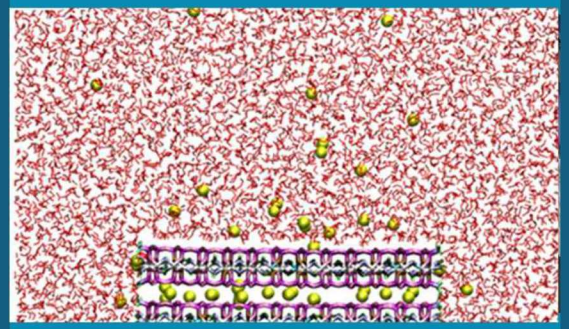
SAND2019-5814C

Mechanism of montmorillonite interlayer hydration from potential of mean force molecular dynamics simulations



PRESENTED BY

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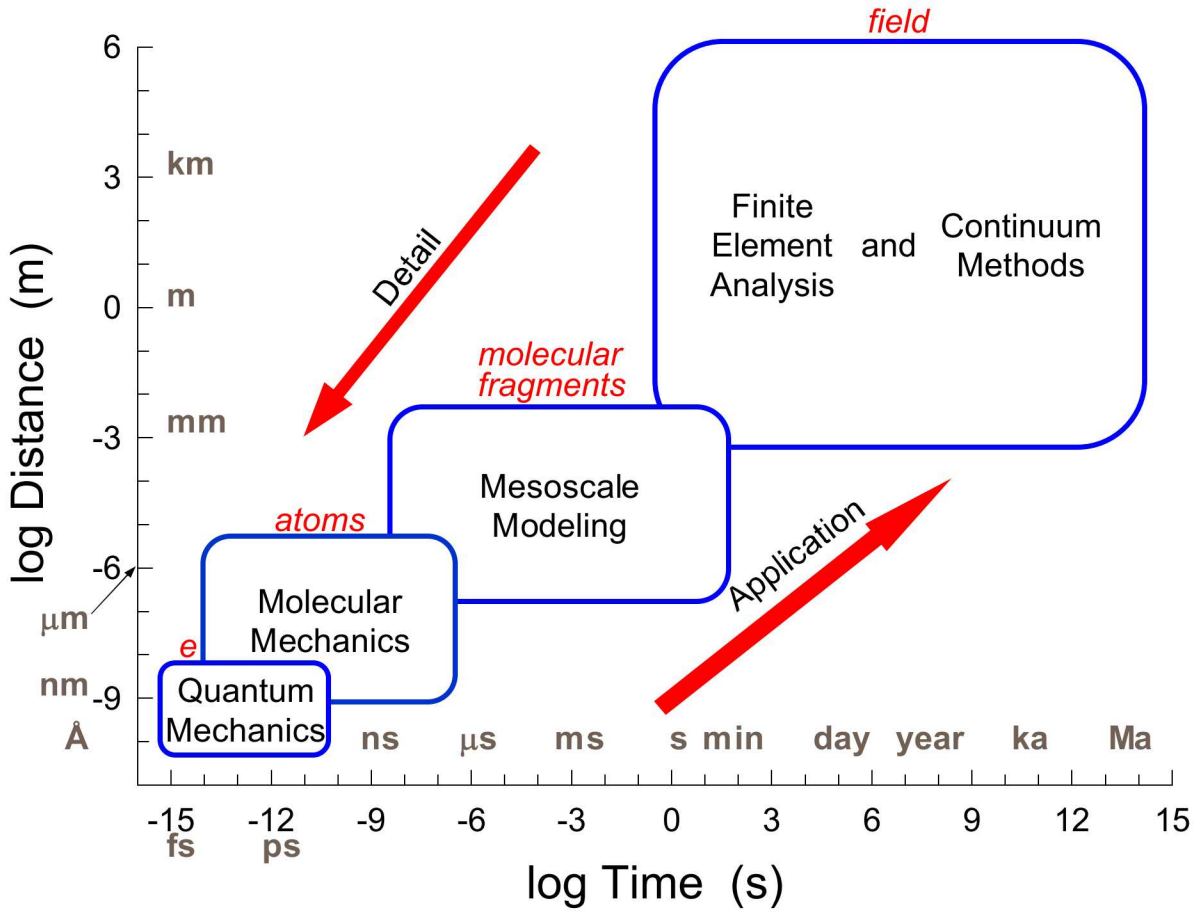
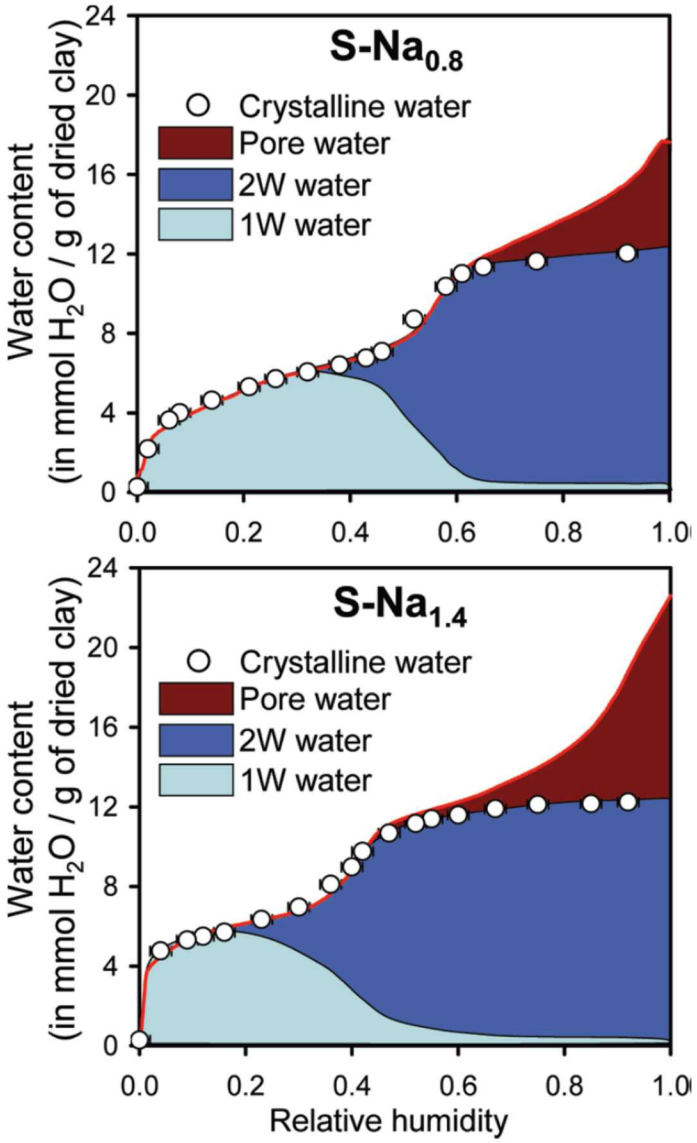
Outline

