SAND2021-10176C

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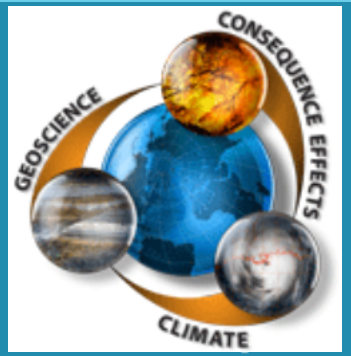
Diffusion Properties of Aqueous Fluids in Mineral Nanopores



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U.S. DEPARTMENT OF ENERGY NNSA

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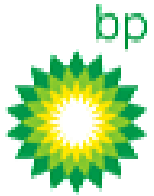
Acknowledgements

Research Sponsored by

BP America



United States Department of Energy
Office of Basic Energy Sciences

Clay Interlayers

Randall Cygan, Sandia (retired)
Joanne Fredrich (BP)
Gary Jerauld (BP)

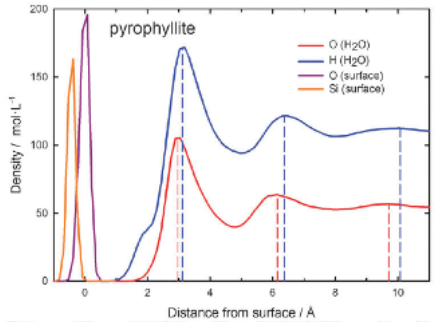
Clay Nanopores

Geoff Bowers, St. Mary's College (Maryland)
Randall Cygan, Sandia (retired)
Andrey G. Kalinichev, Ecole des Mines de Nantes
R. James Kirkpatrick, Michigan State University

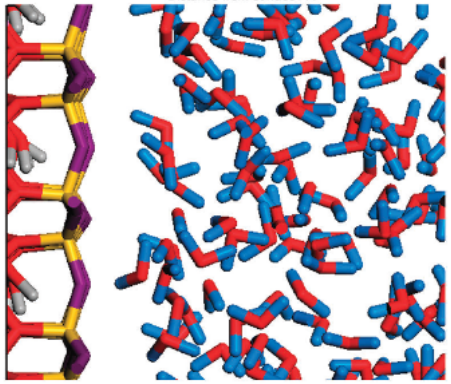
Imogolite

Rafael González (U. Mayor, Chile)
Javier Rojas-Nunez (U. de Santiago de Chile)

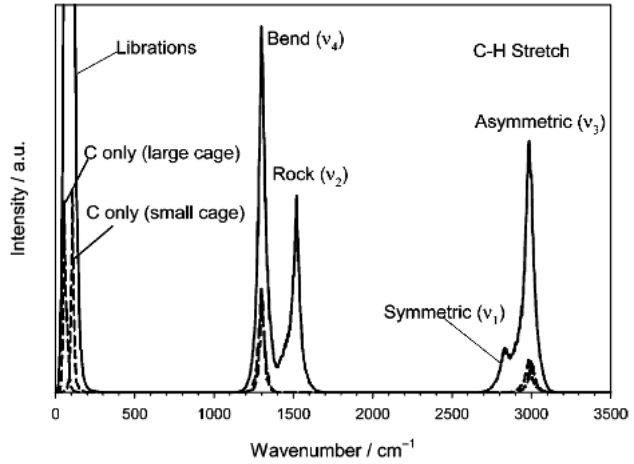
Molecular simulation of dynamical processes at mineral interfaces



Interfacial structure and dynamics

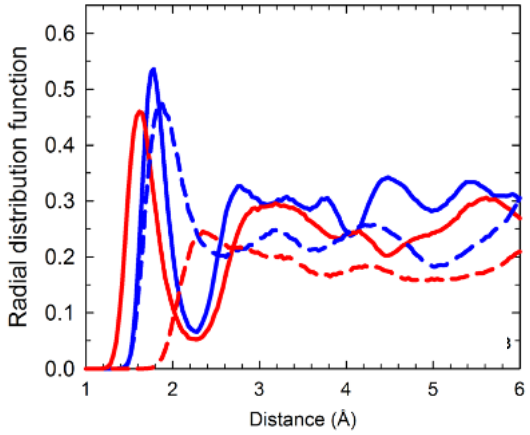


Vibrational motion



Clay Force Field energy expression

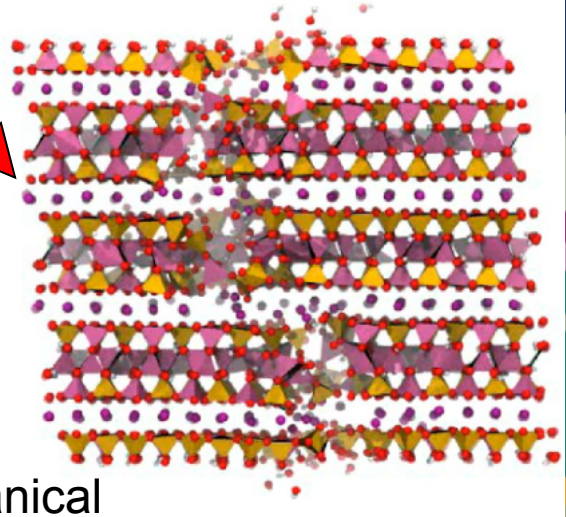
No Image



Local coordination

Further development of Clayff has enabled simulations of hydroxylated mineral surfaces.

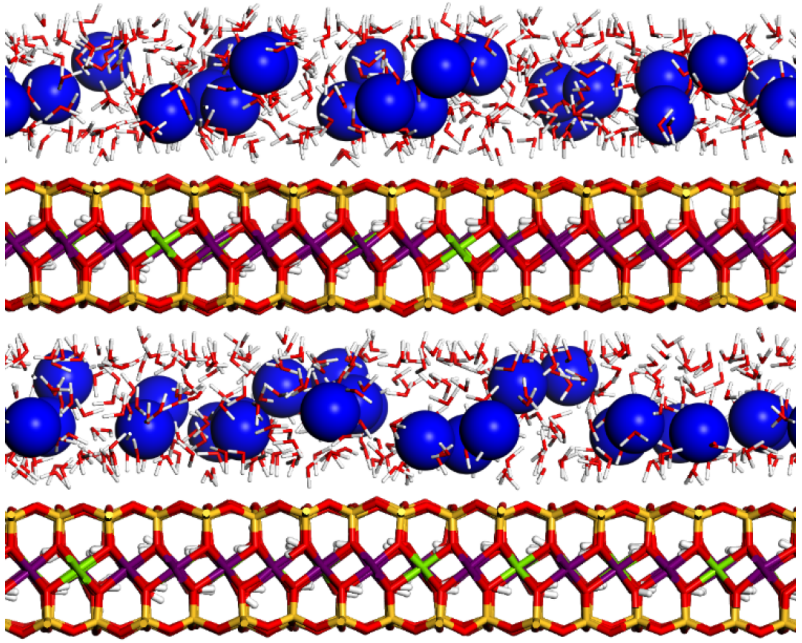
Zeitler et al, *J. Phys. Chem. C* **2014**, *118*, 7946
Pouvreau et al, *J. Phys. Chem. C* **2017**, *121*, 14757
Pouvreau et al, *J. Phys. Chem. C* **2019,** *23*, 11628



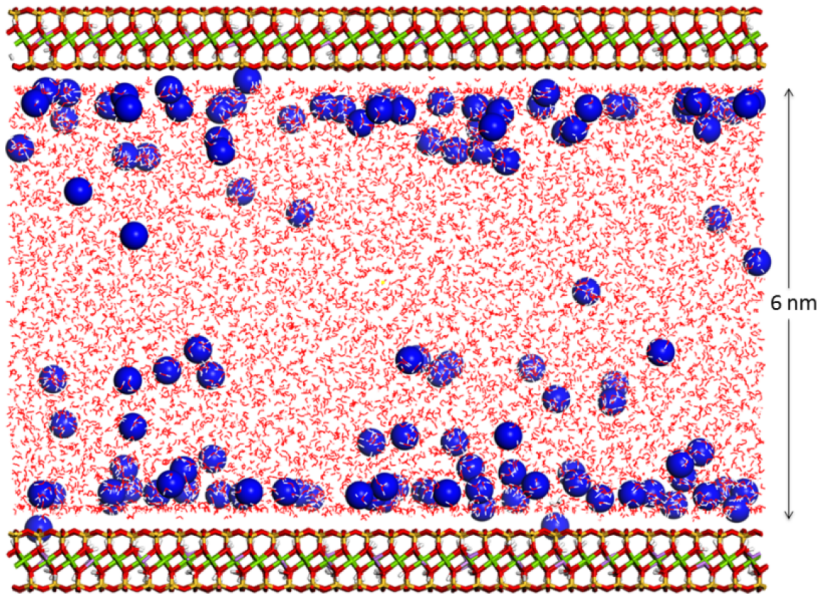
Mechanical properties

Examples of Fluid Diffusion in Mineral Nanopores

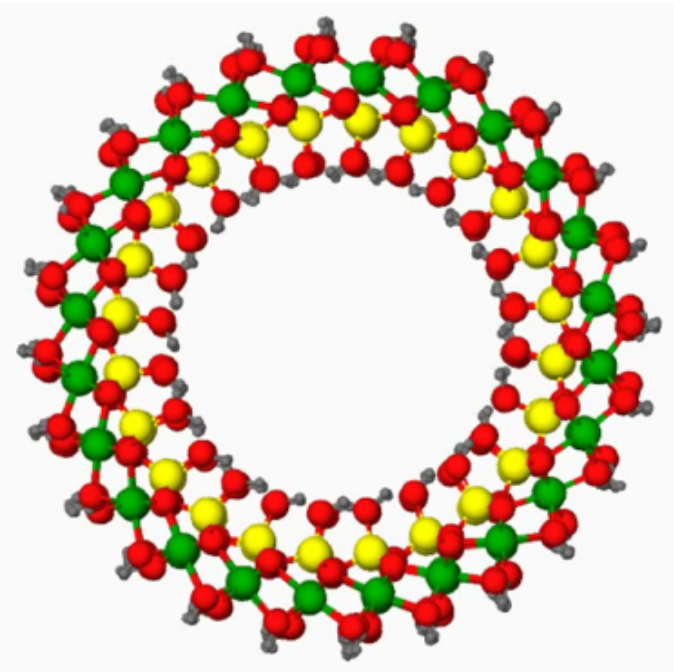
Clay Interlayers



Clay Nanopores



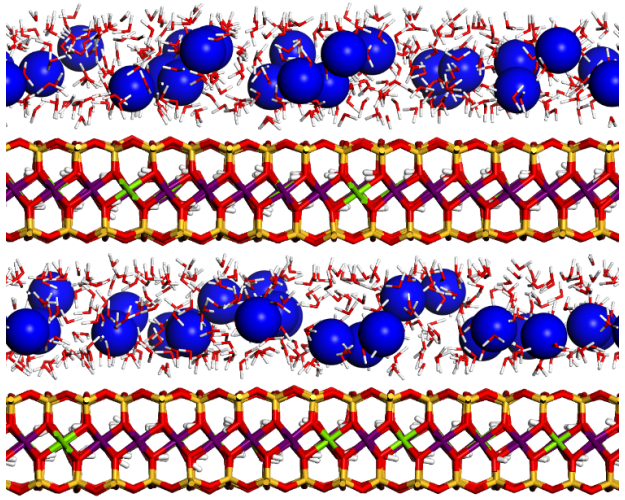
Imogolite Nanotubes



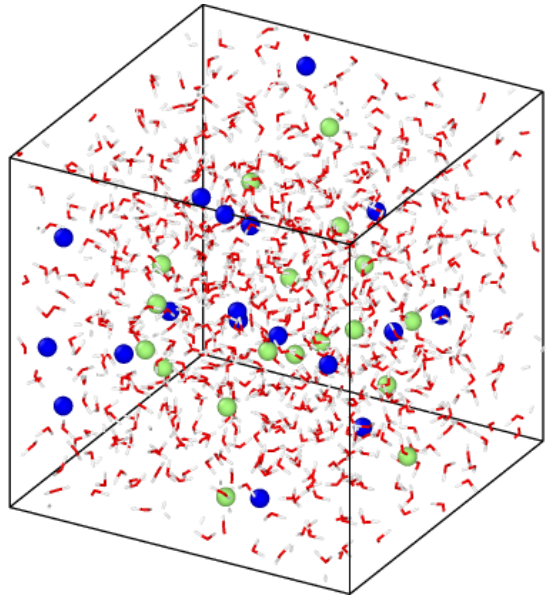
Diffusion in Clay Interlayers

Randall Cygan, Sandia
Joanne Fredrich (BP)
Gary Jerauld (BP)

- Controls adsorption and ion exchange properties relevant to:
  - Contaminant migration
  - Materials properties
  - **Hydrocarbon extraction**
- Provides a critical link between:
  - Molecular simulations
  - Laboratory measurements (NMR, neutron scattering)
  - Field measurements (**conductivity**)
- Simulation models span a range of porosity in natural rock phases:
  - Interlayers (nanoscale porosity)
  - Bulk solutions (mesoscale porosity)



nanoscale porosity

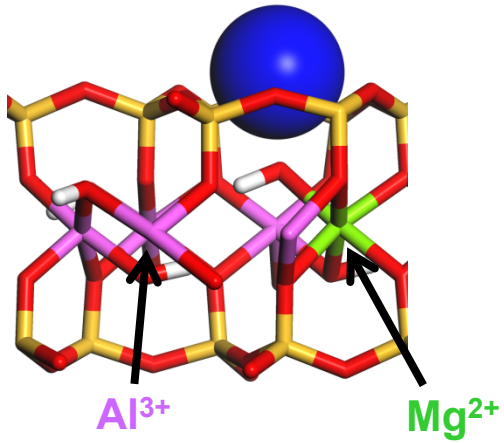


bulk solutions
mesoscale porosity

Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Molecular Dynamics (MD) Simulation Methods

- Montmorillonite
- Bulk fluids with same cation concentration as montmorillonite interlayers.
  - NaCl, 0.05 *M* – 2.78 *M*
  - $CaCl_2$, 0.05 *M* – 0.89 *M*
- Clayff parameters, flexible SPC water (Cygan et al, *J. Phys. Chem. B*, **2004**).
- Constant-pressure simulations (*NPT*), 10 ns production simulation.
- Diffusion analysis: mean-square displacement in 2D (interlayers) or 3D (bulk fluids).
- Conductivity calculated from ion diffusion coefficients (Nernst-Einstein).



