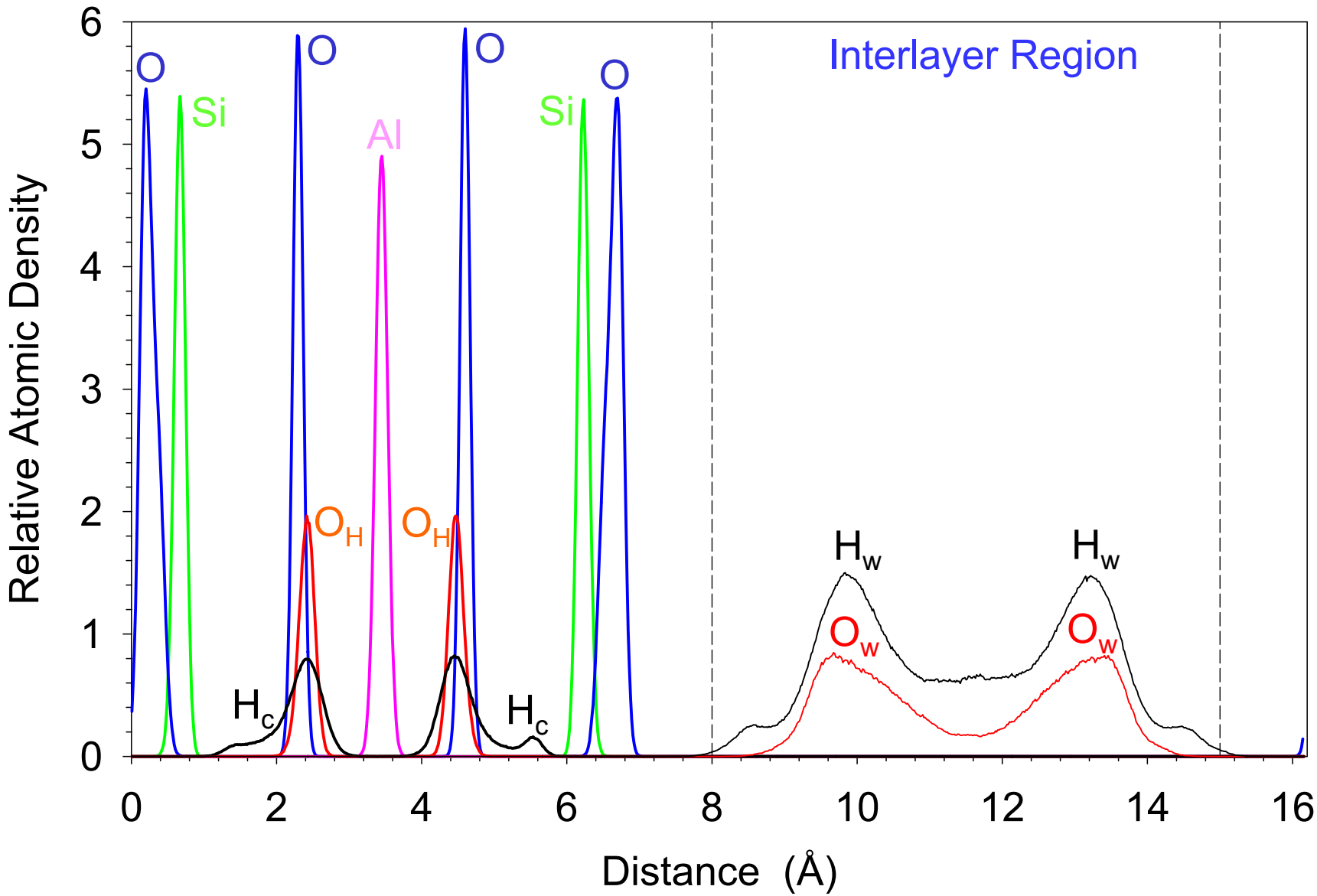
Beidellite



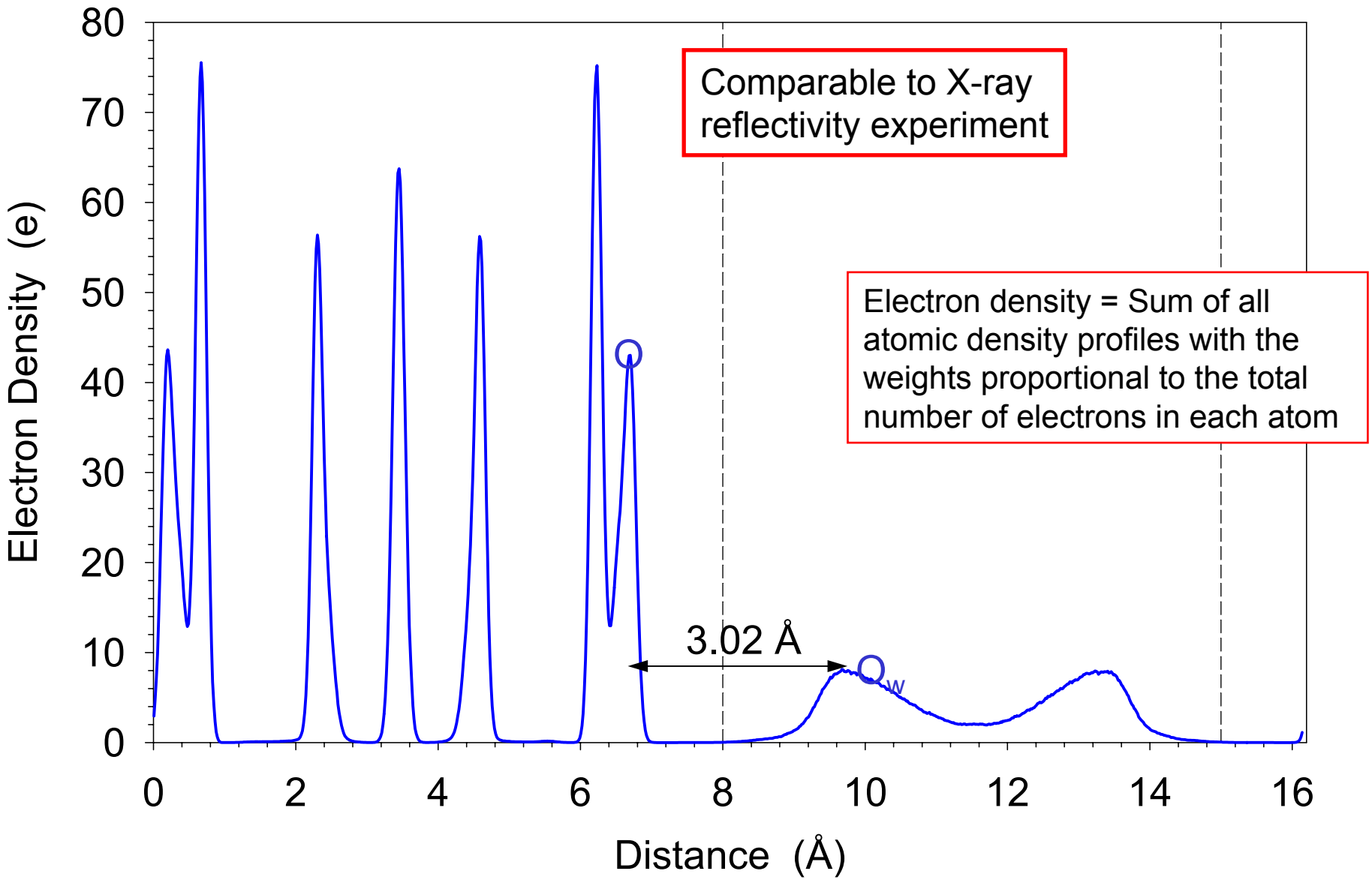
Comparison of Clay Swelling Behavior



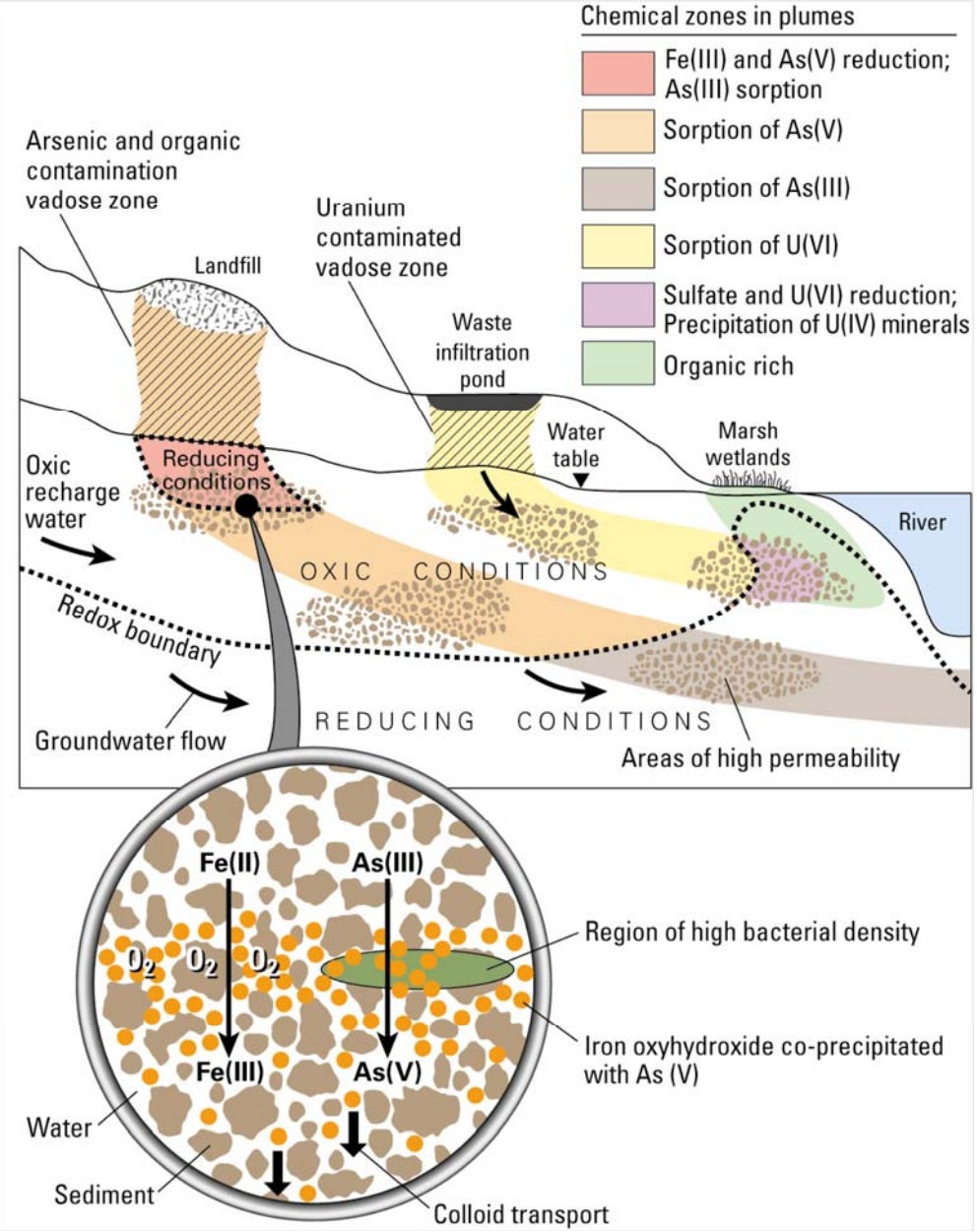