- Motivation
- Molecular Dynamics (MD) Methods
- ClayFF Modification
- Swelling Free Energies
- Proposed Swelling Mechanism



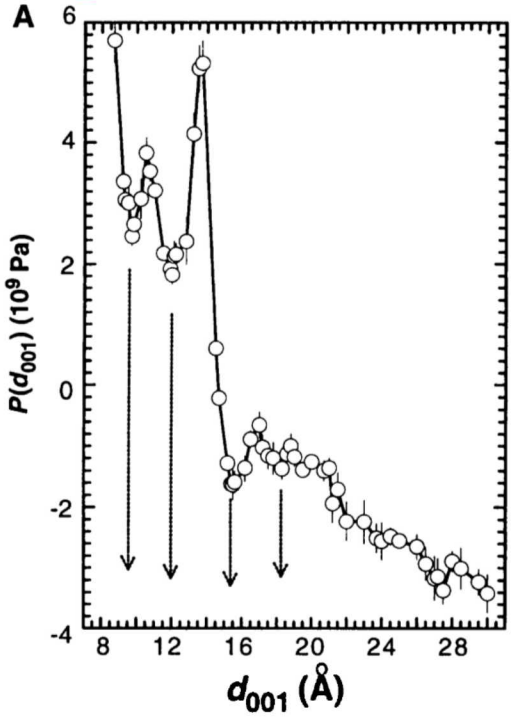
Clay swelling

- Importance of interlayer hydration and intracrystalline swelling in smectite clays:
  - Chemomechanical coupling
  - Fate and transport of contaminants and nutrients
  - Industrial applications
- XRD profile modeling indicates the coexistence of interlayer hydration states (**0W**, **1W**, **2W**)
- **Unresolved issues:**
  - How do water molecules enter interlayer regions from pore fluids?
  - What are the transition states (**0W-1W**, **1W-2W**)?
- **Goal:** Apply enhanced MD simulation techniques (umbrella sampling, potential of mean force) to evaluate relative free energies of interlayer hydration states