Counterion	Na^+, Ca^{2+}
Layer Charge	Low (−0.375 e/unit cell) High (−0.750 e/unit cell)
Water Content	1W – 3W
Temperature	Low (300 K) High (366 K)

Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Validation: Na-montmorillonite, 300 K

Interlayer Water Diffusion Coefficients (D_w, 10^{-10} $m^2 \cdot s^{-1}$)

Method	Water Layers	D_W
MD	1W 2W	5 13
Exp	1W 2W	1 – 3 5 – 10

Malikova et al, *J. Phys. Chem. B* **2006**, *110*, 3206

Na^+ Diffusion Coefficients (D_{Na}, 10^{-10} $m^2 \cdot s^{-1}$)

Method	T (K)	Water Layers	D_{Na}
MD	300	1W 2W	1.6 5.1
Exp	293	30% RH 90% RH	0.5 10

MX-80, Salles et al, *J. Phys. Chem. C* **2015** *119*, 10370

Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

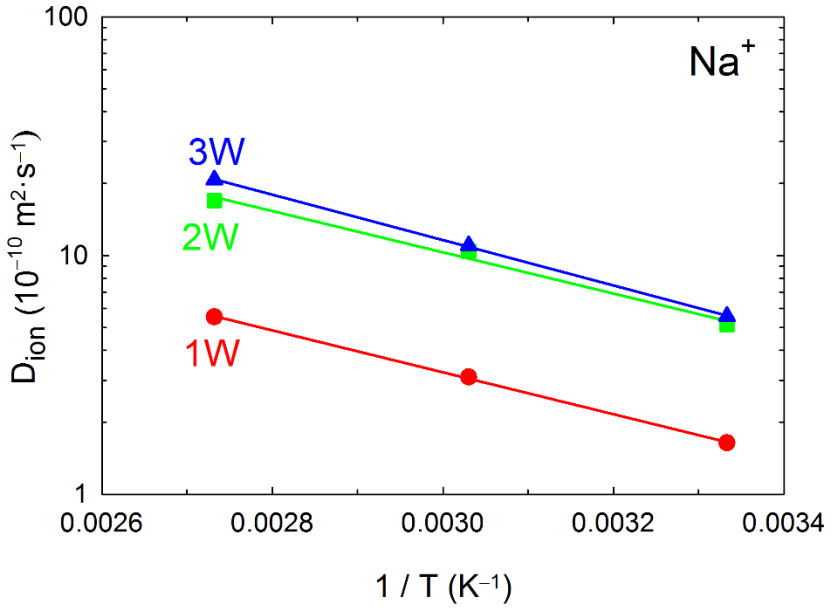
Activation Energies, Na-montmorillonite, 300 K – 366 K

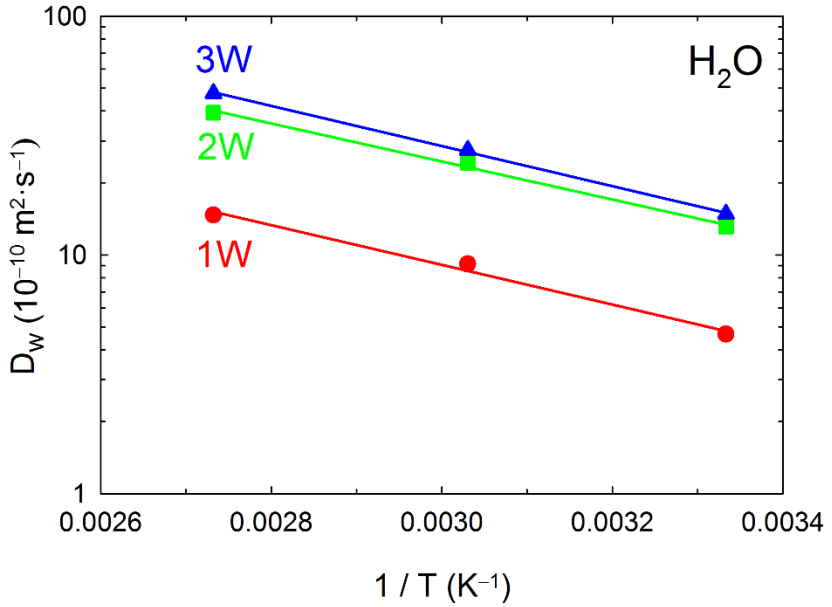
Comparison of E_{act} values (kJ·mol^{-1})

Method	Water Layers	H_2O	Na^+
MD	1W	15.9	16.8
	2W	15.2	16.5
	3W	16.1	18.2
Exp*		11.6	
Exp	Bulk**	16.9	18.4
	H-bond***	20.5	

* Sánchez et al, *ES&T* **2009**, *43*, 3487
** Gates et al, *J. Phys. Chem. C* **2012**, *116*, 5558
*** Feyereisen, et al, *J. Phys. Chem.* **1996**, *100*, 2993

E_{act} values similar to water H-bond energy. Breaking H-bonds is a critical step in interlayer diffusion.

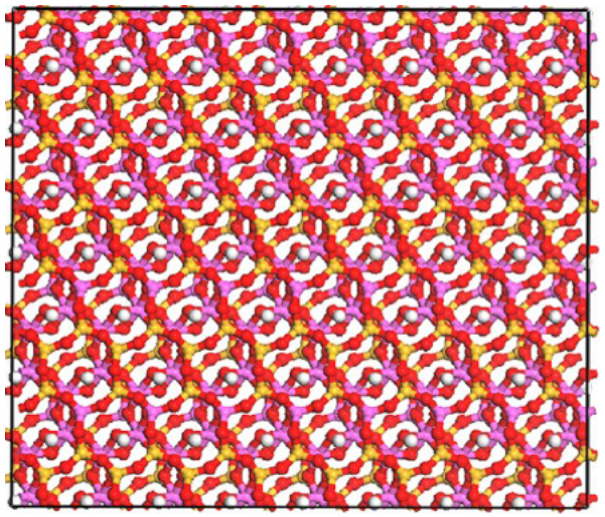


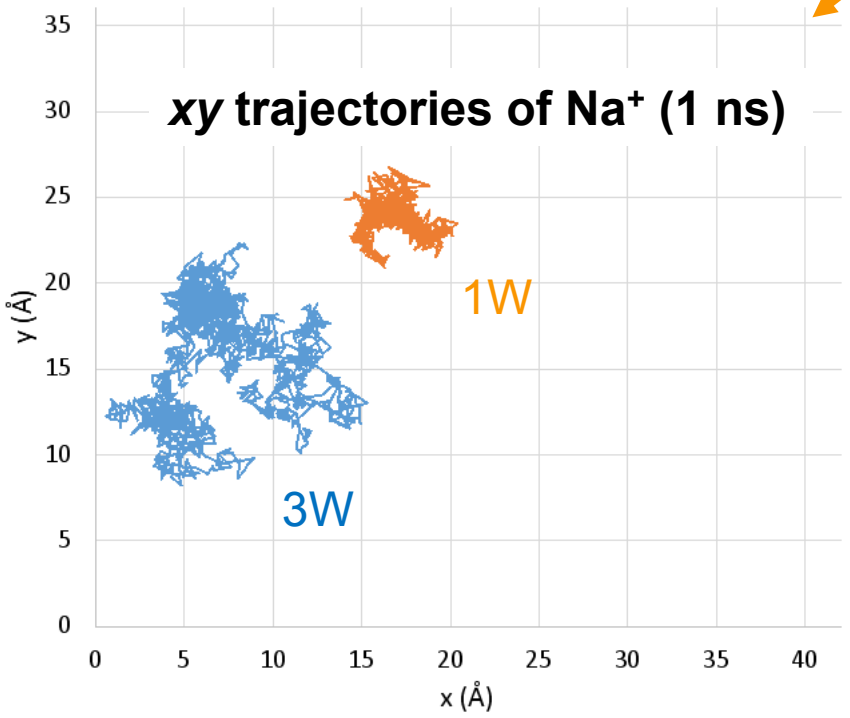


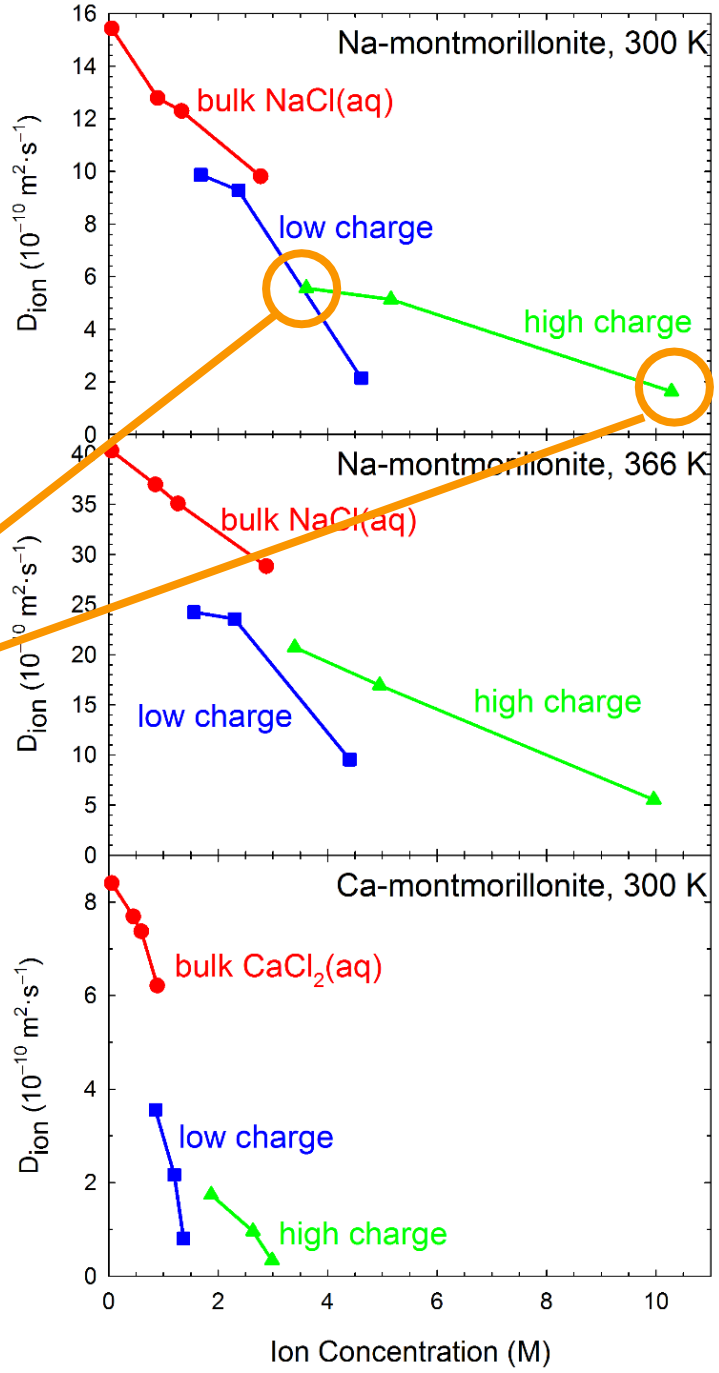
Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Ion Diffusion – Interlayer vs Bulk

- Bulk fluids have equivalent ppm ion concentrations but lower molarity due to reduced accessible volume in clay interlayers.
- Trends: *D* decreases with:
  - Increasing ion concentration (3W > 2W > 1W).
  - Increasing layer charge (more hydrophobic environment at low charge).
  - Decreasing temperature.