Atomic Density Profile for Pyrophyllite



Electron Density Profile for Pyrophyllite



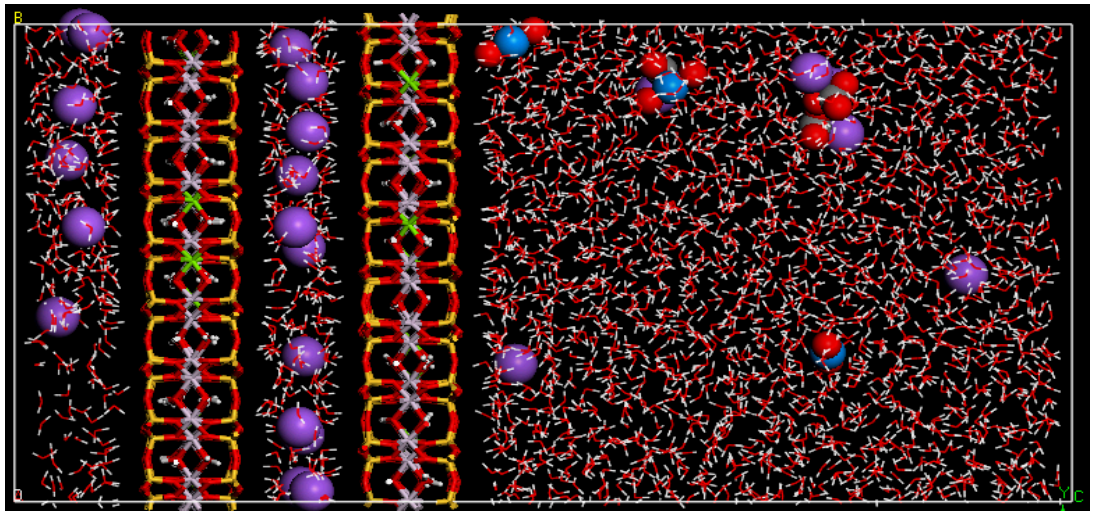
Contaminant Plumes in the Environment



Critical Contaminants

UO_2^{2+}, Cs^+, Sr^{2+}, Th^{4+}, I^-, TcO_4^-
NO_3^-, AsO_4^{3-}, AsO_3^{3-}, ClO_4^-
acetone, toluene, TCE,
methylene chloride