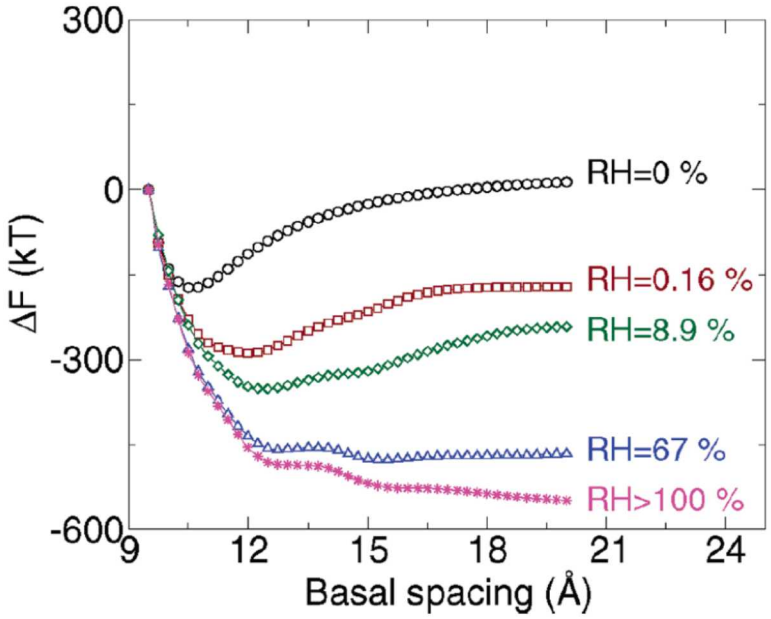


Ferrage et al., *J. Phys. Chem. C* **2010**

Previous molecular simulation studies of Na-montmorillonite swelling

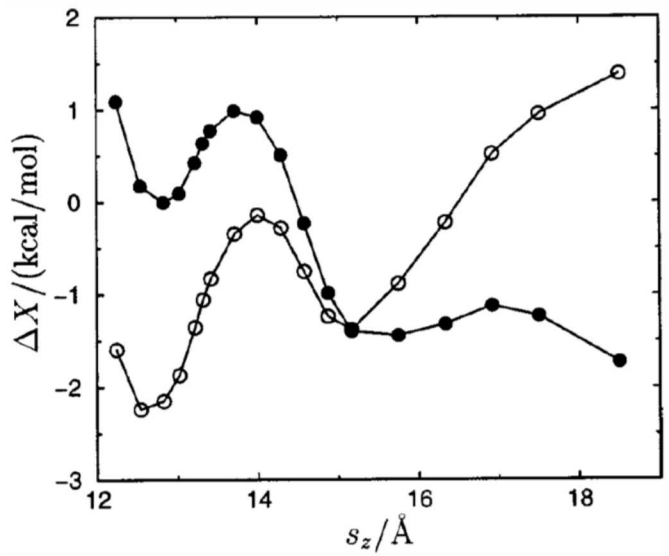


Karaborni et al.
Science **1996**



Tambach et al.
J. Phys. Chem. B **2004**

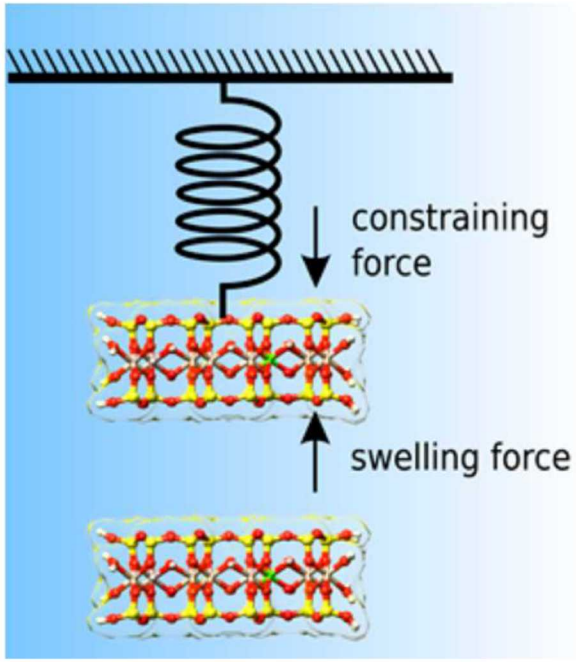
Bulk models



Shroll and Smith
J. Chem. Phys. **1999**

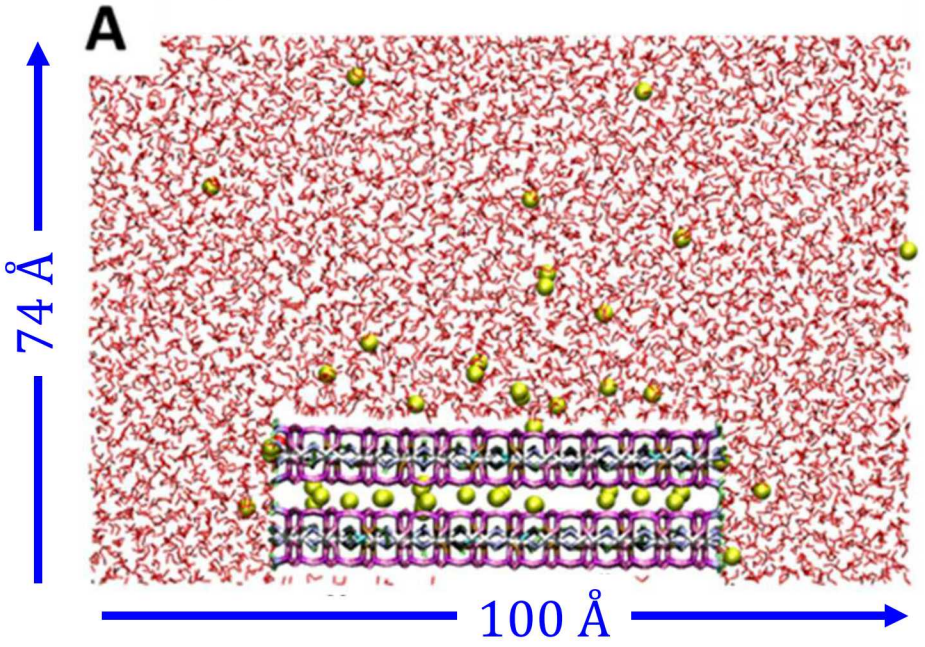
Ribbon model
1D periodic

Sun et al.
J. Phys. Chem. C **2015**

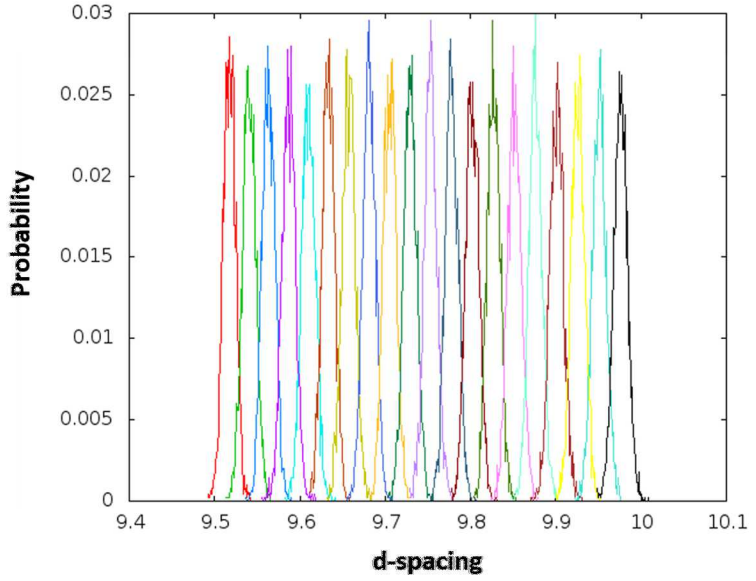


Molecular dynamics with enhanced sampling (Tuan Ho)

- **Na-MMT nanoparticle**
  - 2 TOT layers, 53 Å × 31 Å
  - Negative charge in octahedral sheet (Mg:Al 0.75:3.25)
  - Periodic in 1D
  - Broken bonds completed with -H and -OH
  - Particle immersed in a water box
  - Fully flexible



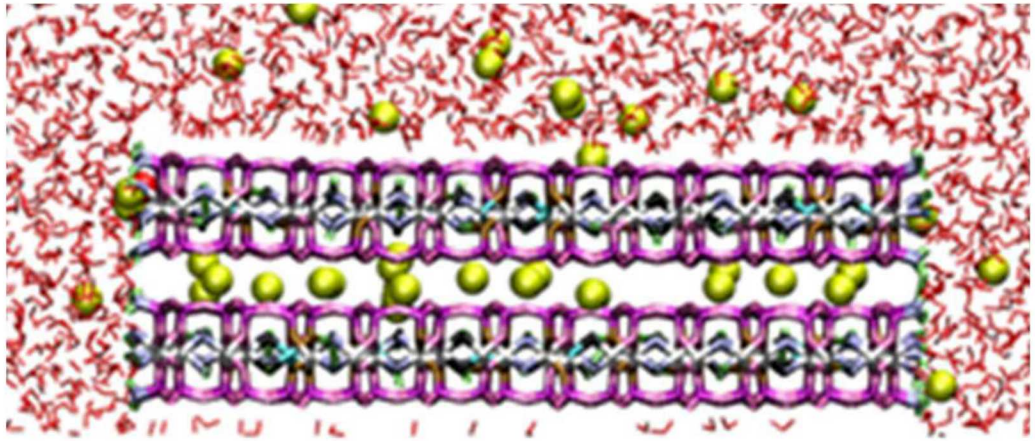
- **MD methodology (LAMMPS)**
  - ClayFF with new SiOH and AlOH angle bending terms (Pouvreau et al, *J. Phys. Chem. C* **2017**, **2019**)
  - Constant pressure ensemble (1 atm, 300 K)
  - Umbrella sampling (COLVARS package)
    - *d*-spacing controlled by layer-layer harmonic interaction (individual windows, 9.5 Å – 17.0 Å)
    - Each window simulated for 3.0 ns
    - Potential of mean force (PMF) calculated using WHAM (Grossfield)