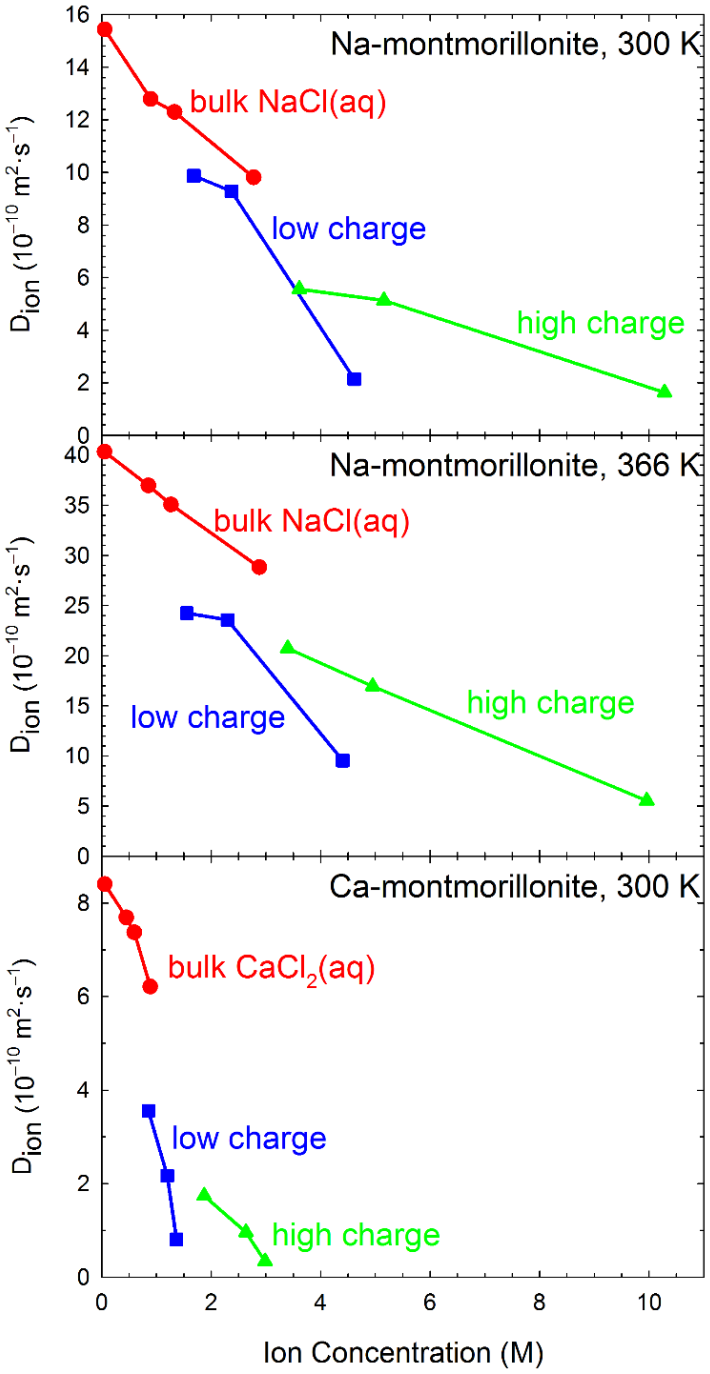


Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Water Diffusion – Interlayer vs Bulk

- Interlayer fluids exhibit similar diffusion behavior as bulk fluids of equivalent concentration.
- Comparison of D_W values with a reference electrolyte solution seems more appropriate than pure water.
- Penetration depth: time required for transport through 1-μm of clay grain (low charge, 300 K):

Water Content	Na^+	H_2O
1W	0.7 ms	0.2 ms
3W	0.2 ms	0.07 ms



Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

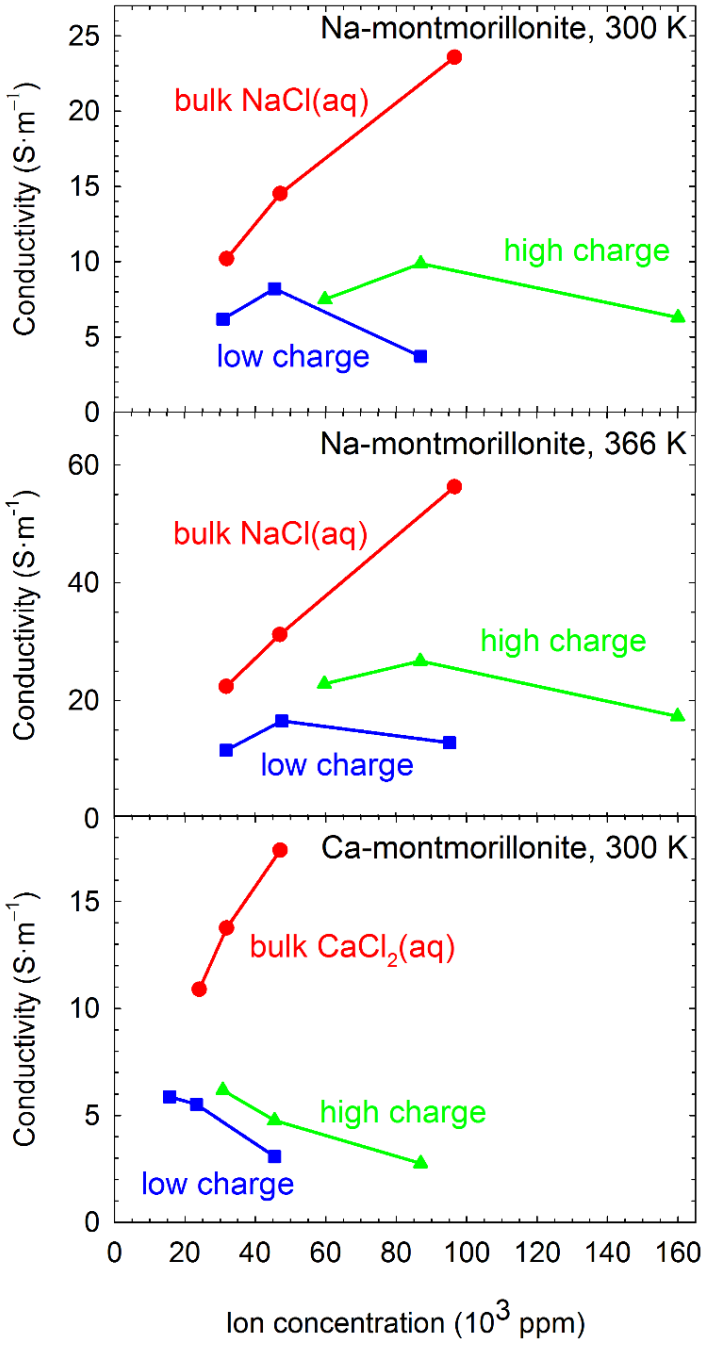
Electrical Conductivities

concentration

diffusion coefficient

Nernst-Einstein: $\sigma = \frac{n z^2 e^2 D}{kT}$

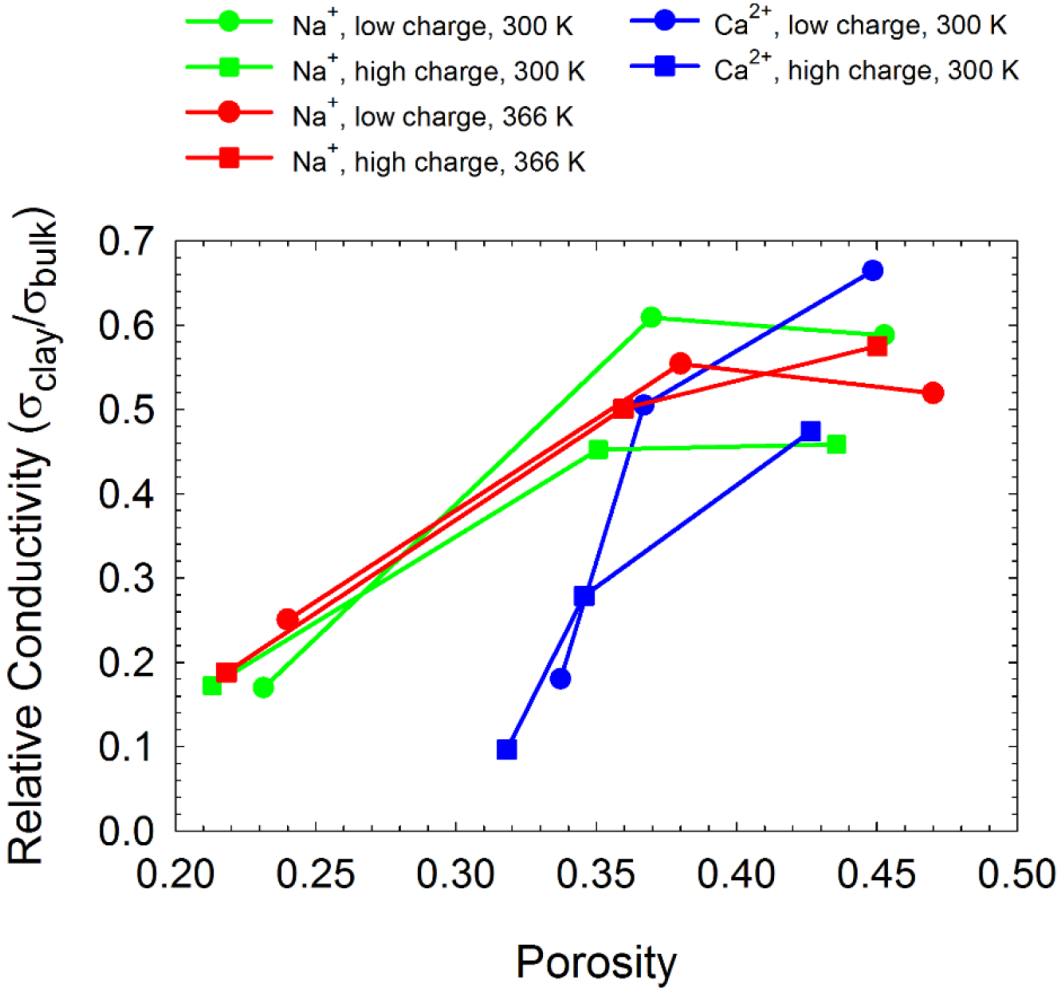
- Concentration units (ppm) consistent with conductivity measurements.
- Bulk solutions contain chloride ions.
- Layer charge has little effect on interlayer conductivity.
- Opposite trends in conductivities:
  - Bulk solutions: σ increases as ion concentration increases (more ions but only a slight decrease in diffusion).
  - Interlayers: σ decreases as ion concentration increases due to reduced ion mobility (3W > 2W > 1W).



Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Effect of Porosity on Conductivity

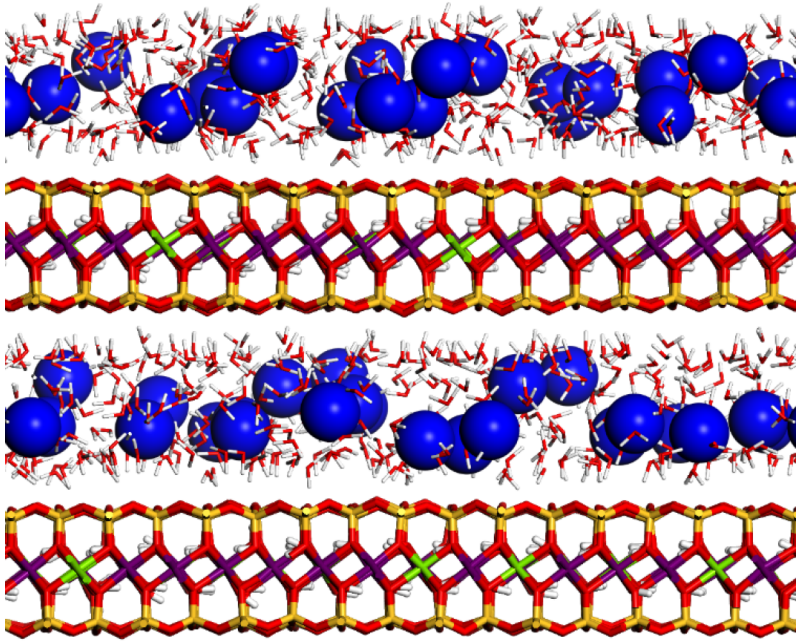
- Allows for direct comparison between clays with different counterions and layer charges.
- σ_{bulk} values (same ppm concentration as the interlayer) estimated from linear trend in bulk solution conductivities.
- At higher humidity (2W state), higher layer charge results in lower relative conductivity.
- For Na-montmorillonite, very little effect due to temperature.
- This methodology can be used to estimate relative conductivities in clay-bearing rocks for any given reference solution (pore fluid).