Uranium Adsorption onto Clay Surfaces



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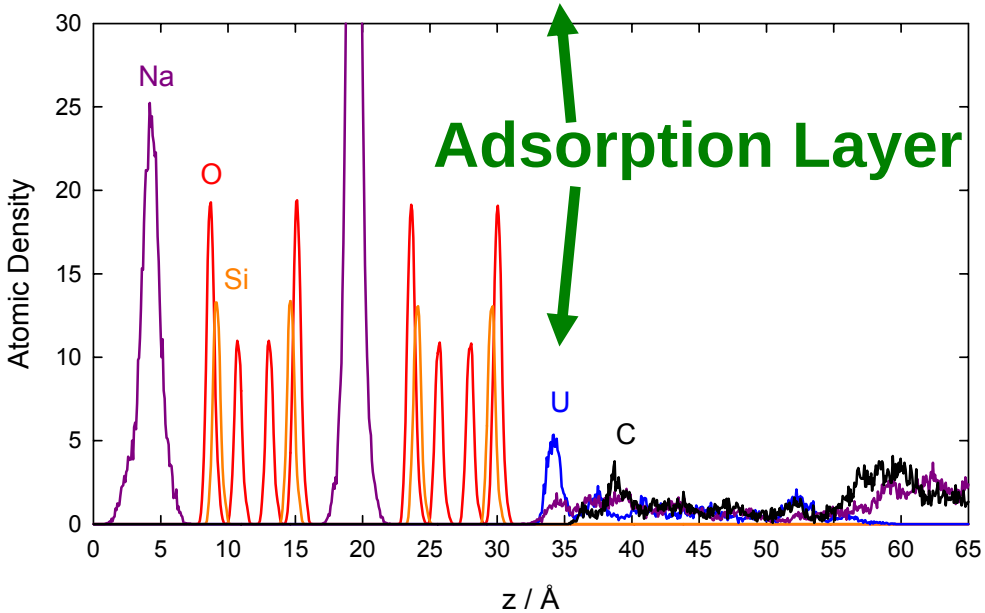


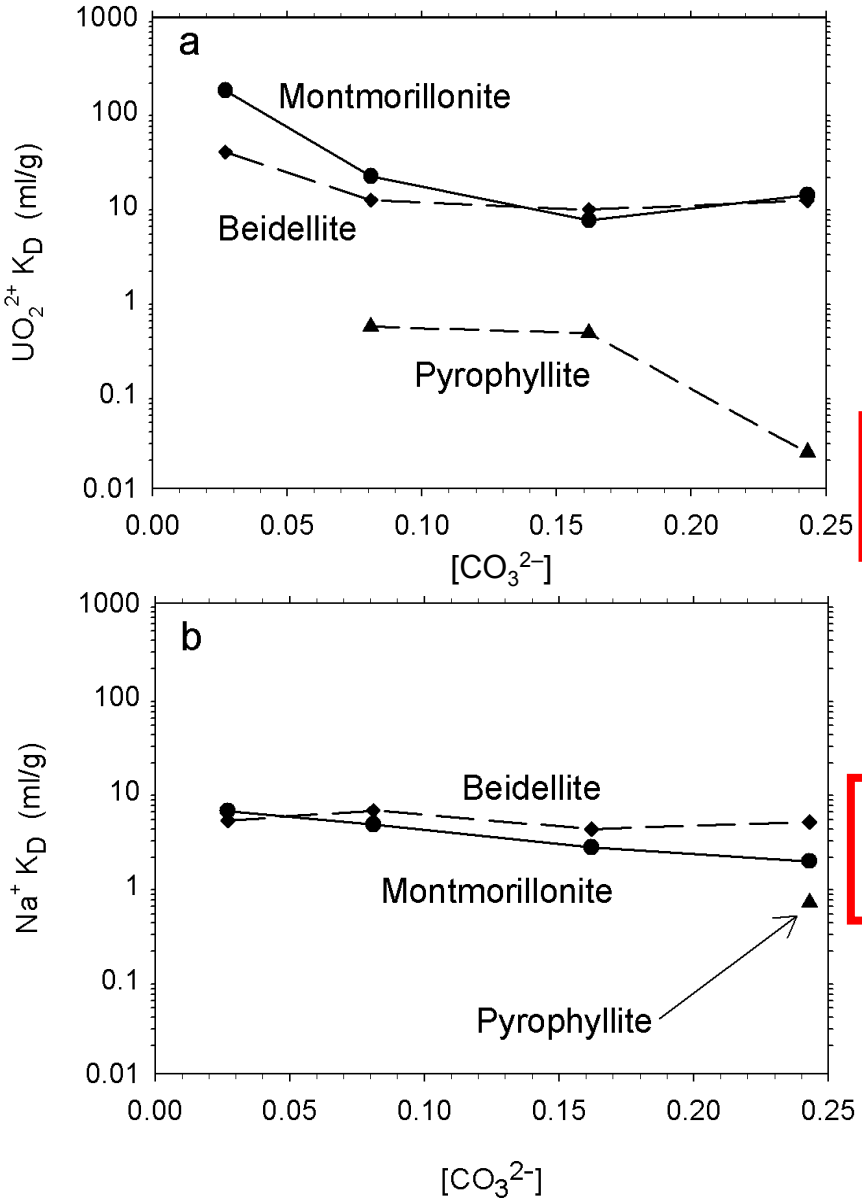
"low charge" montorillonite
x = −0.375 *e* / unit cell