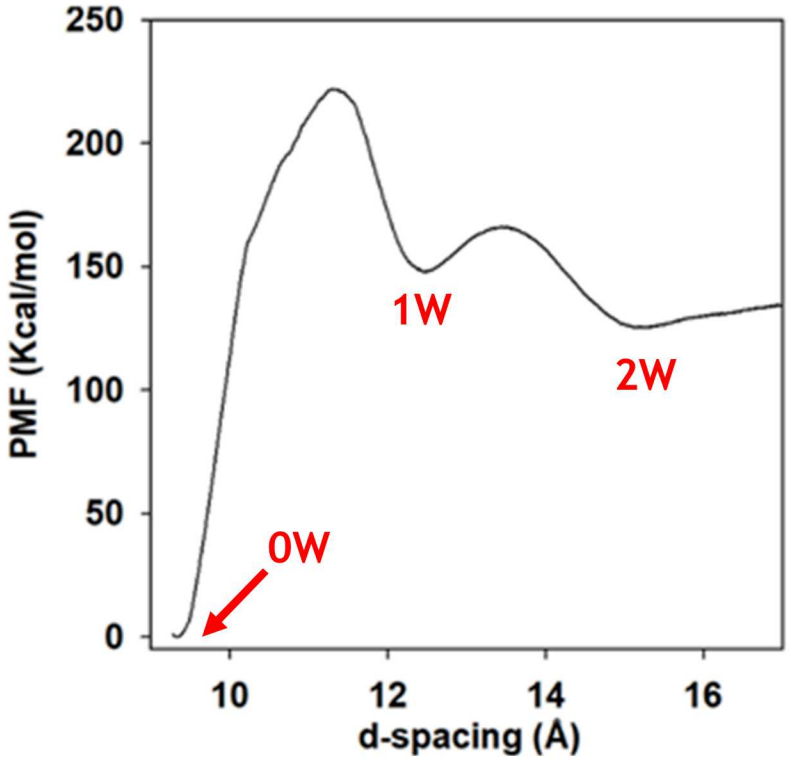
Initial results

Unconstrained MD:

- No waters enter the dry interlayer
- Some Na^+ reside deep in siloxane cavities



Initial PMF shows unusually stable dry state

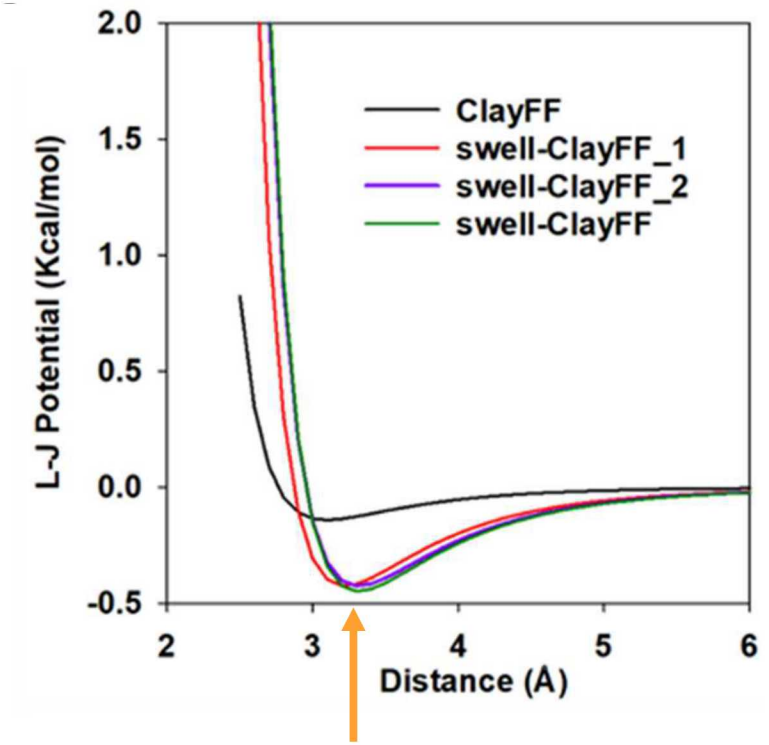


ClayFF modifications: Lennard-Jones interactions

- Clay O atoms to fit XRD data (Ferrage et al., *J. Phys. Chem. C* **2011**)
- Surface O atoms to fit IR spectra (Szczerba et al., *Clays Clay Miner.* **2016**)
- We modified only the Na-$O_{bridging}$ interaction for particle stability and consistency with original ClayFF

