Molecular simulation of structure and diffusion at smectite-water interfaces: Using expanded clay interlayers as model nanopores

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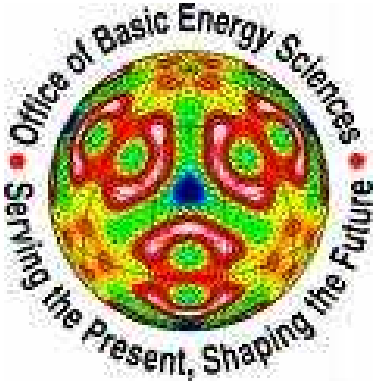

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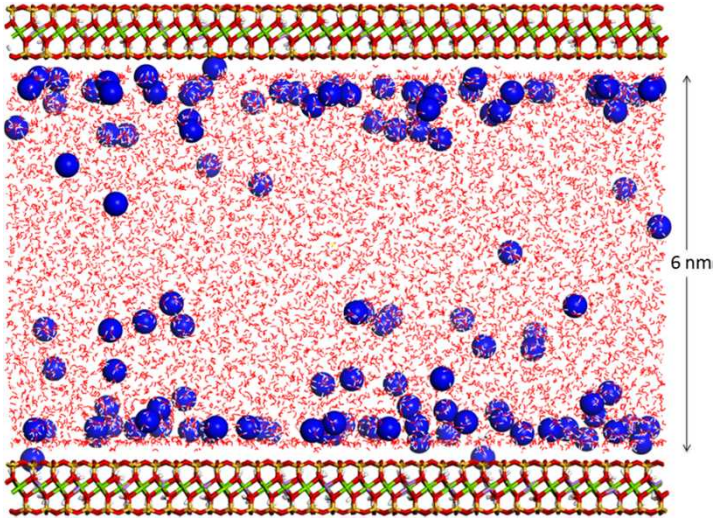
Solution Dynamics at Clay Interfaces

- Solution structure and transport in clay nanopores is key to:
  - Fossil energy extraction from unconventional geological reservoirs.
  - CO_2 sequestration in the subsurface.
  - Nuclear waste storage in geological formations.
  - Reactive transport and flow in soils and sediments.



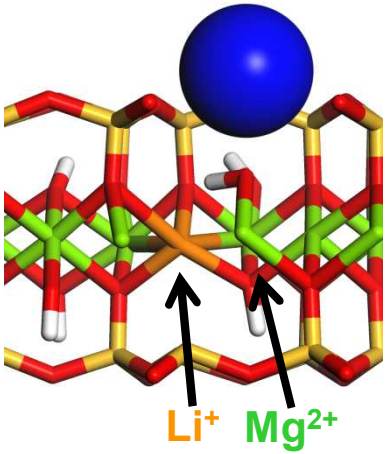
- Understand structural factors controlling aqueous transport at clay mineral-solution interfaces. How is water and ion mobility affected by:
  - Clay structure (layer charge and location).
  - Solution composition, ion hydration, surface complexes formed.

- Follows from recent work by BES collaborators Kirkpatrick and Bowers:
  - Variable temperature ^{23}Na and ^{2}H NMR of Na-hectorite pastes (Bowers et al, *JPCC* **2011**).
  - Molecular dynamics simulation of Na-hectorite interlayers (Morrow et al, *JPCC* **2013**).

Simulation Methods

- MD simulations of clay nanopores (external basal surfaces) similar to paste samples used in NMR experiments.

Na-hectorite



Na-montmorillonite

Hectorite	Montmorillonite
Trioctahedral	Dioctahedral
Li/Mg substitution	Mg/Al substitution
−0.5 *e* per $O_{10}(OH)_2$	−0.5 *e* per $O_{10}(OH)_2$
OH perpendicular to basal plane	OH parallel to basal plane

- Clayff parameters, flexible SPC water.
- Large system sizes and run times to thoroughly sample all possible adsorption sites and surface complexes:
  - NPT to equilibrate pore width, NVT for analysis, 298 K
  - 80 x 70 x 90 Å^3, 50k atoms, 6 nm pore width
  - 10 x 10 ns per clay
  - **200 ns simulation time (10 CPU years) completed in 1 week**