Percent Ion Adsorption

[Na]	[UO_2]	% UO_2	% Na
0.162	0.027	37.4	10.4
0.162	0.081	21.8	8.5
0.162	0.162	10.2	7.6
0.324	0.162	3.9	8.1

Greathouse and Cygan, *PCCP* **2005**

Adsorption Equilibria (K_D)



Distribution Coefficient

$$K_D = S / C$$

S = sorbed concentration (mol/g)

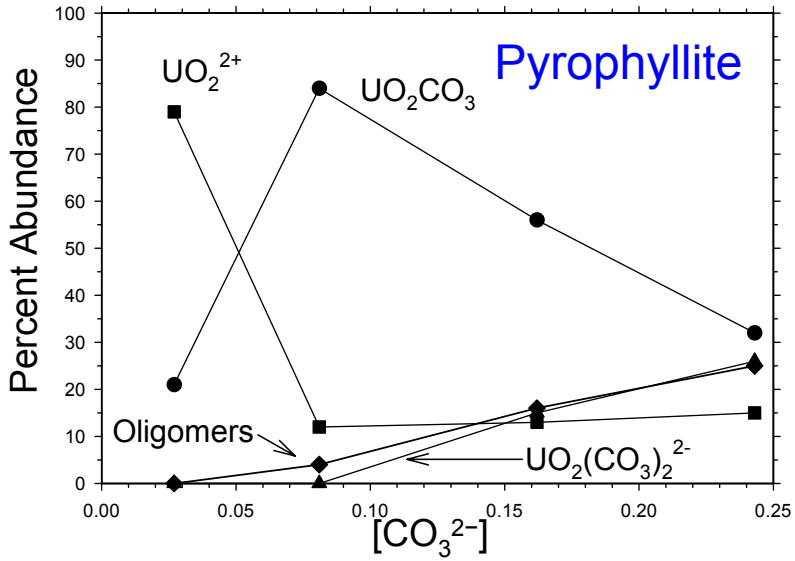
C = dissolved concentration (mol/cm^3)

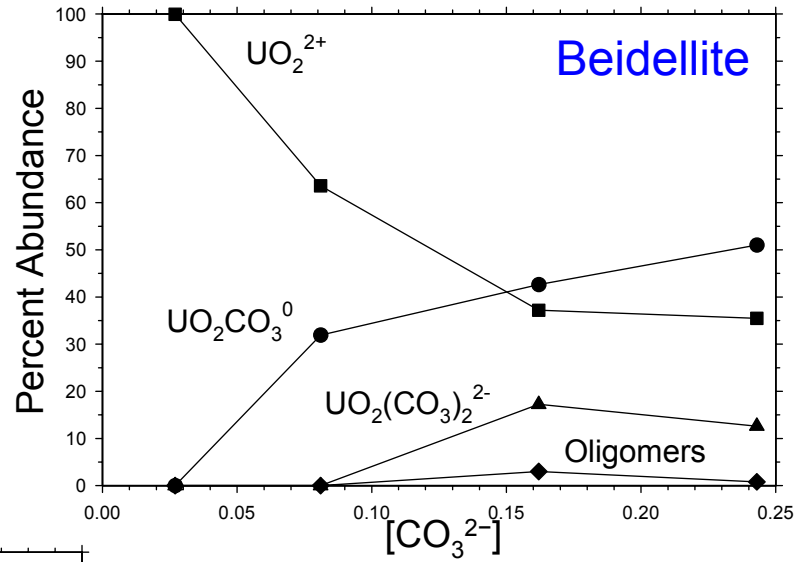
UO_2^{2+} sorption is influenced by solution concentration

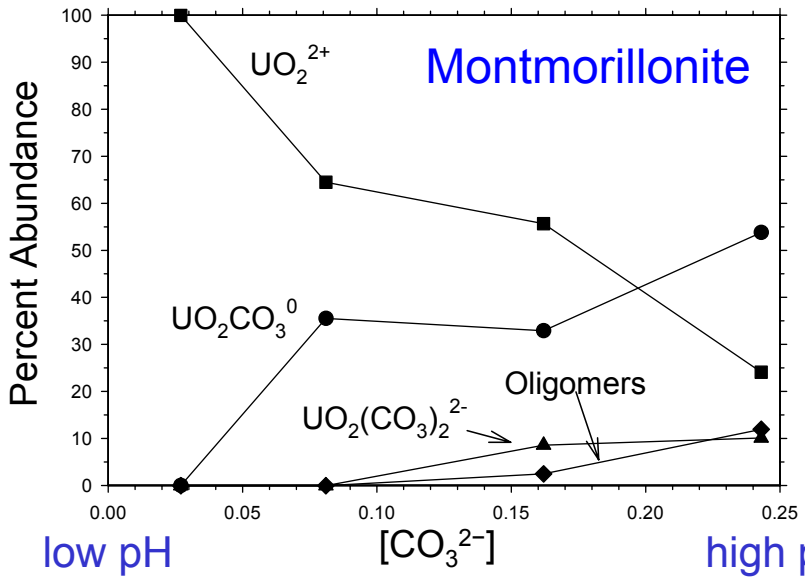
Na^+ sorption is unaffected by solution concentration