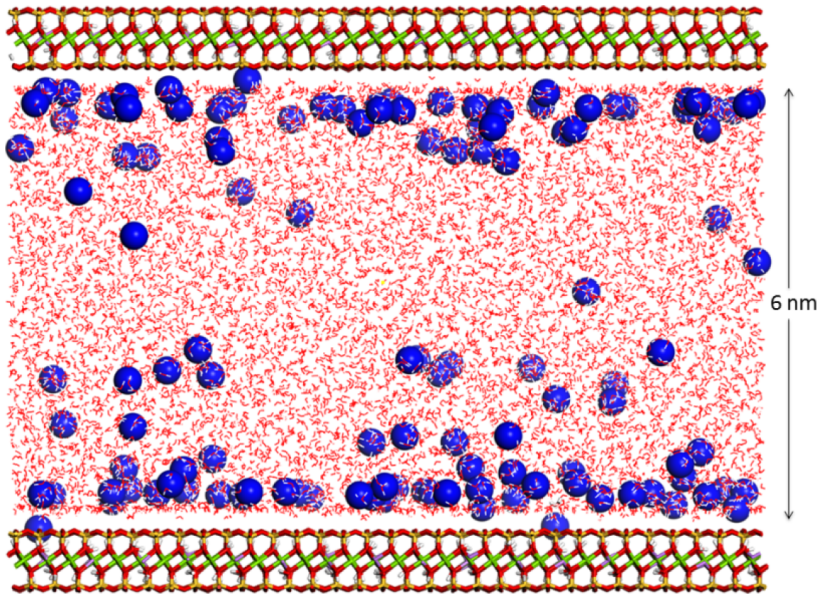
Greathouse et al., *J. Phys. Chem. C* **2016**, *120,* 1640

Examples of Fluid Diffusion in Mineral Nanopores

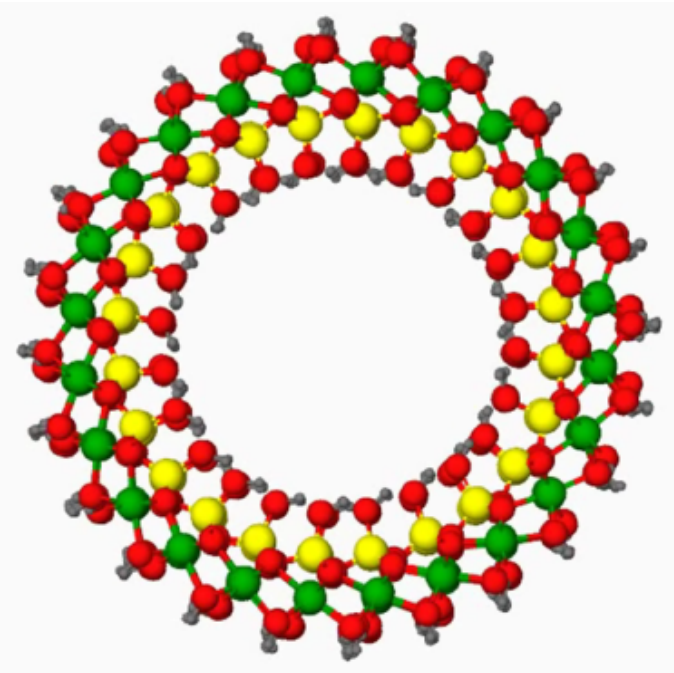
Clay Interlayers



Clay Nanopores



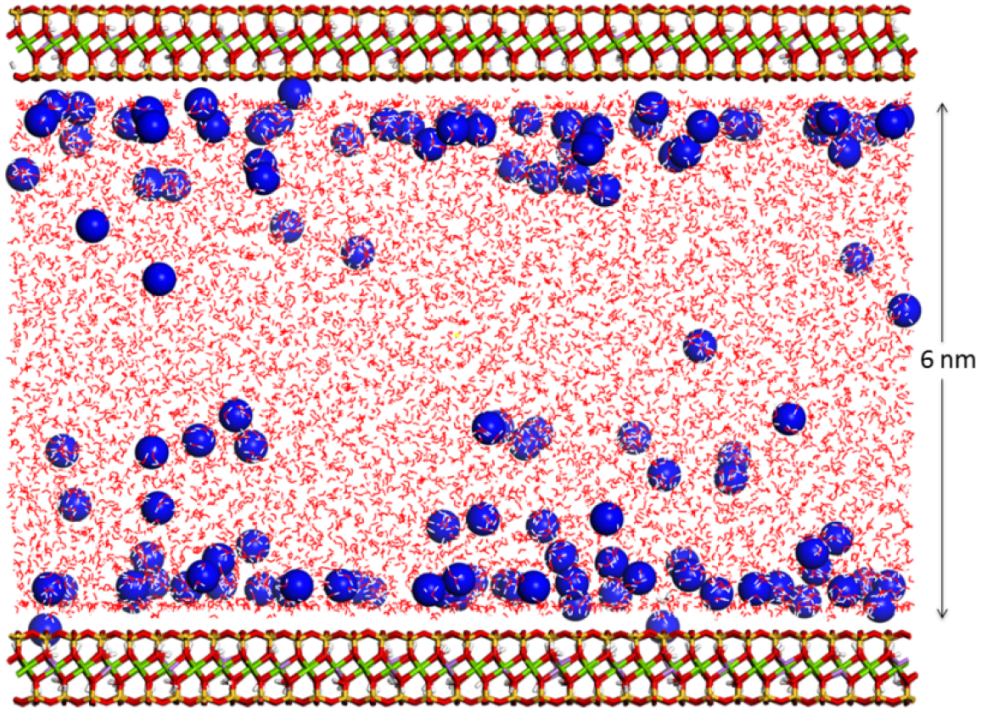
Imogolite Nanotubes



Solution Dynamics at Clay Interfaces

Geoff Bowers, St. Mary's College (Maryland)
Randall Cygan, Sandia
Andrey G. Kalinichev, Ecole des Mines de Nantes
R. James Kirkpatrick, Michigan State University

- 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**, *115*, 23395).
  - Molecular dynamics simulation of Na-hectorite interlayers (Morrow et al, *JPCC* **2013**, *117*, 5172).

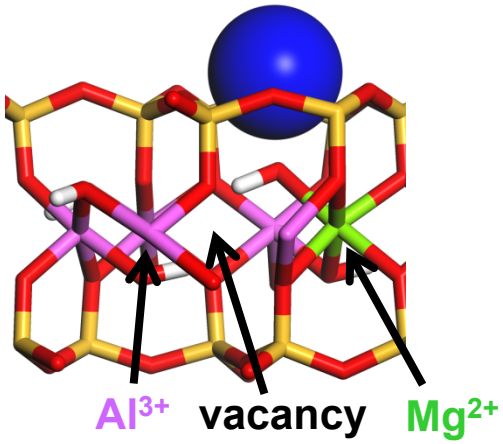
Greathouse et al, *J. Phys. Chem. C* **2015**, *119*, 17126.

Simulating Fluid Diffusion in Clay Nanopores

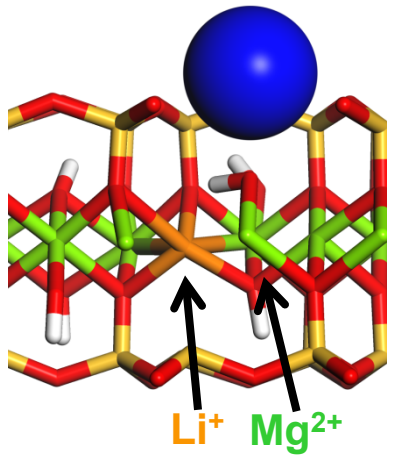
- MD simulations of clay nanopores (external basal surfaces) similar to paste samples used in NMR experiments.
- Clayff parameters, flexible SPC water.
- Large system sizes and run times to thoroughly sample all possible adsorption sites and surface complexes:
  - NPT to equilibrate pore width, NVT for analysis, 298 K
  - 80 x 70 x 90 Å^3, 50k atoms, 6 nm pore width
  - 10 x 10 ns per clay

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

Na-montmorillonite



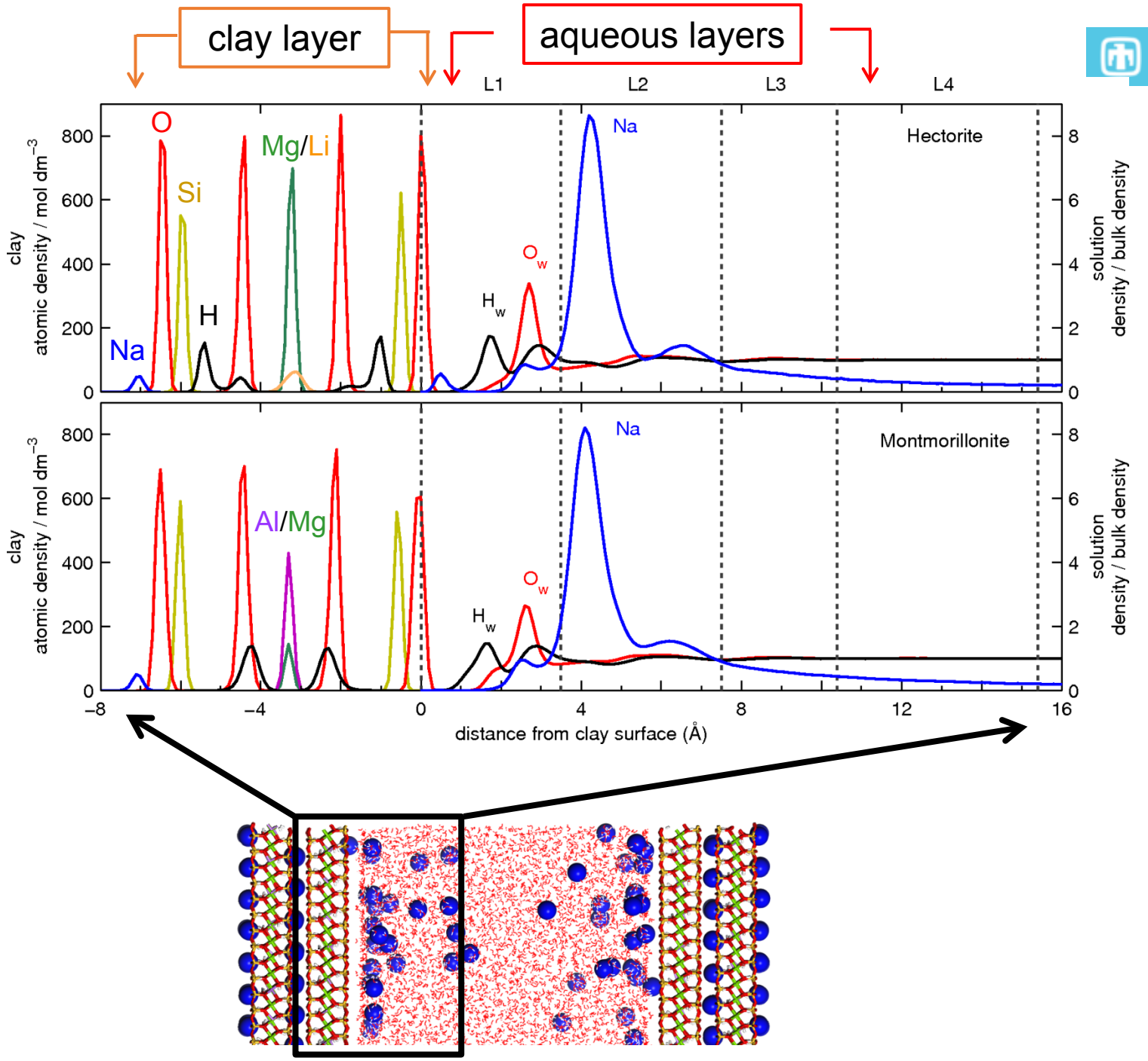
Na-hectorite



Greathouse et al, *J. Phys. Chem. C* **2015**, *119*, 17126.

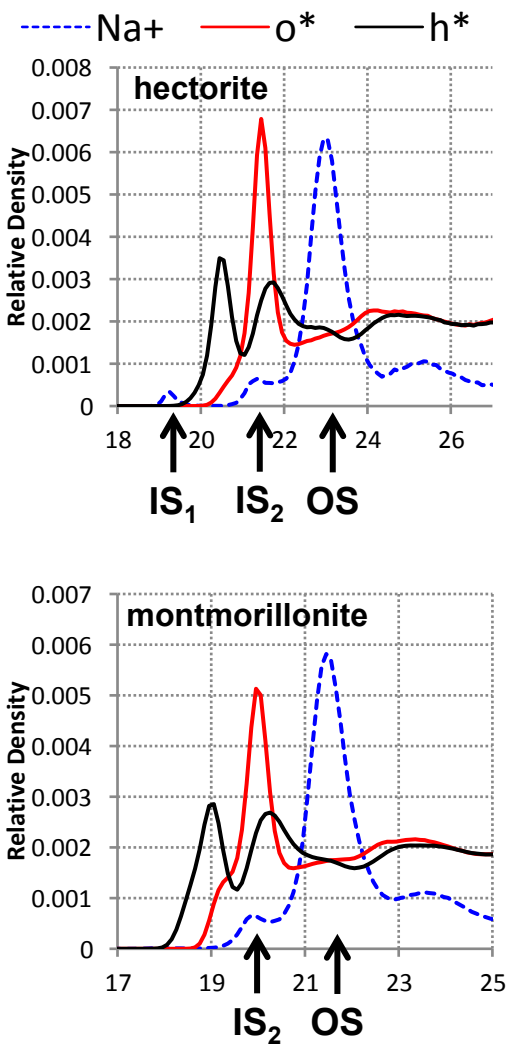
1D Structure

- 1D atomic density profiles averaged over 10 separate simulations.
- Aqueous regions defined by water peaks: L1, L2, L3, L4, Diffuse.