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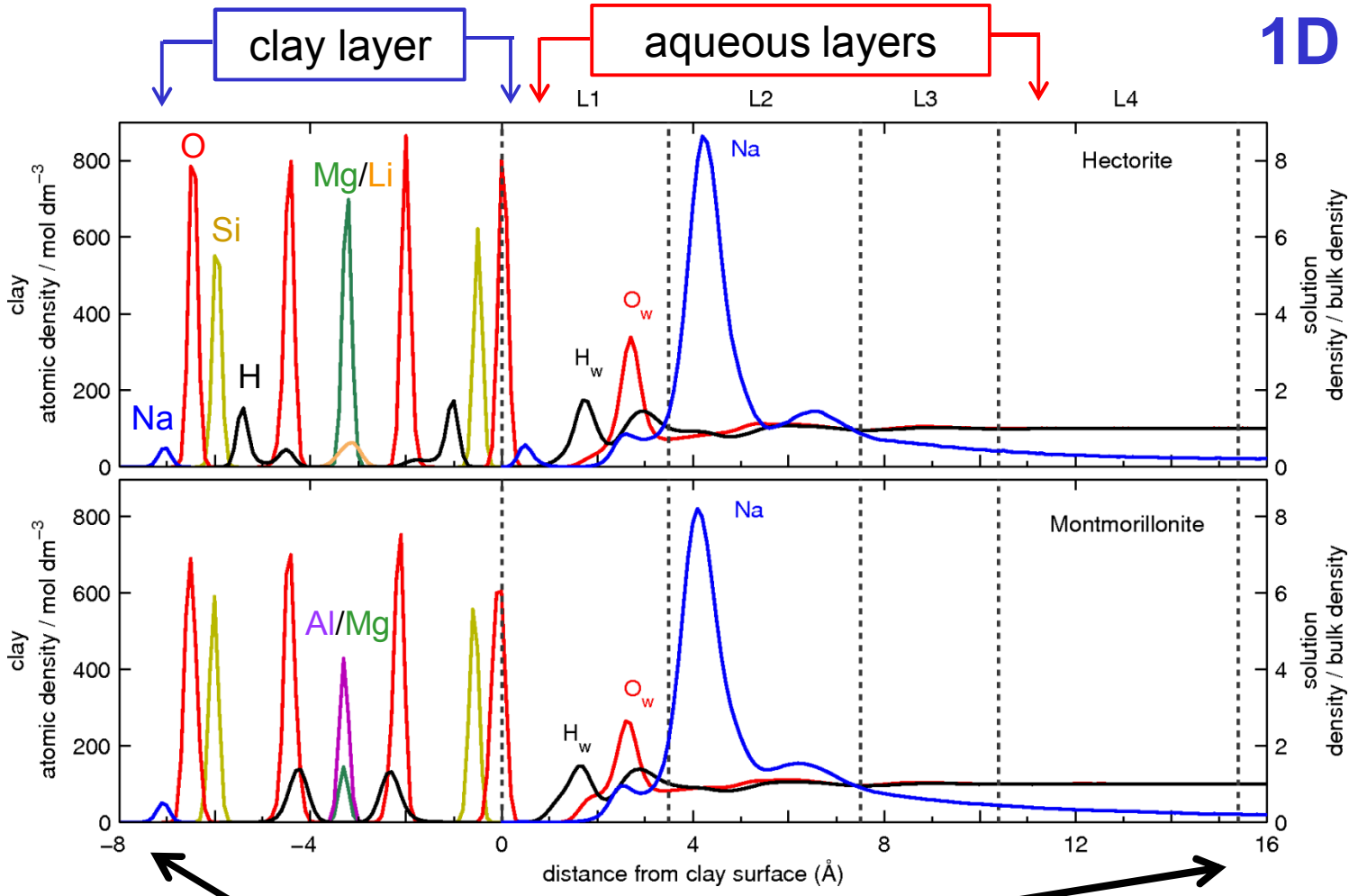
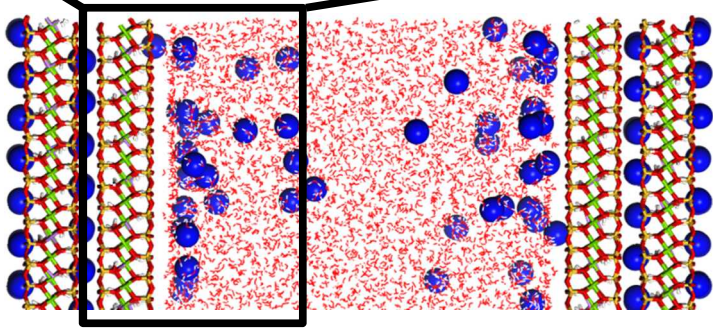
1D Structure





- 1D density profiles averaged over 20 interfaces.
- Aqueous regions defined by water peaks: L1, L2, L3, L4, Diffuse.