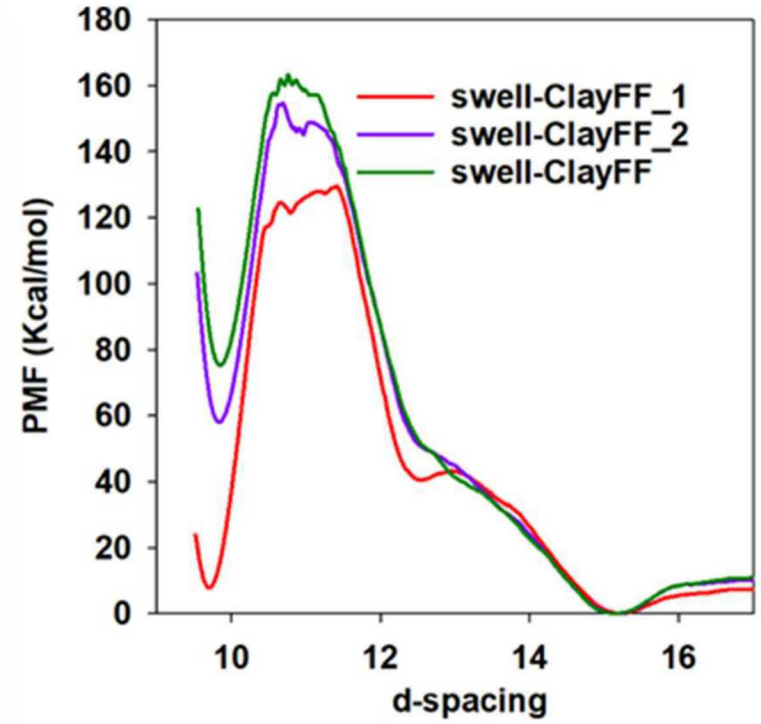
ClayFF modification

Several choices of Na-$O_{bridging}$ interaction were examined



More repulsive at short distances

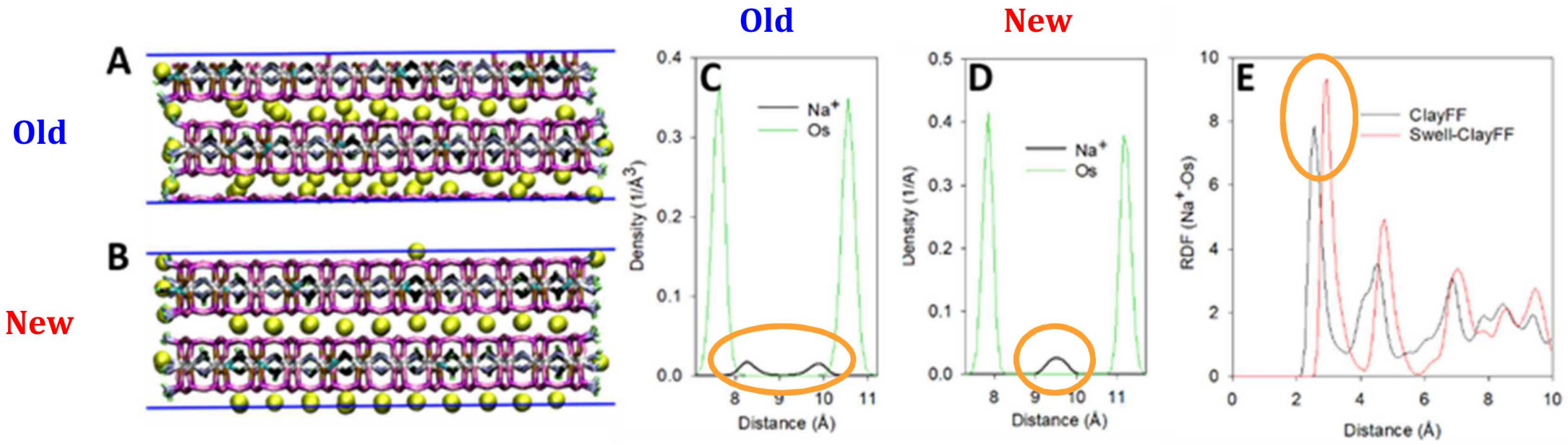
Dramatic effect on hydration properties



Final parameters (green) give expected trend for Na-MMT in contact with water (**2W < 1W < 0W**).