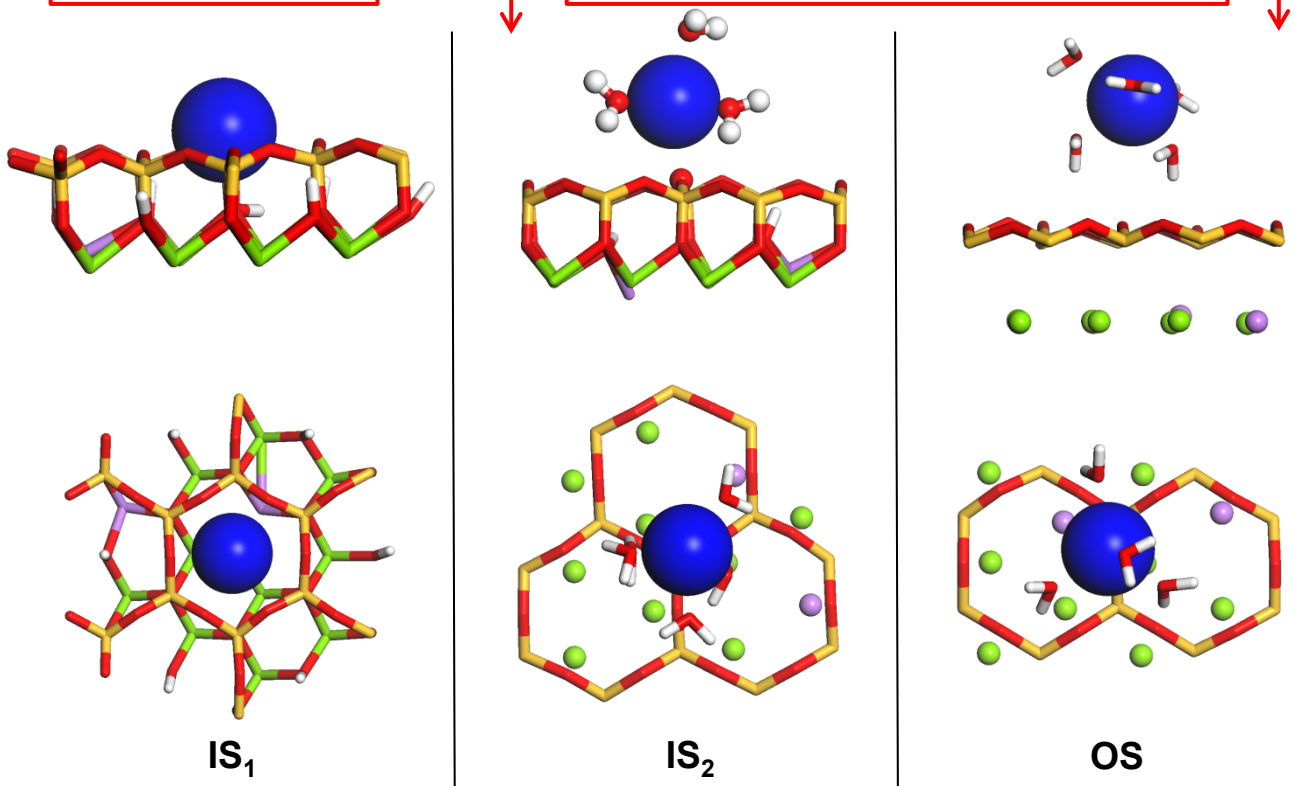
Greathouse et al, *J. Phys. Chem. C* **2015**, *119*, 17126.

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)

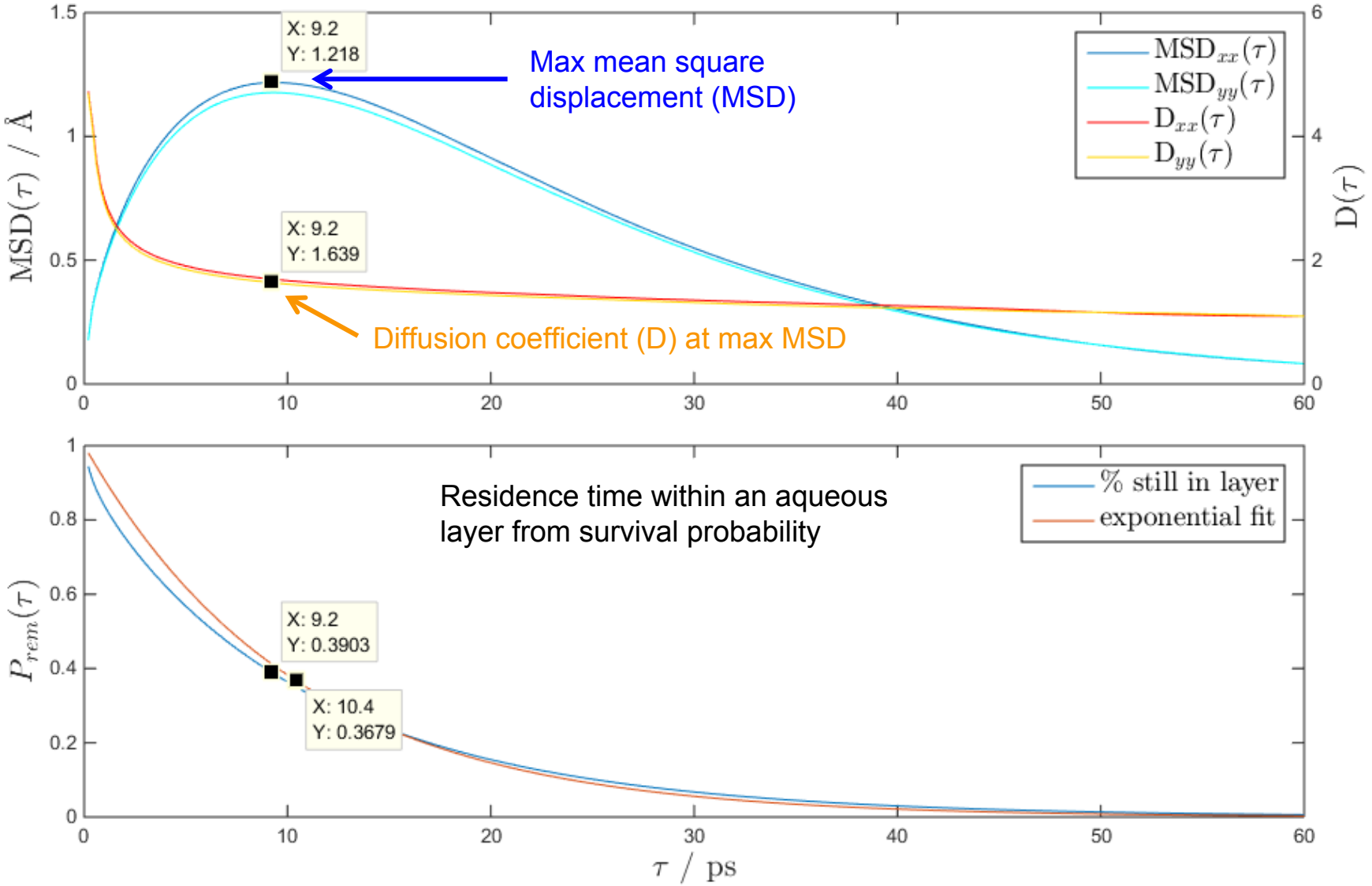
Greathouse et al, *J. Phys. Chem. C* **2015**, *119*, 17126.

Hectorite results consistent with NMR results (Bowers et al, *JPCC* **2011** *115*, 23395).

Diffusion and Residence Time Analysis

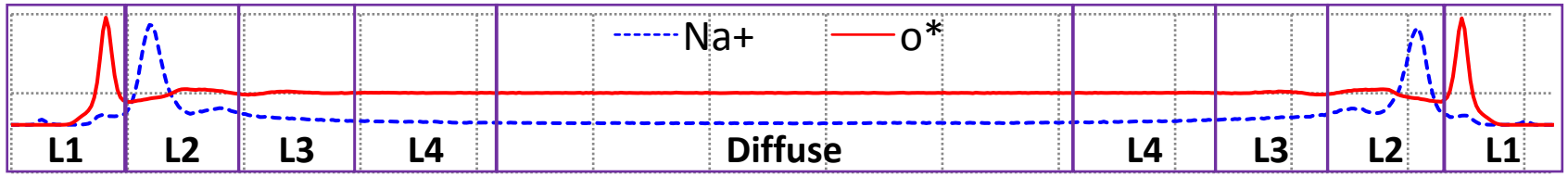
Diffusion coefficients and residence times calculated as a function of distance from mineral surface.

Rotenberg et al, *J. Phys. Condens. Matter* **2010**, *22*, 284114



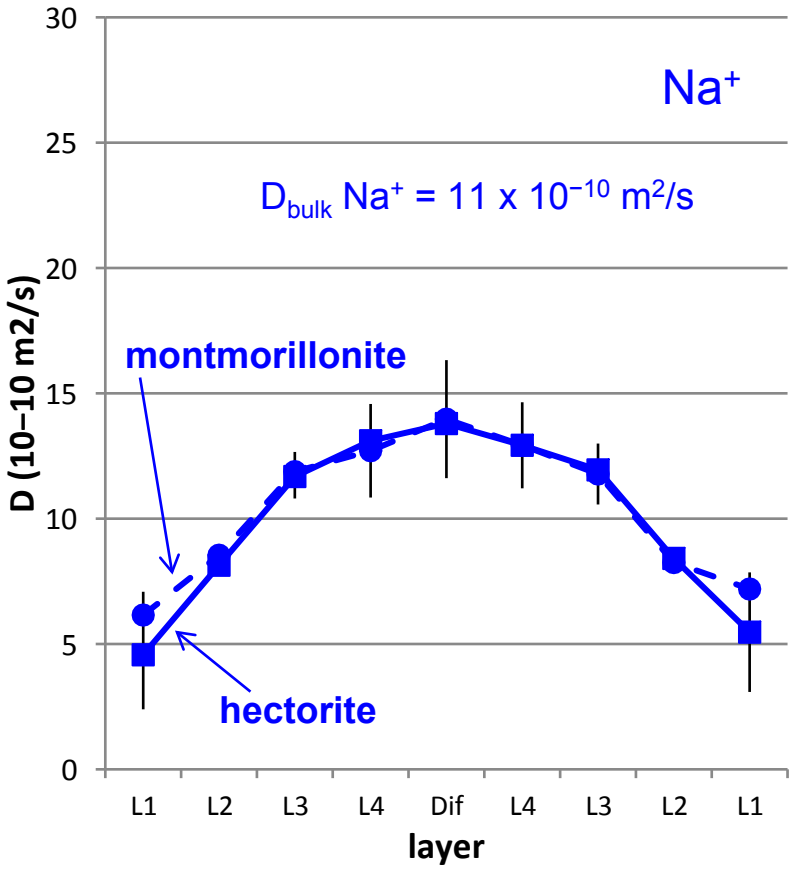
Greathouse et al, *J. Phys. Chem. C* **2015**, *119*, 17126.

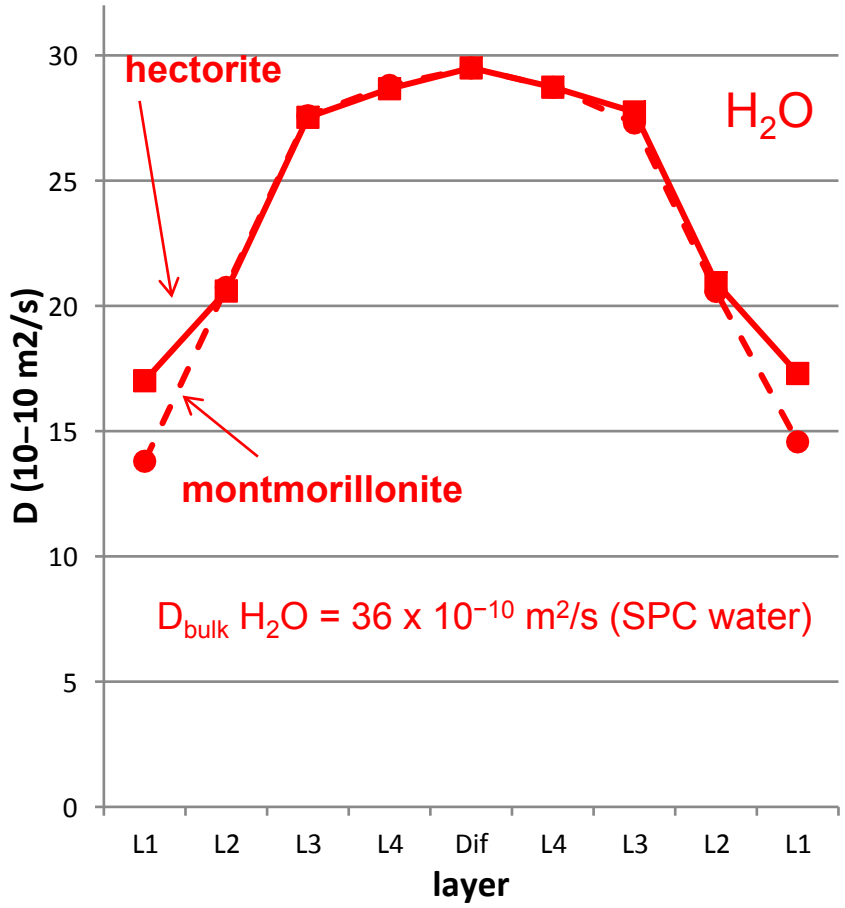
Water and Ion Diffusion at Clay Surfaces



Identical diffusion behavior beyond the first water peak.

Bulk-like structural and diffusion properties beyond 10 Å from the surface.