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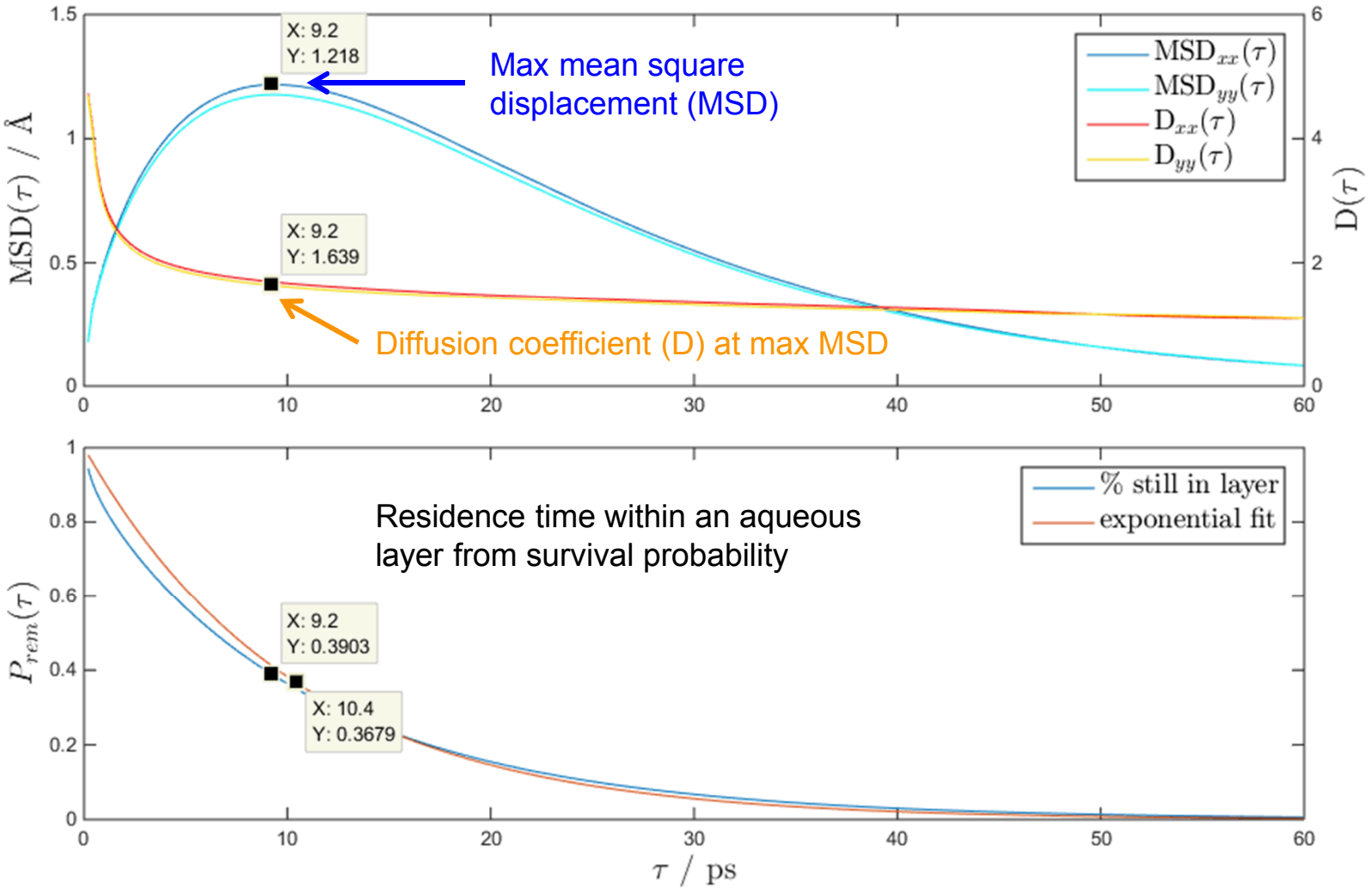
Diffusion and Residence Time Analysis



Diffusion coefficients and residence times calculated as a function of distance from mineral surface (Rotenberg et al, *J. Phys. Condens. Matter* **2010**).