UO_2^{2+} Speciation

MD Results for Aqueous Region (uranyl that is not adsorbed)



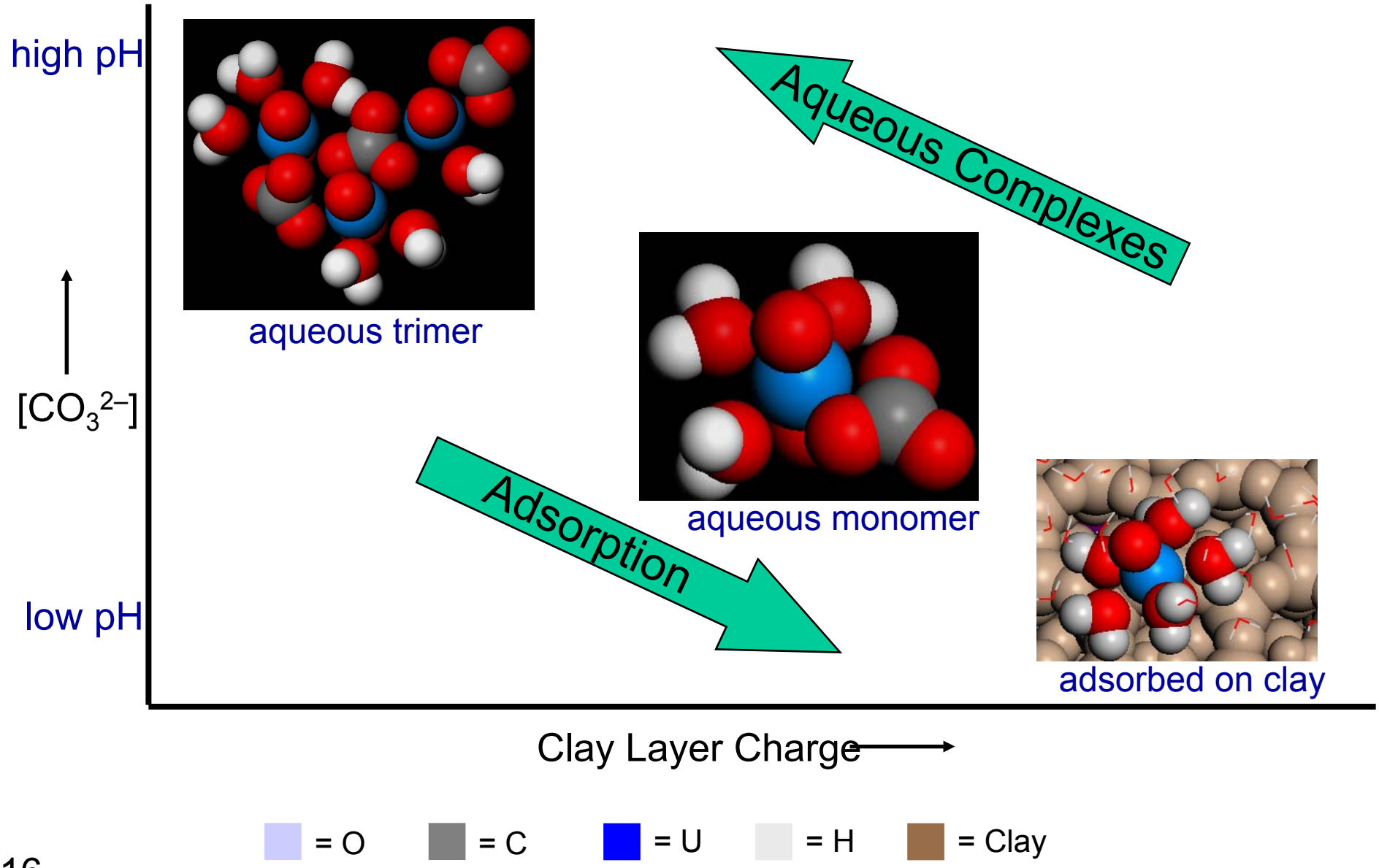




low pH

high pH

Summary of Uranium Adsorption and Complexation



Computational resources for large-scale simulations

Geochemistry Facility