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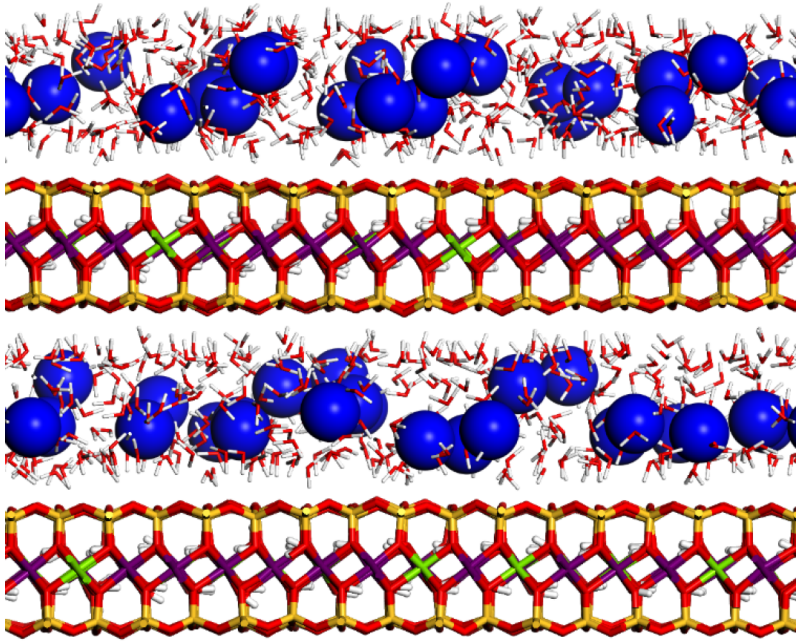
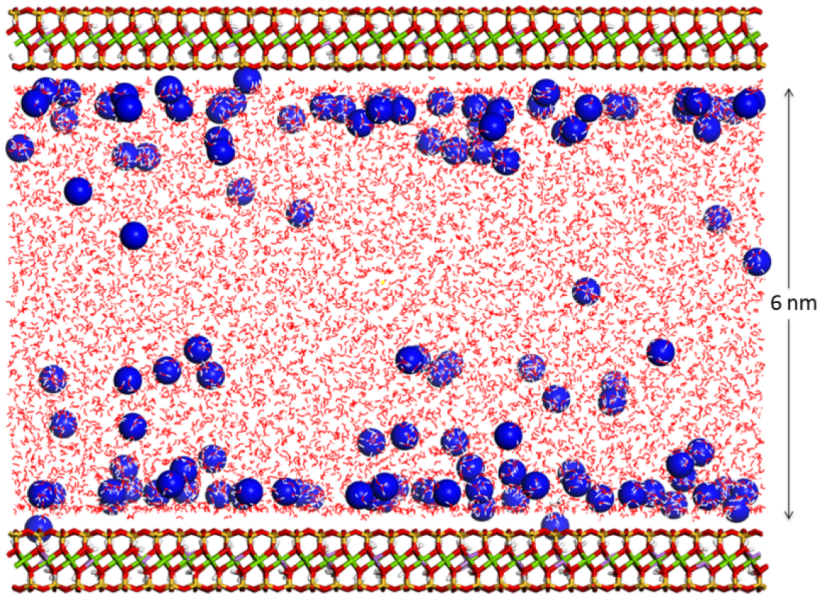
Examples of Fluid Diffusion in Mineral Nanopores

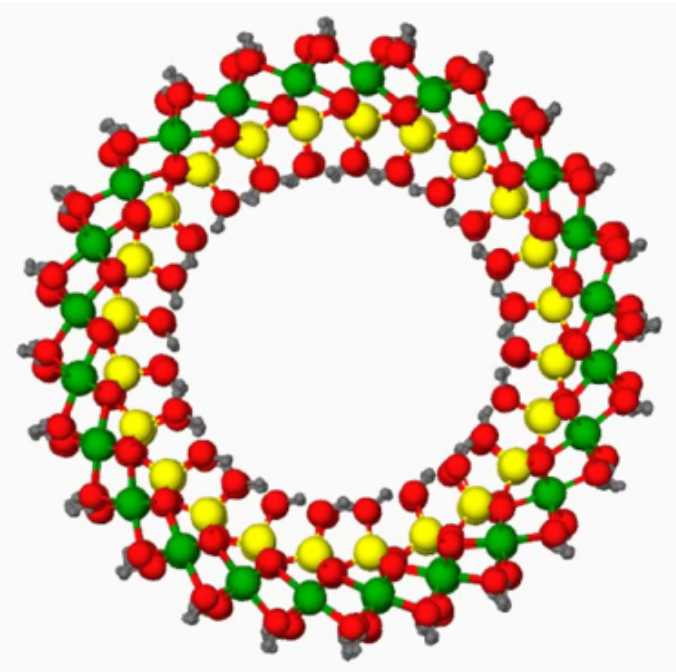
Clay Interlayers



Clay Nanopores

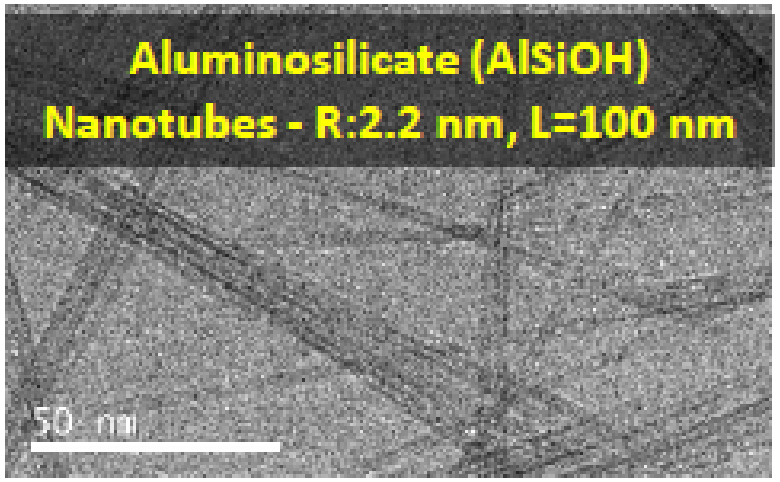


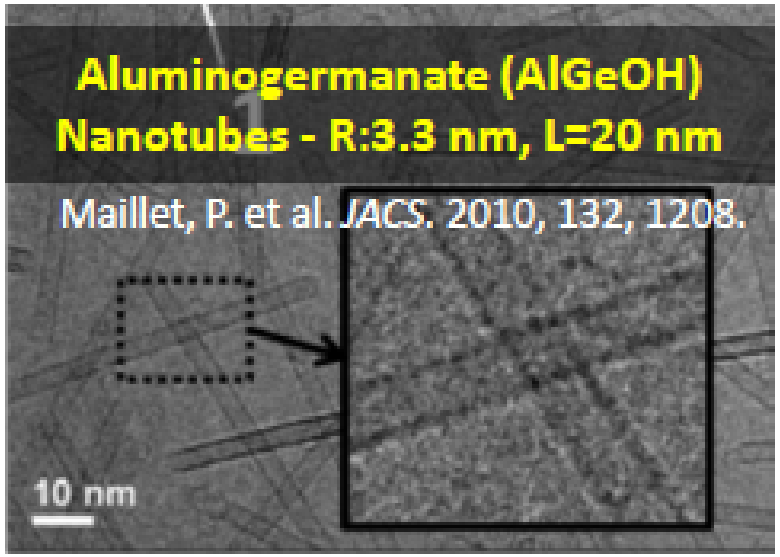
Imogolite Nanotubes



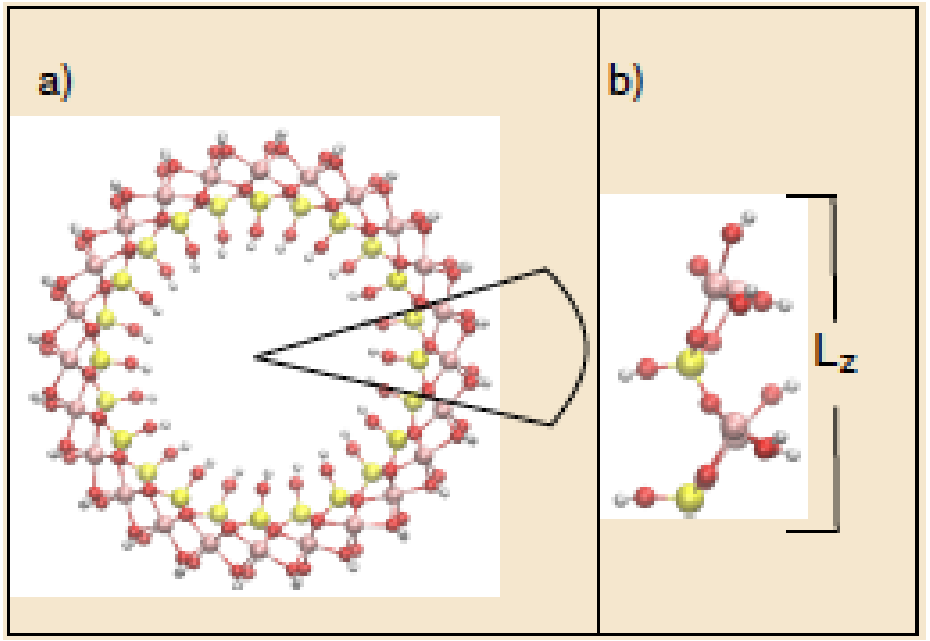
Imogolite, $(OH)_3Al_2O_3SiOH$

Rafael González (U. Mayor, Chile)
Javier Rojas-Nunez (U. de Santiago de Chile)



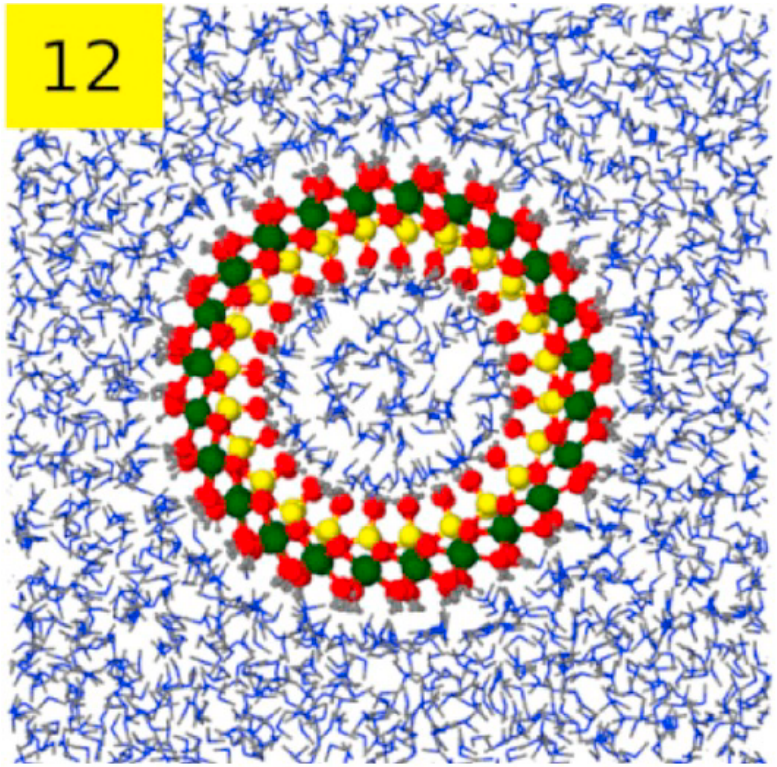


- Aluminosilicate nanotubes of volcanic origin discovered in Japan (1960s).
- Monodisperse
- Relatively simple synthesis with Si or Ge.