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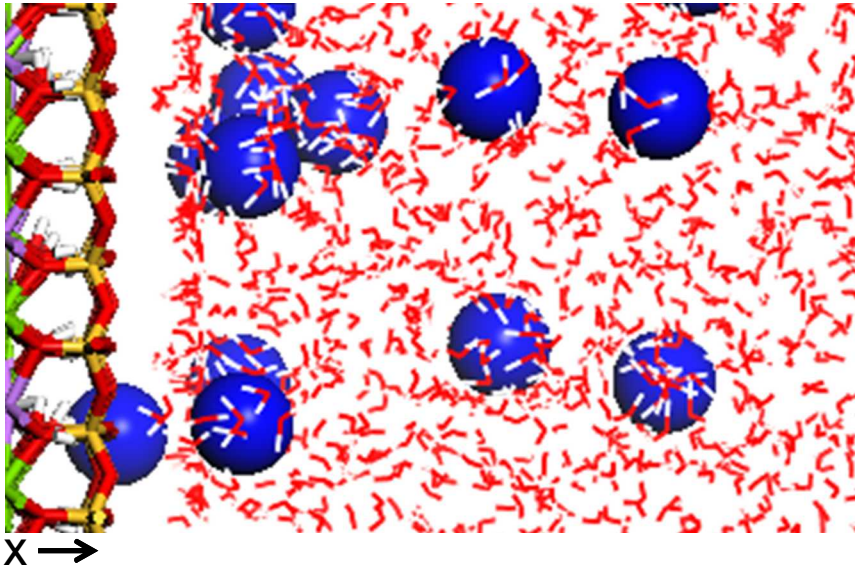
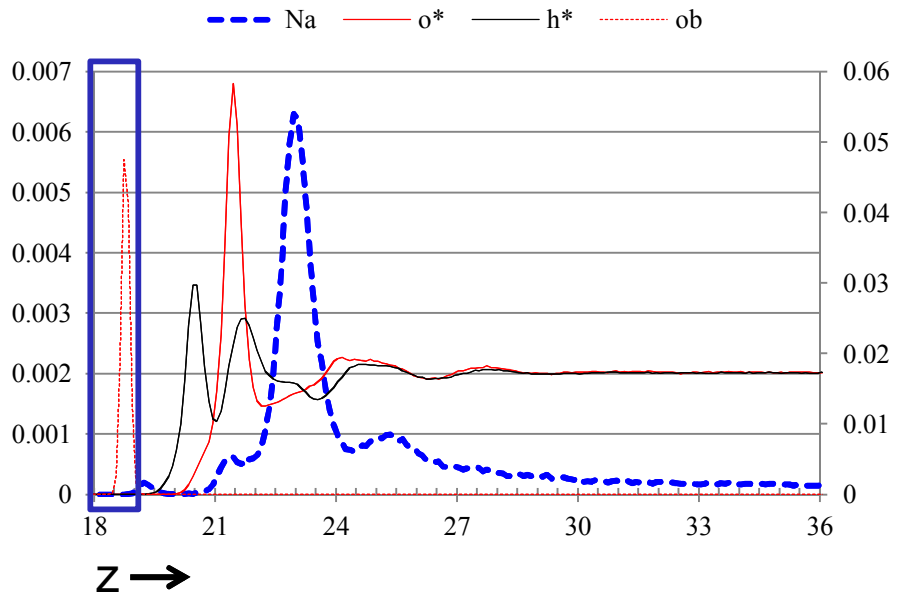
Sodium Density Profiles (Hectorite)

2D profiles: surface adsorption sites (Na^+)