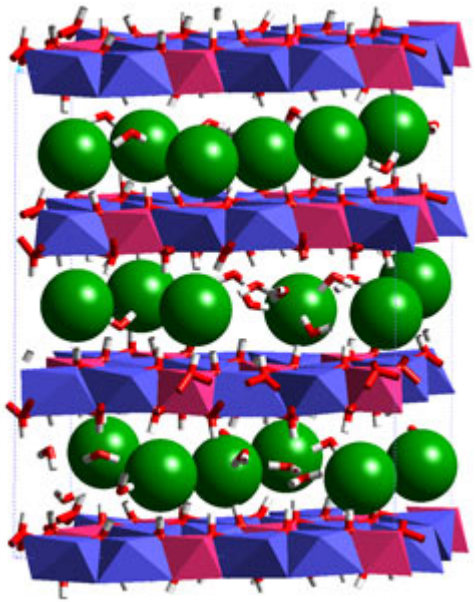
- AMD and Apple clusters
- 100 processors

Sandia Thunderbird Supercomputer

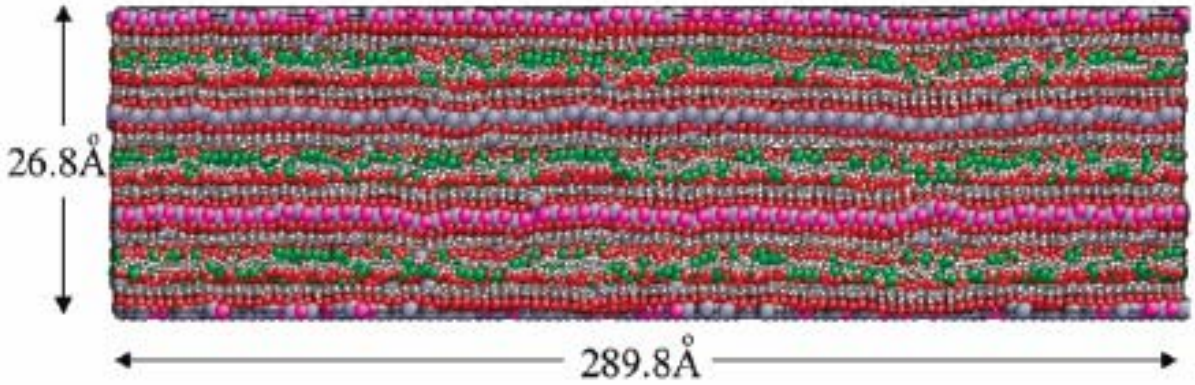
- 8960 processors
- Dual 3.6 GHz Intel EM64T processors with 6 GB RAM
- Performance: 53 Teraflops