Validation of new LJ parameters

Result: longer Na-$O_{bridging}$ distances

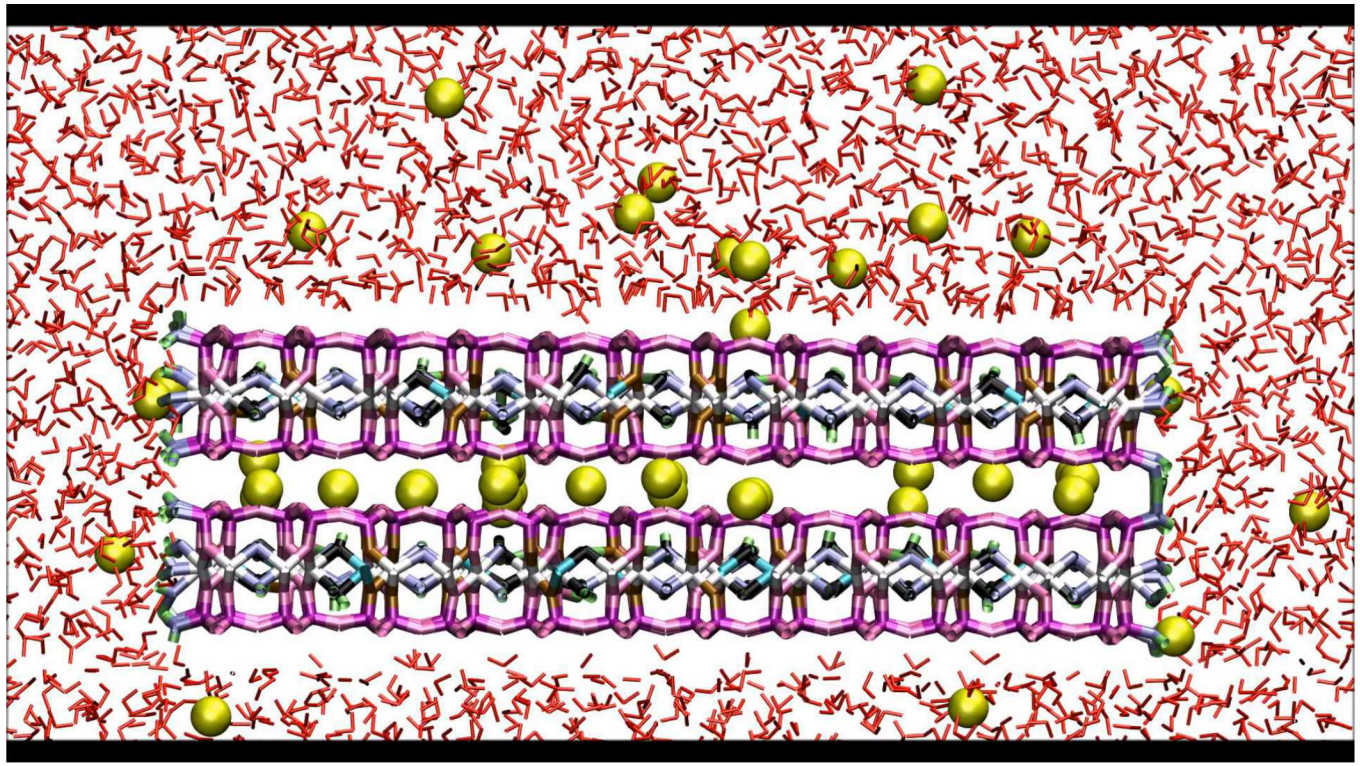


Final parameters show good agreement with DFT* and XRD**

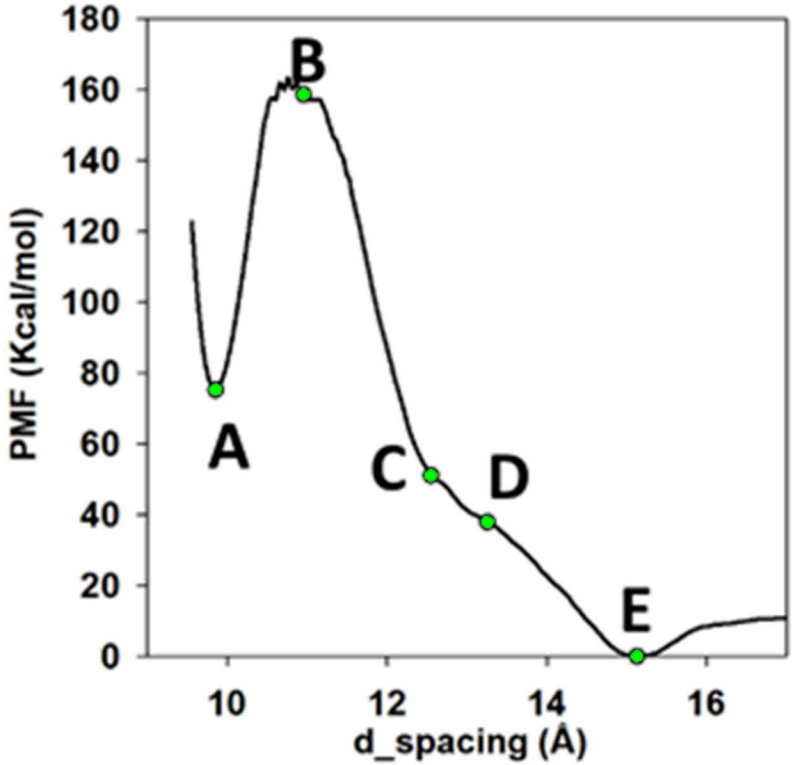
*DFT (Berghout *et al.*, *Clays Clay Miner.* **2010**)
XRD (Mooney et al **1952; Cases et al **1995**; Chiou et al **1997**; Rutherford et al **1997**; Calvet et al **1973**)

Method	Na-O distance (Å)	dry *d*-spacing (Å)
ClayFF	2.2-3.5	9.4
swell_ClayFF	2.4-4.0	9.8
Comparison	2.4-3.9*	9.6-9.8**

Na-montmorillonite hydration



Movie shows interlayer expansion as layers are separated at a rate of 5 Å/ns.



A 0W
B 0W-1W transition
C 1W
D 1W-2W transition
E 2W

Details of stable states and possible transition states

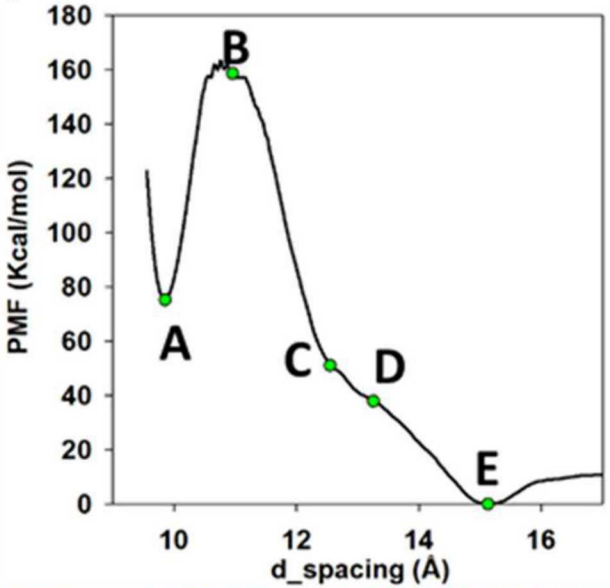
A 0W
- Single layer of Na^+

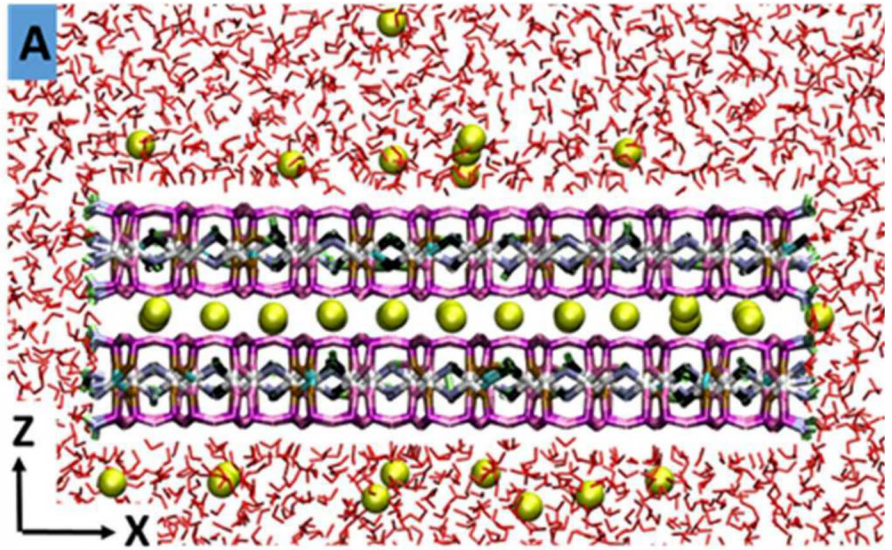
B 0W-1W transition
- Waters enter interlayer, hydrate Na^+
- Water concentration gradient
- Unequal *d*-spacing
- Bending of TOT layers