y

x





1D profiles: adsorption layers

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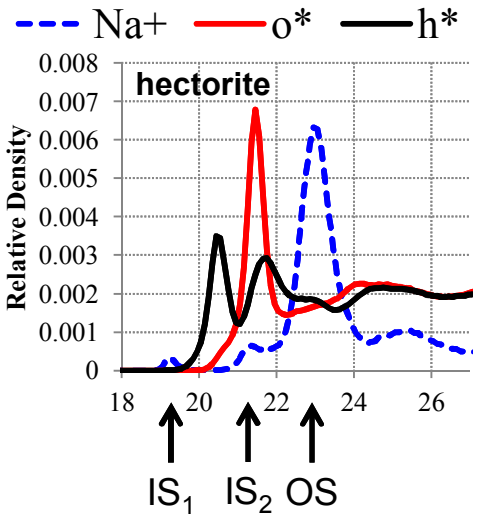
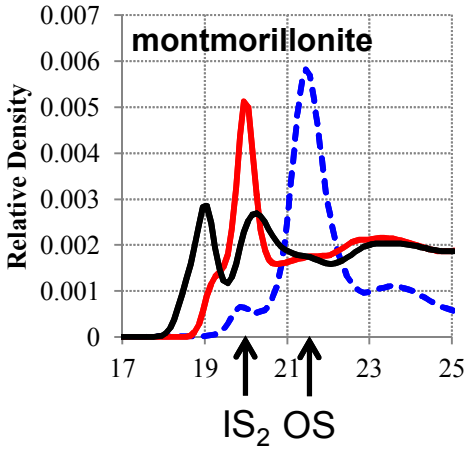
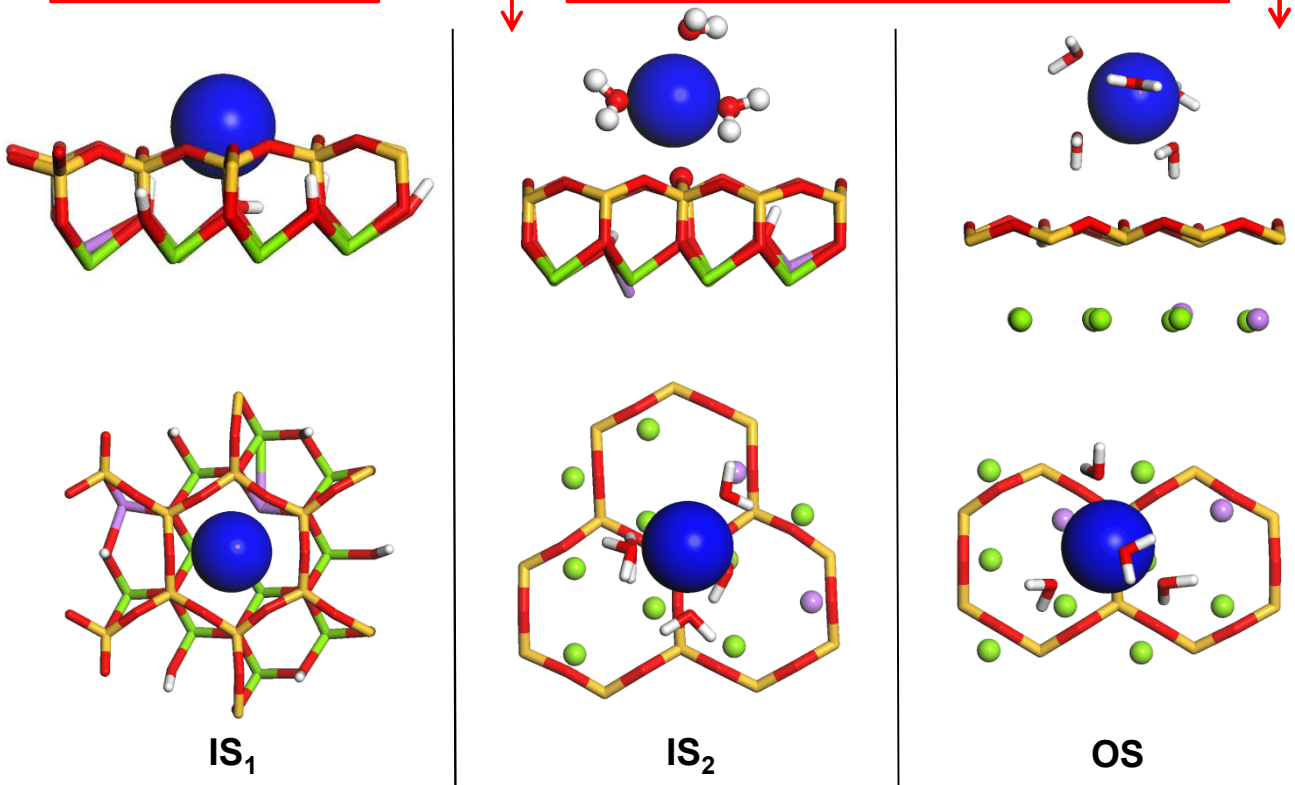
Inner-Sphere and Outer-Sphere Surface Complexes





hectorite only

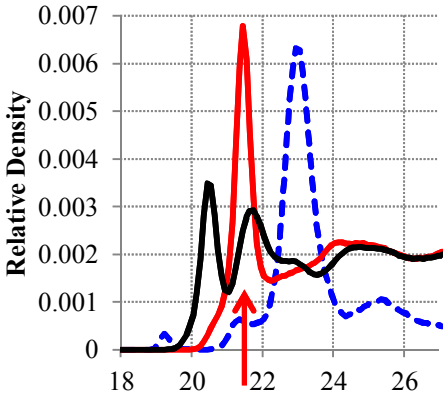
hectorite and montmorillonite

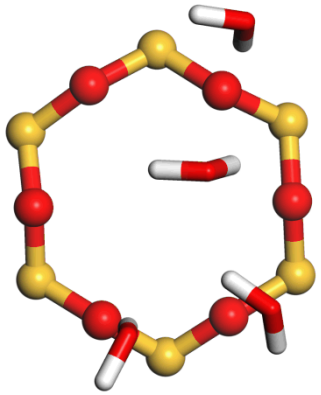


	IS$_1$	IS$_2$	OS
Abundance	0.1 %	3-4 %	52-55 %
Residence times (ps)	65(22)	Na^+ 2.3(1) H_2O 11.0(2)	Na^+ 31.1(5) H_2O 93.0(1)