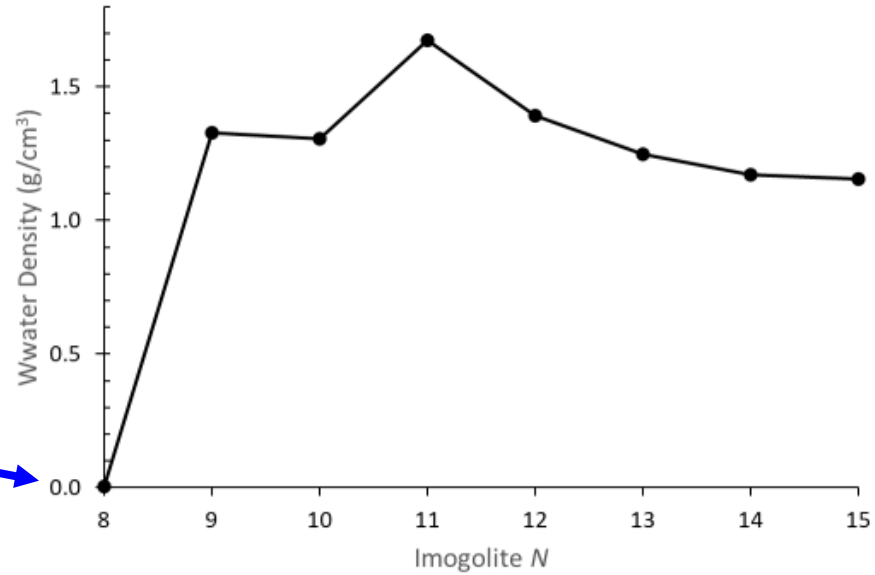
- Unit cell: diameter ≈2.5 nm, length ≈0.85 nm.
- Nanotube length ≈100 nm.
- Natural N = 10 (repetitions of the circular sector), synthetic N = 12

MD Simulations of Water-Imogolite Interfaces



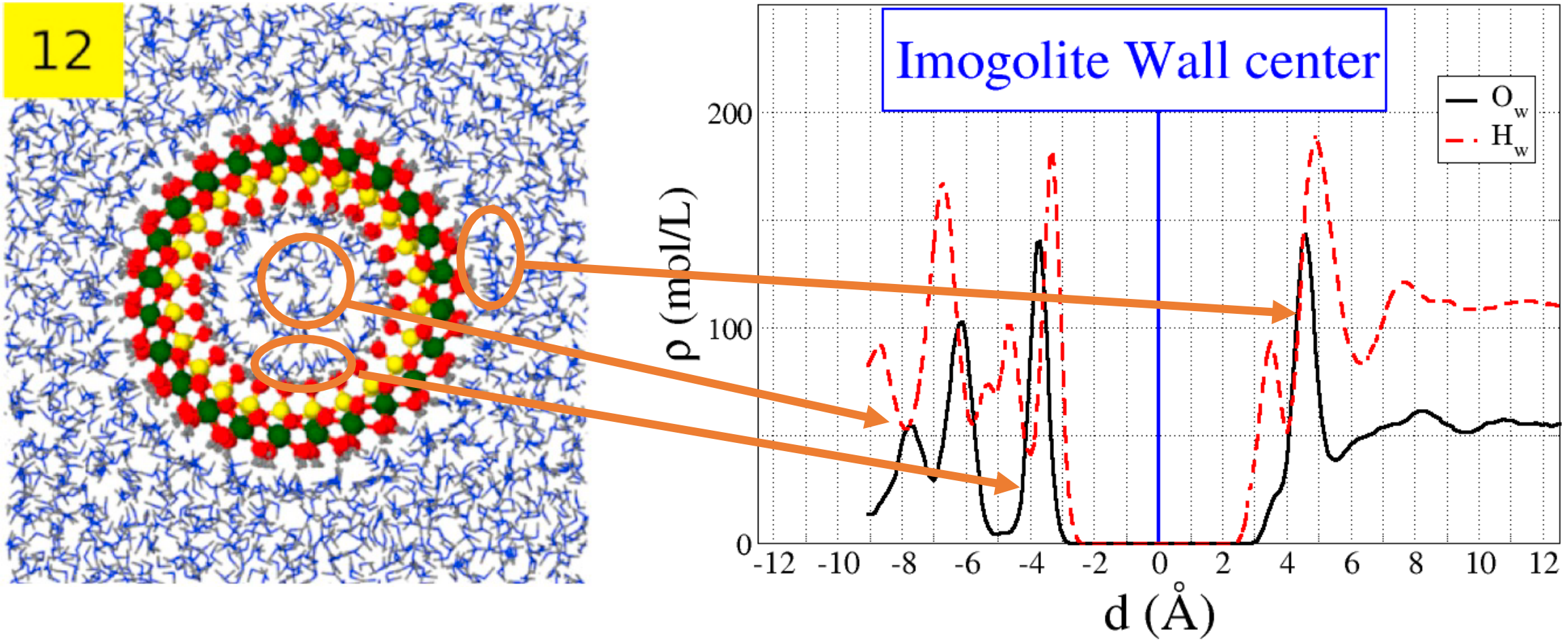
- Inner pore water content from Grand Canonical Monte Carlo (GCMC) simulations (Towhee).
- MD protocol
  - 3D periodic boundary conditions (infinitely long nanotubes).
  - ClayFF + SPC/Fw water model.
  - NPT (*xy*) simulations at 1 atm and 300 K to relax the system.
  - NVT simulations at 300 K up to 2 ns.
- Range of pore diameters ($9 < N < 15$), and planar configuration.
- Calculation of water density profiles and diffusion coefficients.

No water insertion in N = 8 nanotube
(GCMC results)



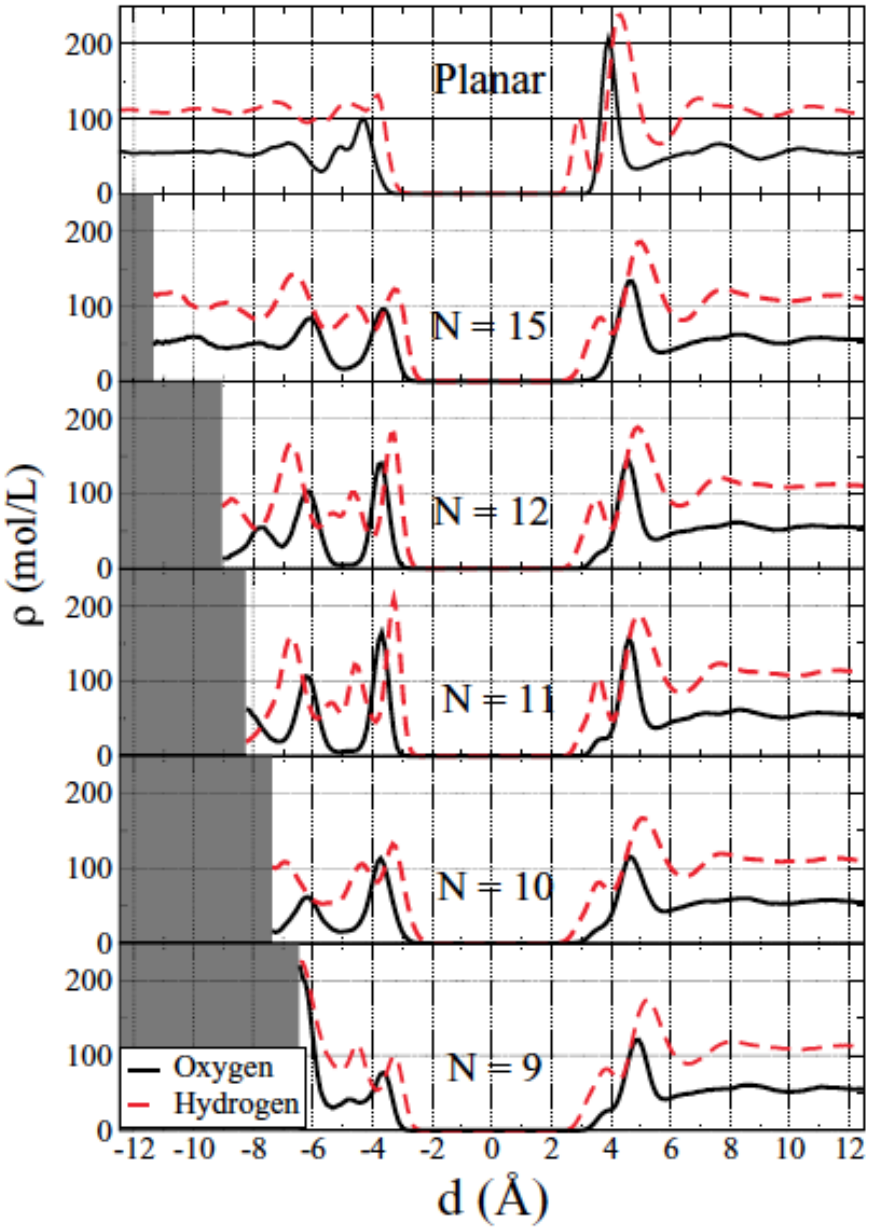
González et al., *Appl. Clay Sci.* **2020**, *191, 105582*

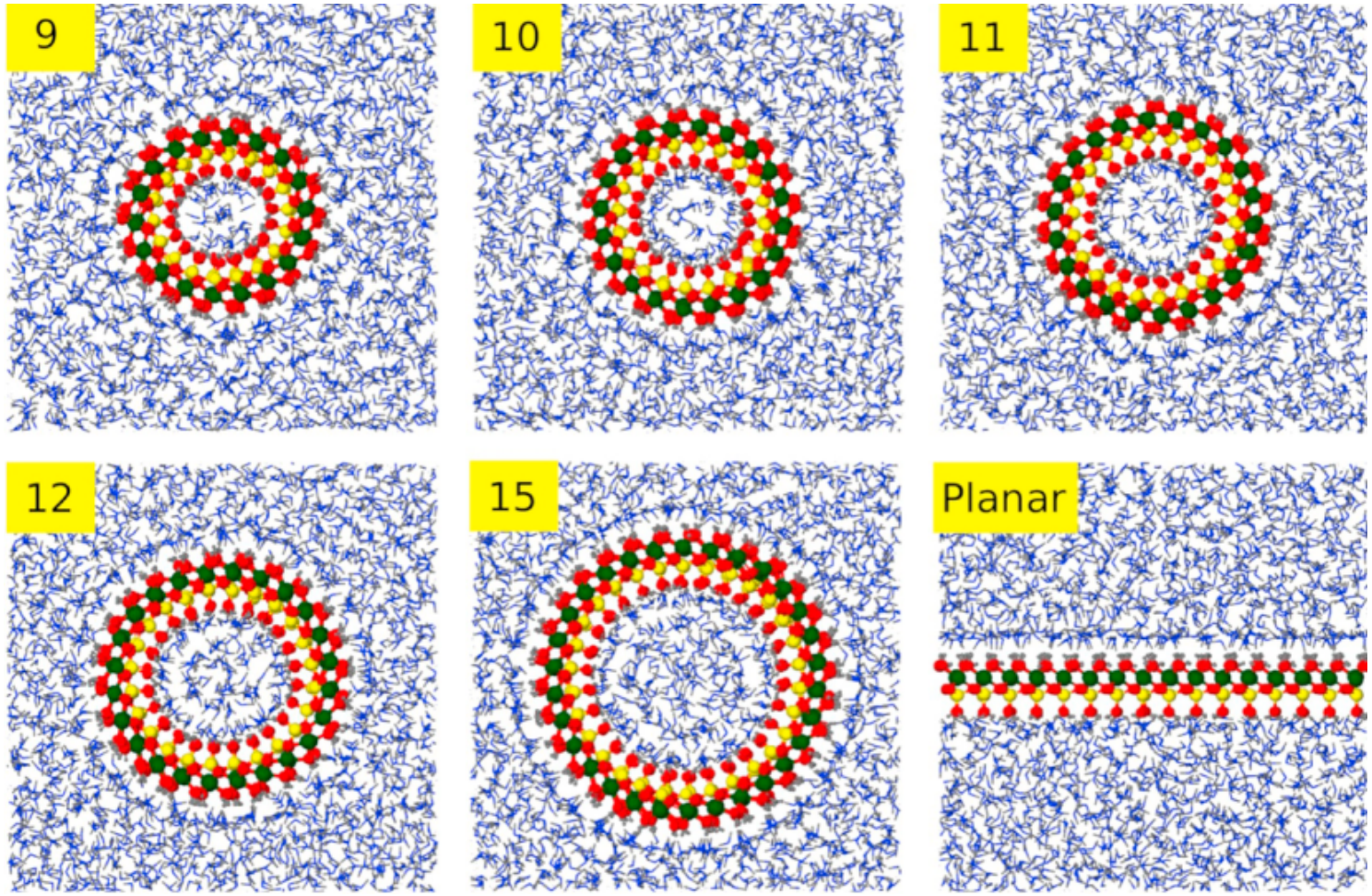
Water Structure from 1D Radial Density Profiles



González et al., *Appl. Clay Sci.* **2020**, *191, 105582*

Water Structure from 1D Radial Density Profiles





- Water structure at outer wall is mostly invariant to surface curvature.
- Surface curvature and pore size significantly affect water structure in the nanotube interior.

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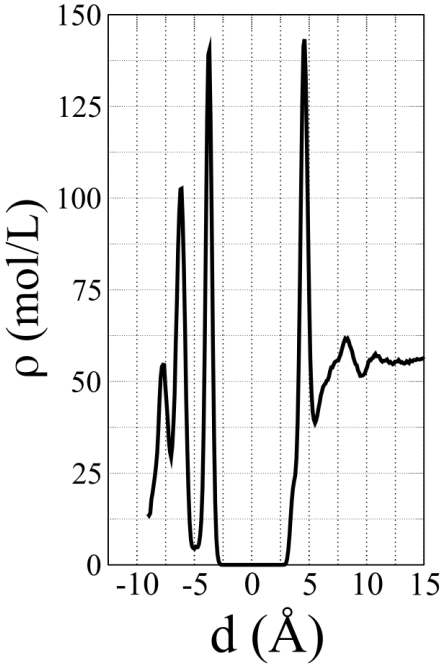
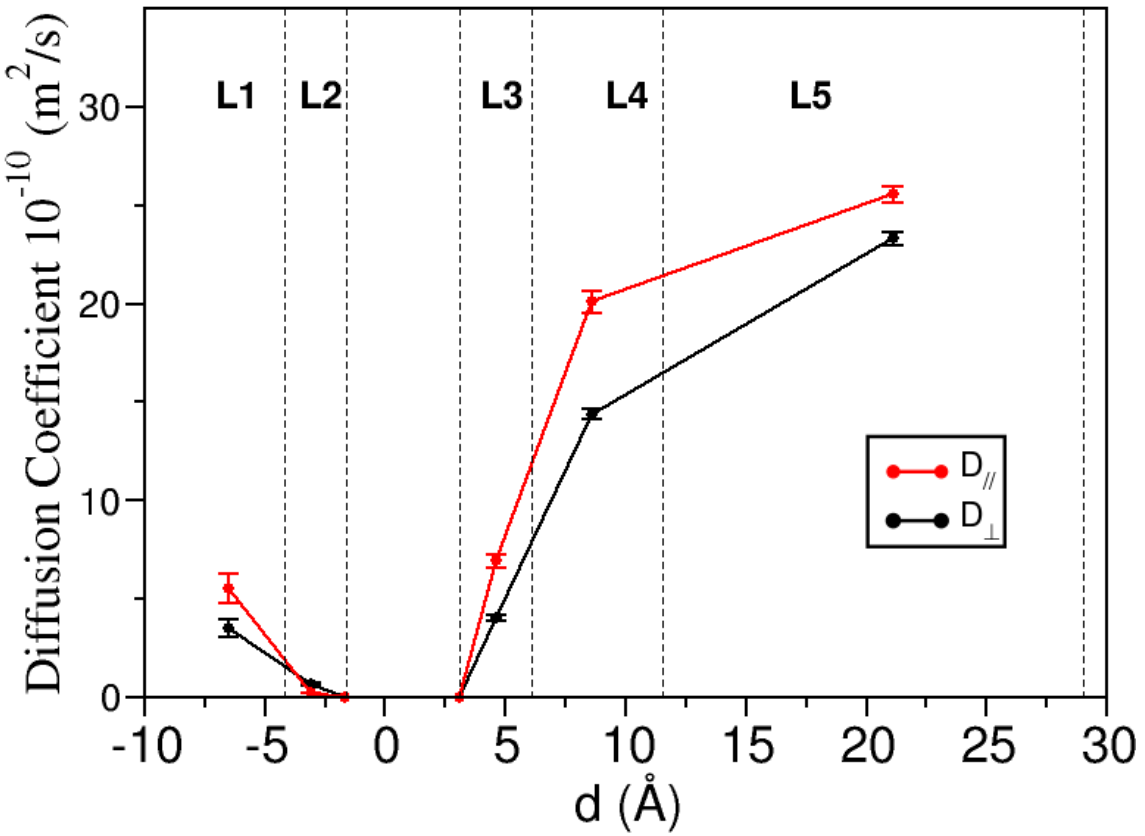
Water Self-Diffusion for N = 12 Nanotube