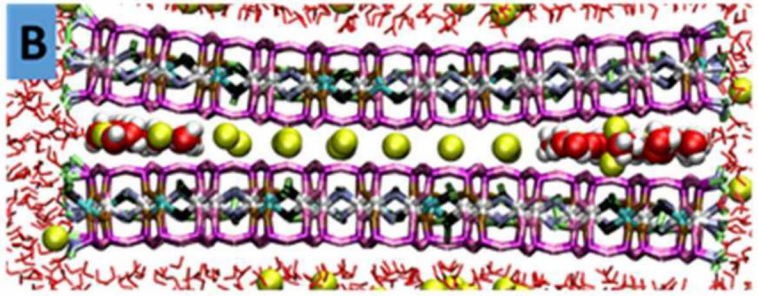
C 1W
- Single layer of Na^+

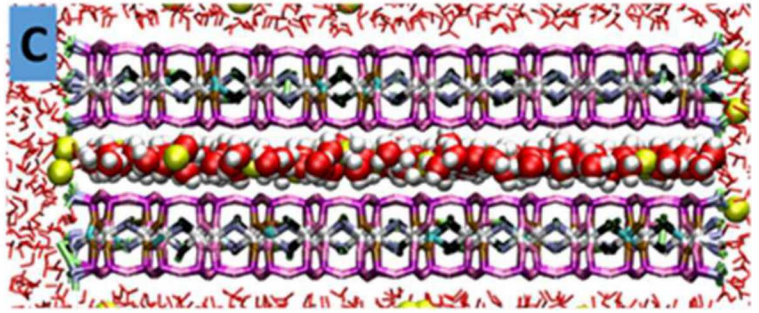
D 1W-2W transition
- Water concentration gradient