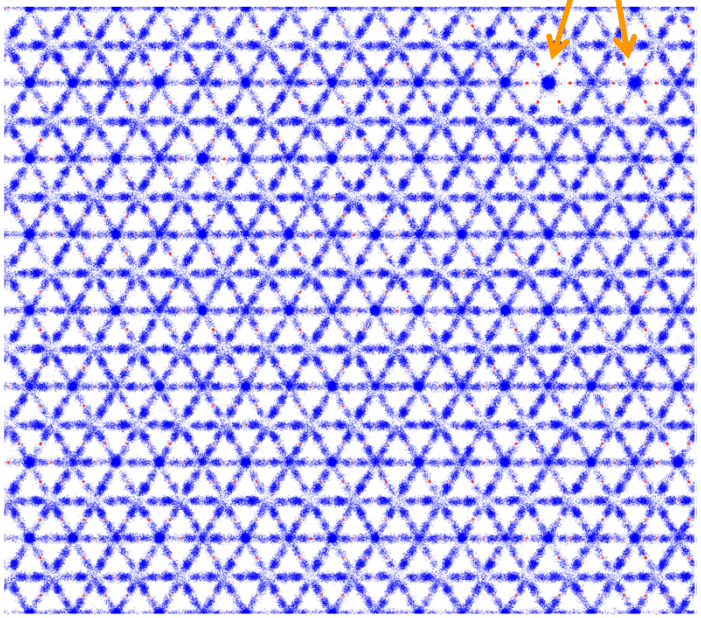
Hectorite results consistent with NMR results (Bowers et al, *JPCC* **2011**).

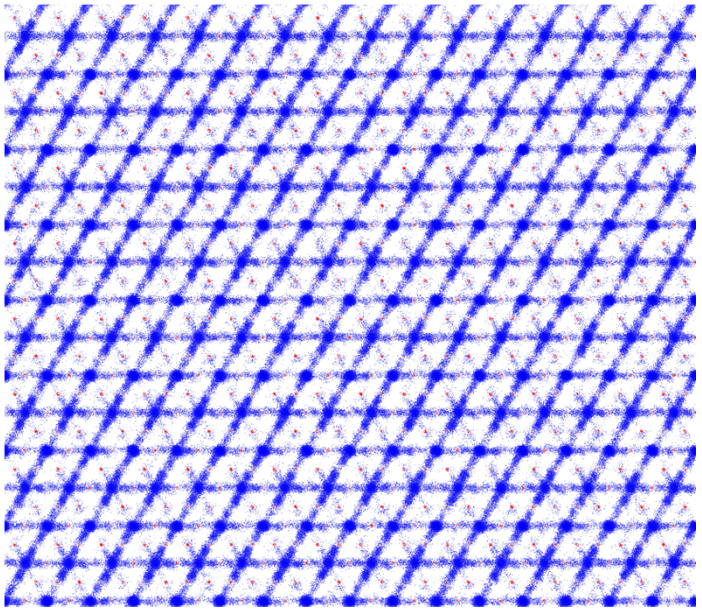
Structure of Adsorbed Water First Aqueous Layer





anhydrous Na^+ inner-sphere sites





hectorite

- Trioctahedral
- “Vertical” layer OH groups
- More water adsorption sites

montmorillonite

- Dioctahedral
- “Tilted” layer OH groups
- Fewer but dense adsorption sites

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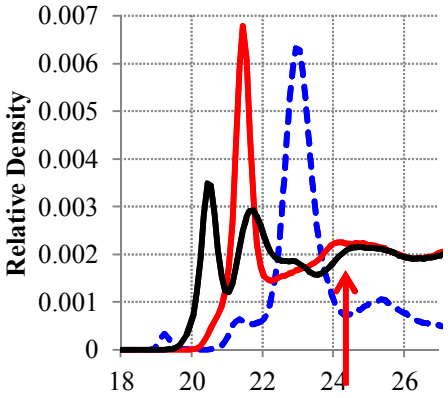
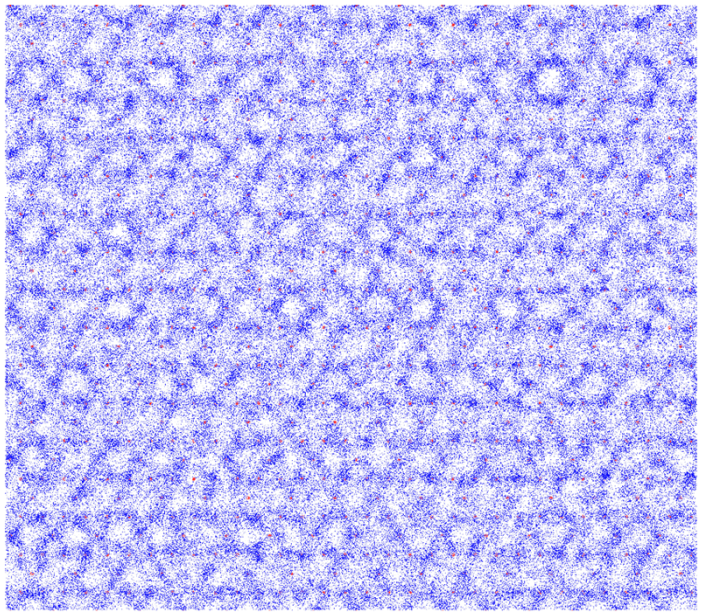
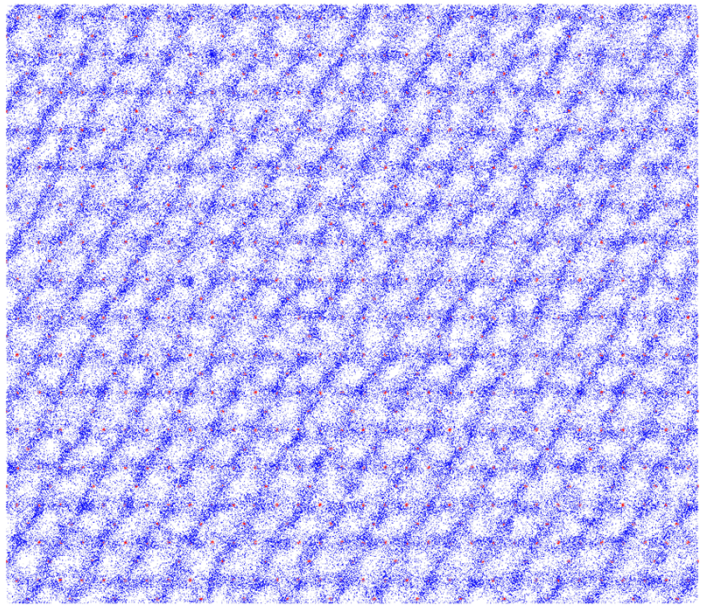
Structure of Adsorbed Water Second Aqueous Layer