Elastic Moduli

$[Mg_2Al(OH)_6]Cl \cdot 2H_2O$

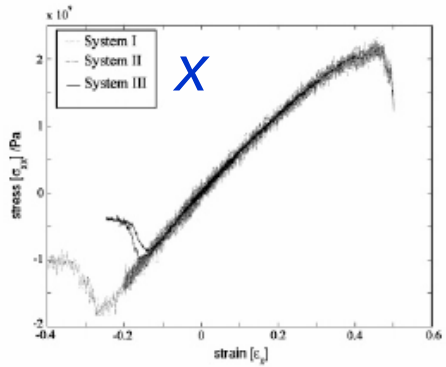


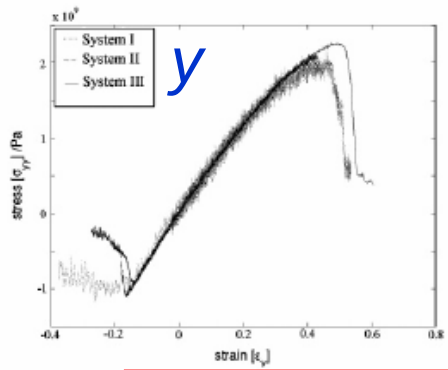
> 10^6 atoms



Stress-Strain

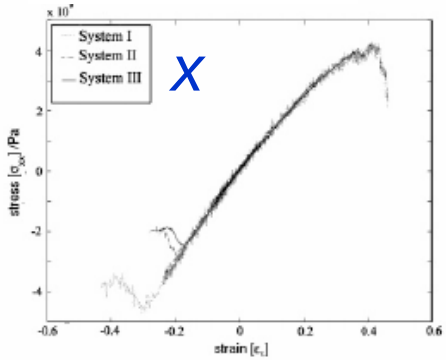
LDH sheet and interlayer

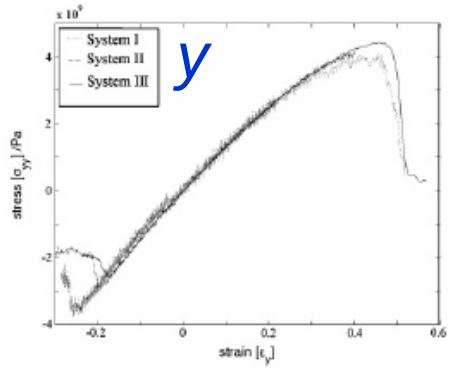




slope = Young's modulus

LDH sheet only





macroscopic stress

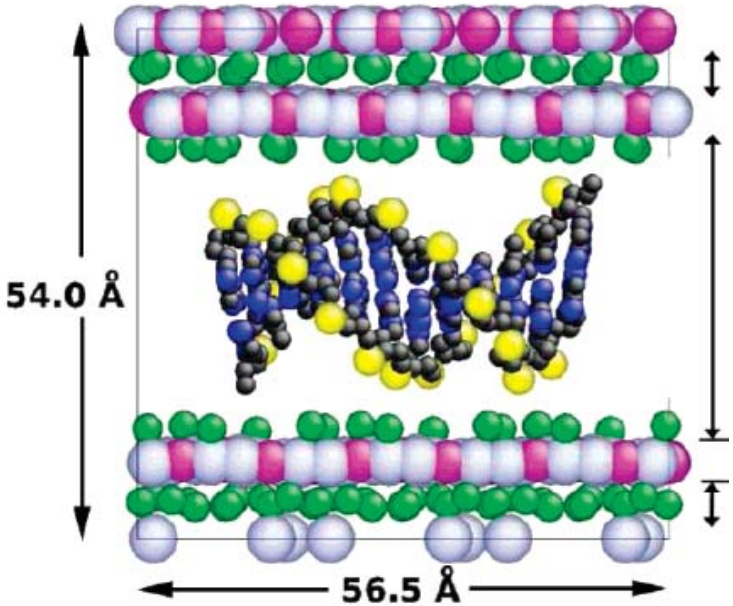
$$\sigma_{ij} = \frac{1}{V}\left(\frac{\partial E}{\partial \epsilon_{ij}}\right)_S$$

atomistic stress

$$\sigma_{kl} = \frac{1}{V}\sum_{i=1}^{N}\left(\frac{m_i}{2}\mathbf{v}_i\mathbf{v}_i + \frac{1}{2}\sum_{j=1}^{N}\mathbf{F}_i\mathbf{r}_{ij}\right)_{kl}$$

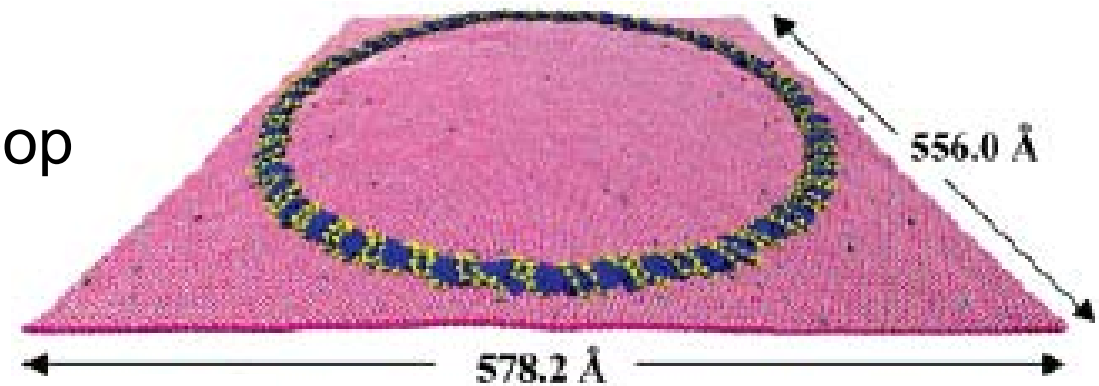
Thyveetil et al. *Chem. Mater.* 2007

Large-Scale Simulations of Mineral-Organic Interactions Using CLAYFF



DNA dodecamer strand intercalated in a layered double hydroxide (LDH)

DNA double strand loop adsorbed on LDH surface



Thyveetil et al, *J. Am. Chem. Soc.* 2008

Summary: What Molecular Modeling Can Provide

- **Nanoscale description of interfacial structure and dynamics**
  - mineral-fluid interactions (aqueous or organic)
  - sensor-fluid
  - mineral-sensor
  - fluid-fluid (immiscible fluids)
- **Adsorption and reaction phenomena**
  - isotherms and K_d
  - ion exchange
- **Dynamics of fluid species**
  - transport (bulk diffusion, surface diffusion)
  - vibrational motion
  - other physical chemical properties (dielectric behavior, time correlation functions)
- **Mechanical properties**
  - stress-strain
  - elastic constants