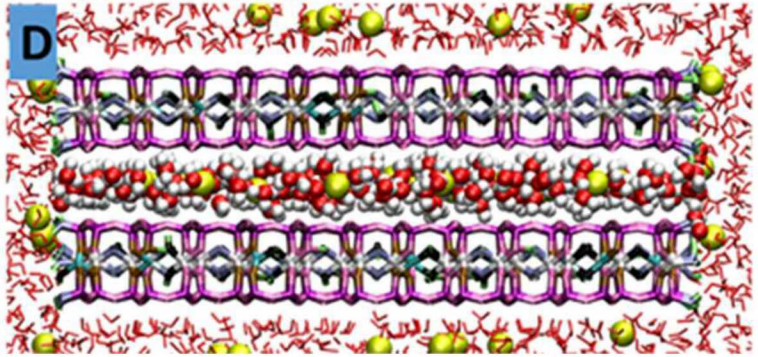
E 2W

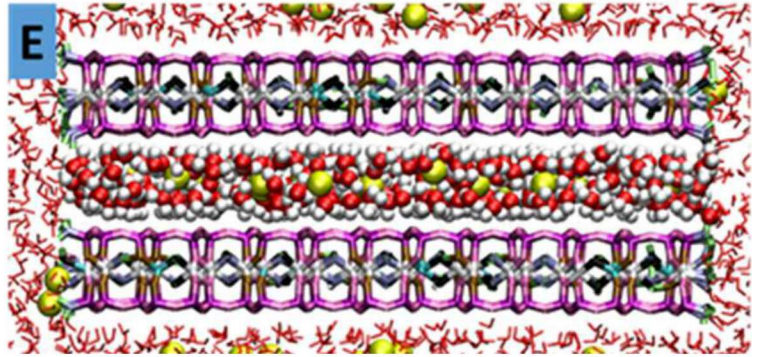






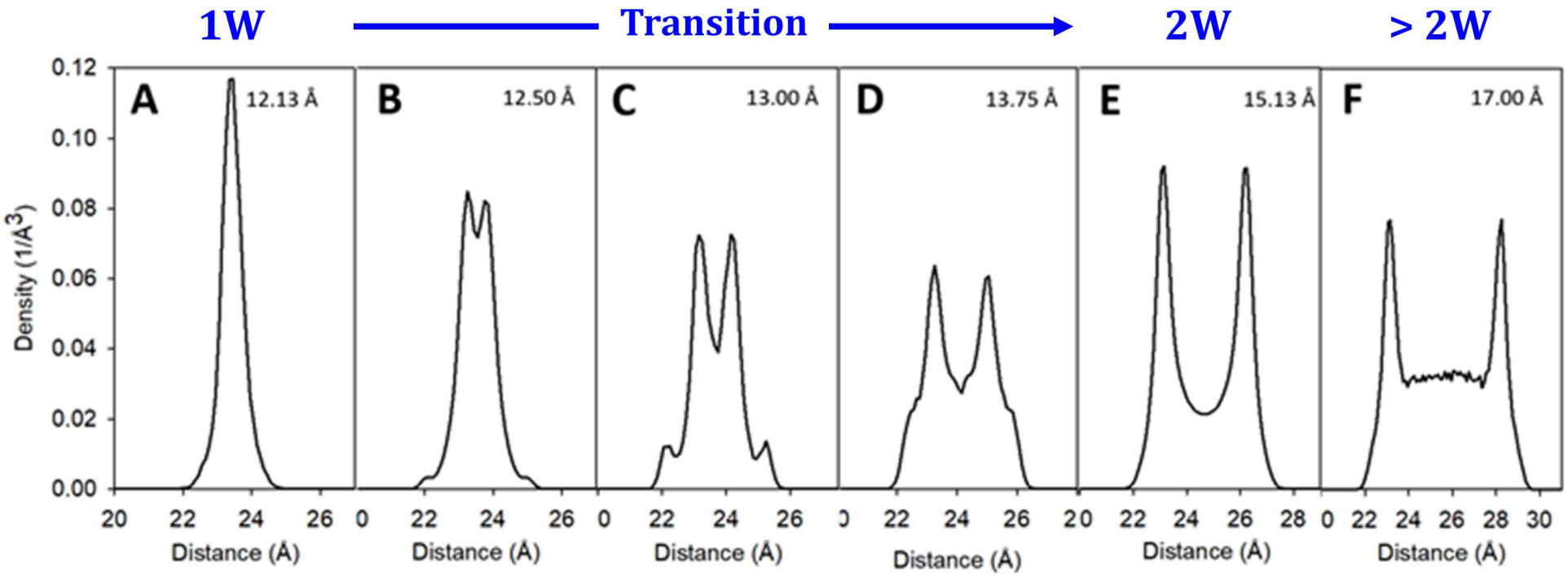






A closer look at the 1W-2W transition

Density profiles of water O atoms

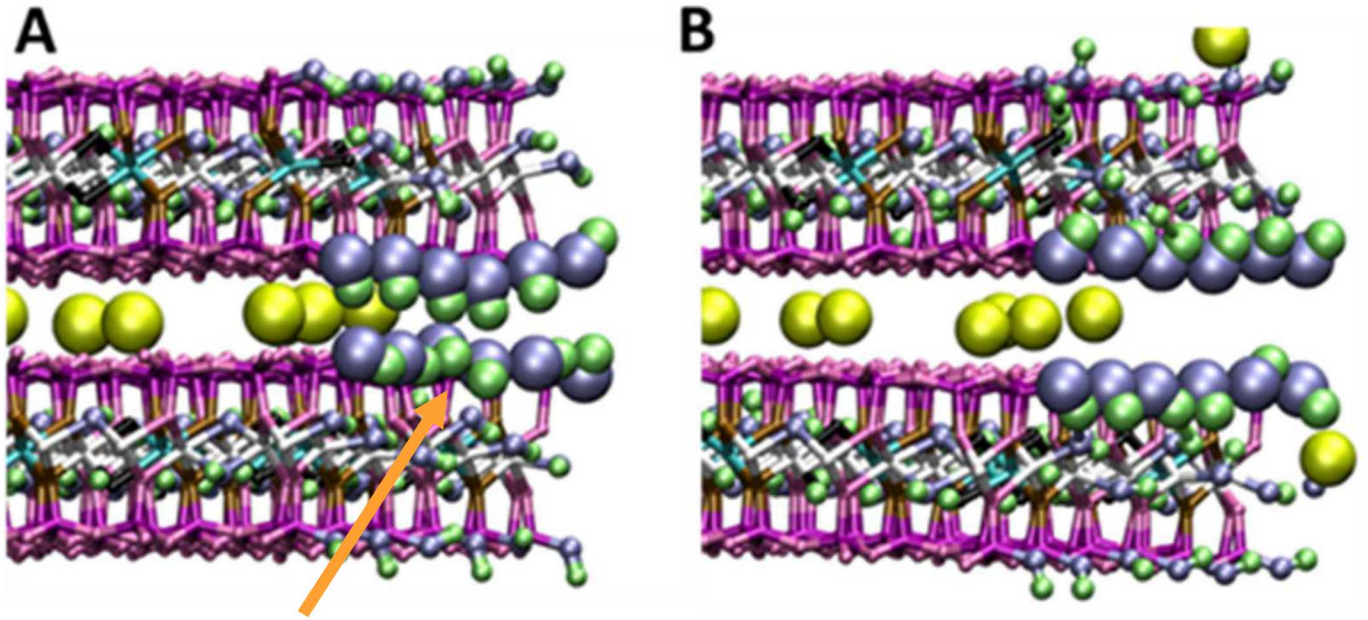


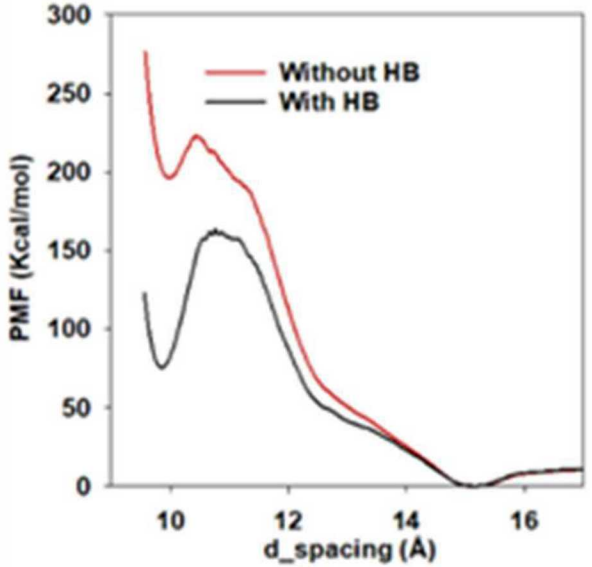
Important role of layer-layer HBs

HBs between layer –OH groups contribute to the 0W-1W energy barrier

Layer-layer HBs included

Layer-layer HBs not included

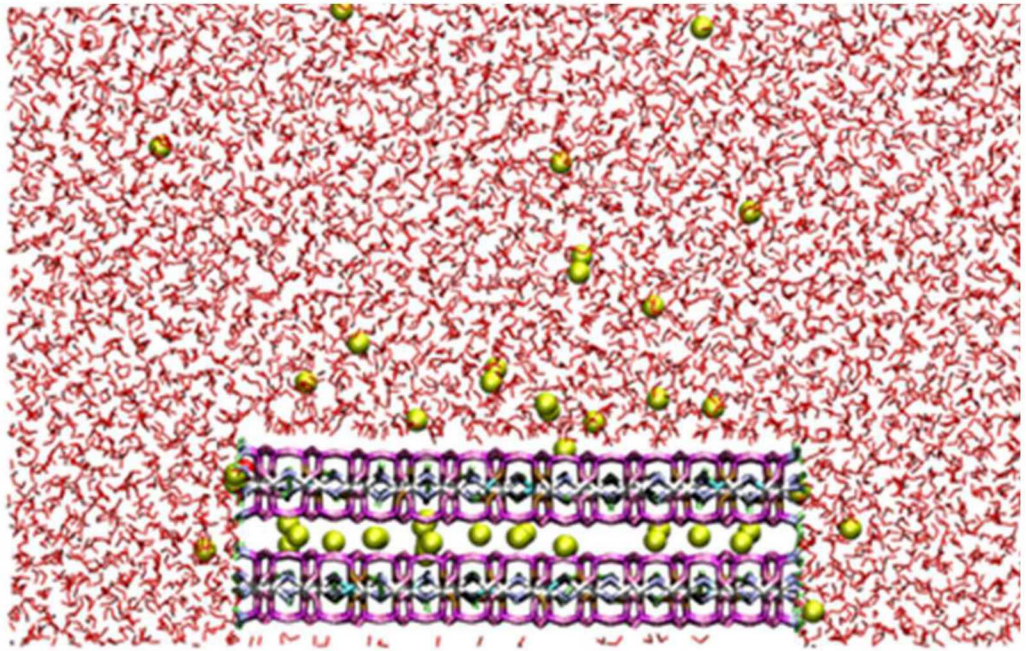




Gate effect
High energy barrier
for water passage

No layer-layer HBs
Edges are open
Low energy barrier

Conclusions



- The mechanism of interlayer hydration and swelling of smectite clays is still a challenging problem.
- MD simulations provide insight based on an idealized Na-MMT particle immersed in water.
- Enhanced sampling techniques to examine **stable hydration states and possible transitions**.
- **Modifications to ClayFF parameters** (cation-clay interactions) are needed to obtain the expected trend in free energies.
- **Hydrogen bonding** between layer edge groups appear to play a key role in interlayer hydration.

Merci beaucoup!