y

x →

hectorite

montmorillonite

- Substantially less ordering in the second layer.
- Traces of the hexagonal structure (L1) still visible.

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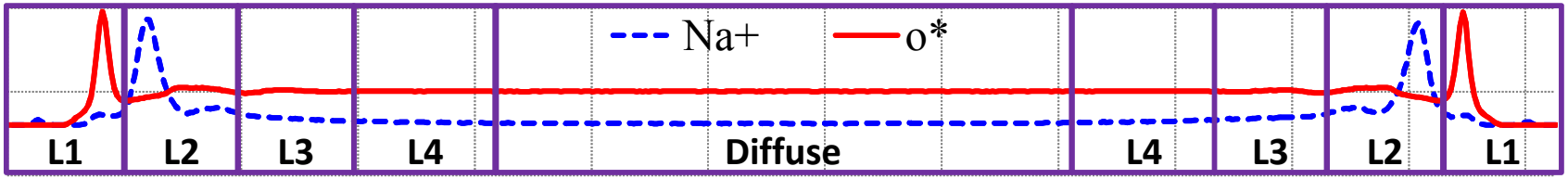
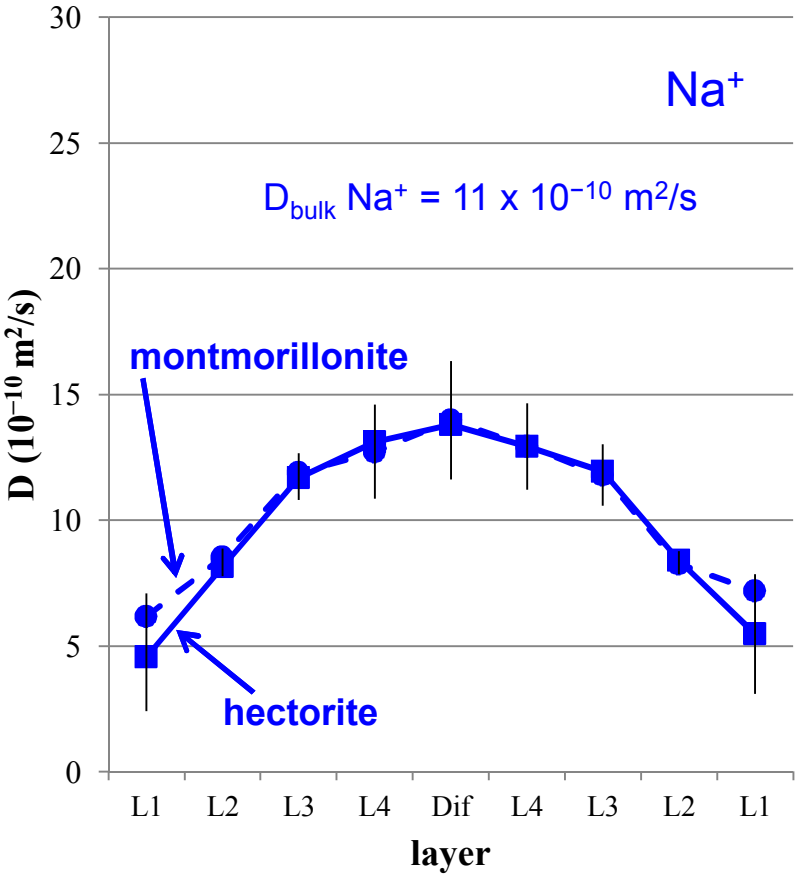
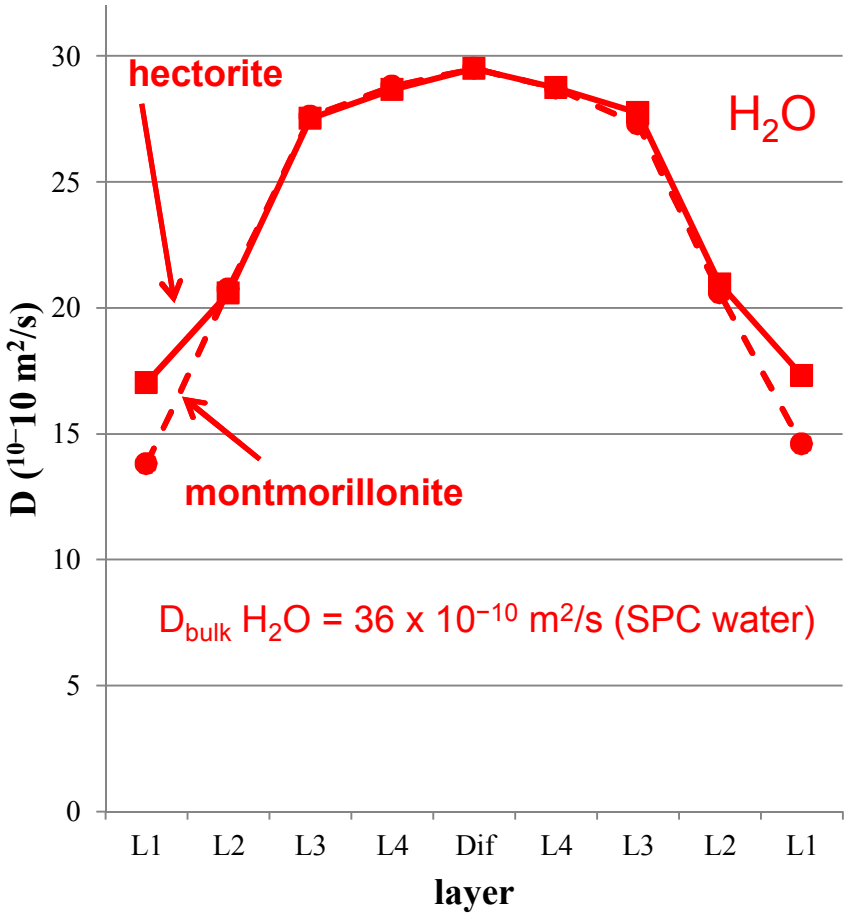
Water and Ion Diffusion at Clay Surfaces







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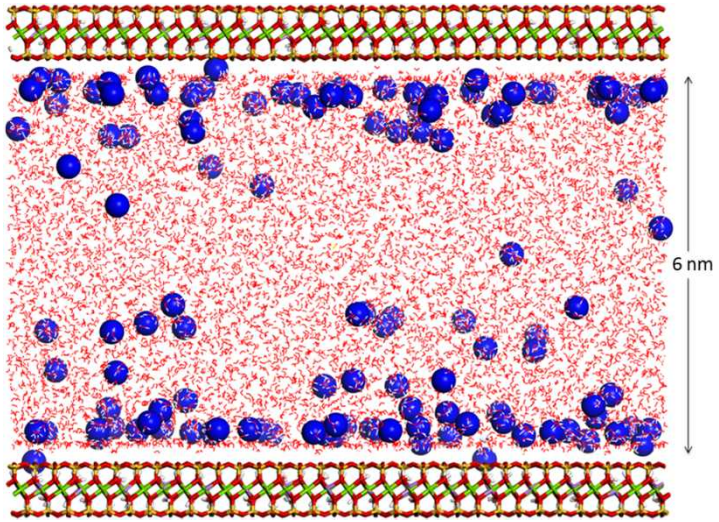
Identical diffusion behavior beyond the first water peak.

Conclusions

- MD simulations of clay nanopores used clay minerals with equivalent layer charge in the octahedral sheet but with different octahedral composition.
- Qualitative agreement with NMR studies of hectorite pastes. Sporadic appearance of anhydrous Na+ at the hectorite surface (easily missed with smaller system sizes or shorter run times).
- Effects due to clay structural features (octahedral vacancy sites, orientation of layer hydroxyl groups) have limited influence on interfacial structure (< 2.5 Å).
- There is a remarkable difference in the 2D structure of adsorbed water, likely due to the presence of vacancies in the octahedral sheet of montmorillonite.
- Analysis of the diffusion behavior in each aqueous layer shows clear differences in Na^+ and H_2O behavior in the first layer, but nearly identical behavior beyond that.
- Both nanopores show bulk-like structural and diffusion properties within 10 Å of the surface.



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