Water density



Water diffusion in each layer



D's calculated from survival probabilities, separately for motion parallel and perpendicular to the pore walls.

Limited diffusion at pore walls (L2 and L3 layers).

Bulk-like diffusion away from the walls.

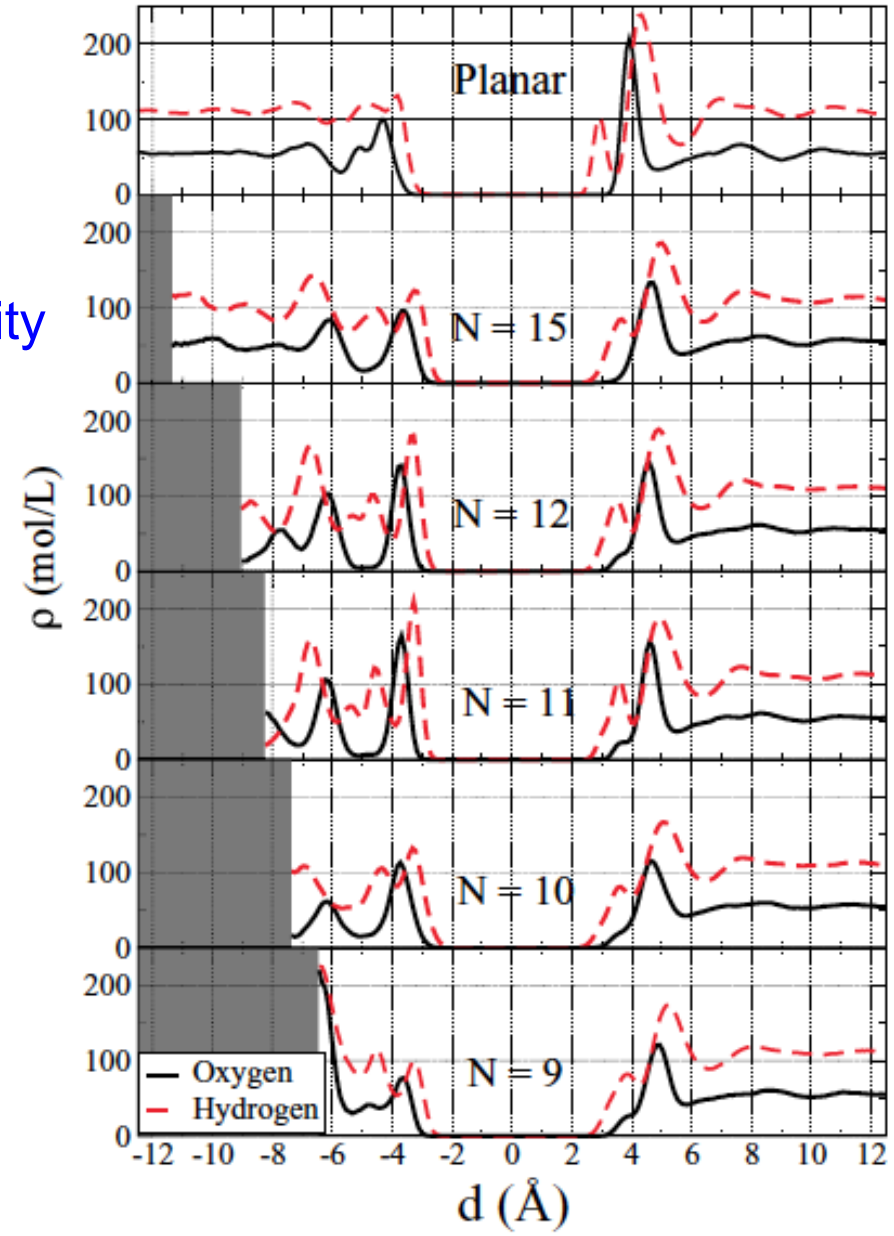
D_{bulk} for SPC/Fw water: 23.2×10^{-10} m^2/s

Wu et al, *J. Chem. Phys.*, **2006**, *124*, 024503

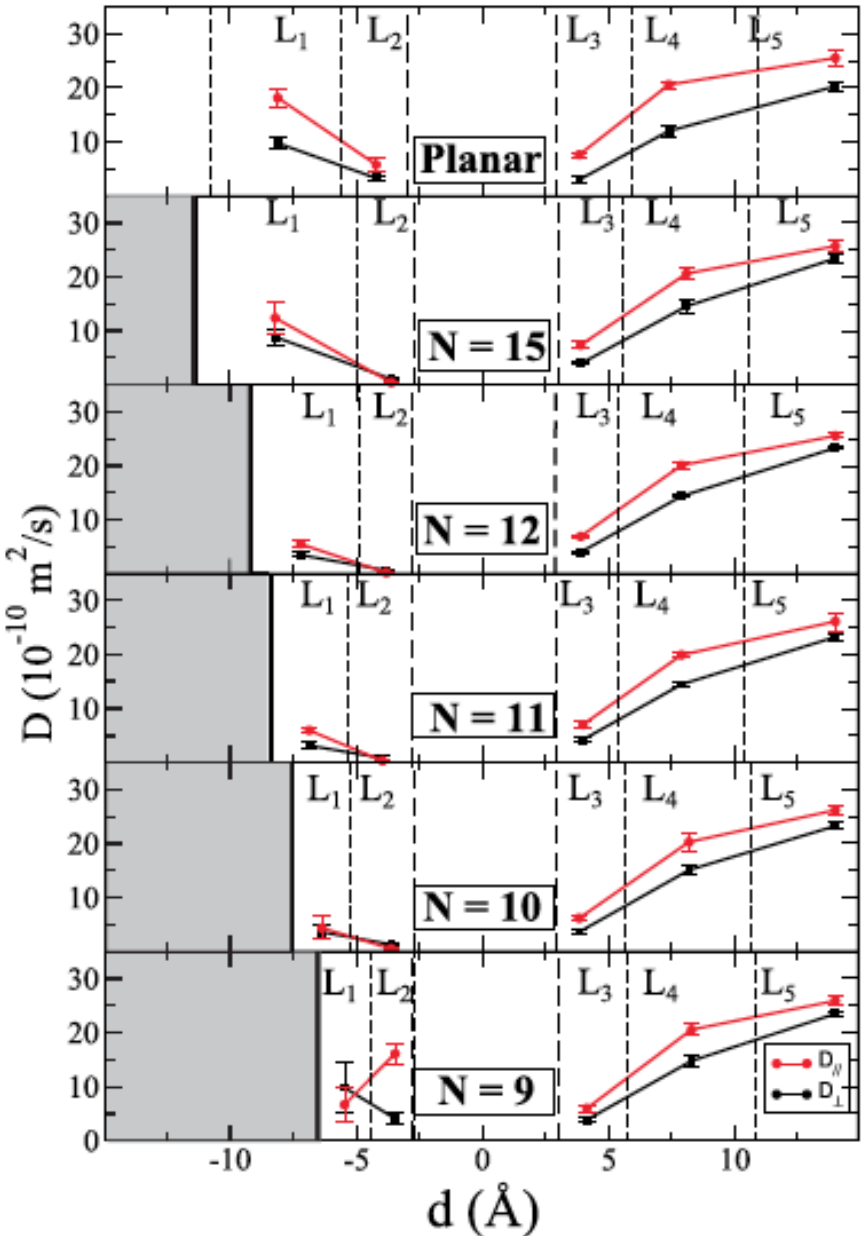
González et al., *Appl. Clay Sci.* **2020**, *191, 105582*

Water Self-Diffusion vs. Pore Size

Density

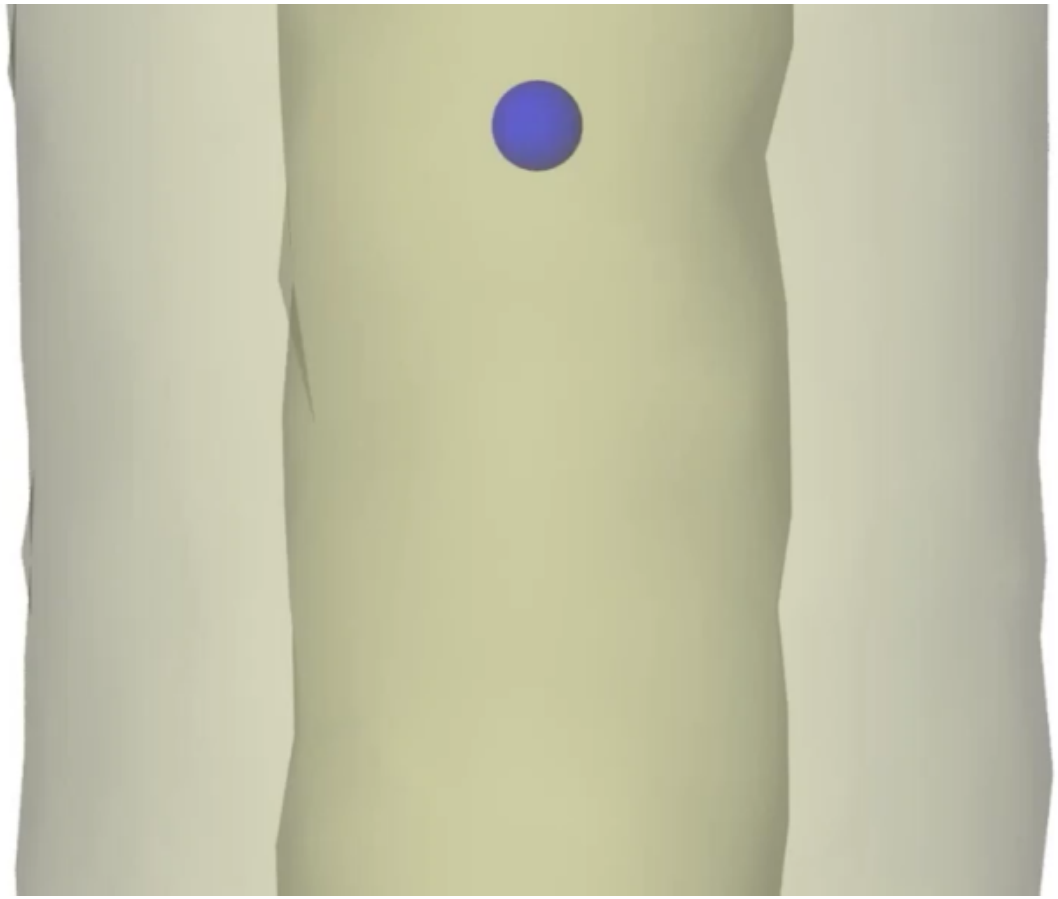


Diffusion



Water Mobility in $N = 12$ Nanotube

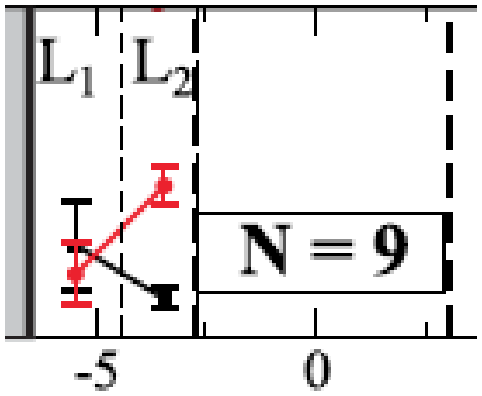
Trajectory of a water oxygen atom over 0.5 ns

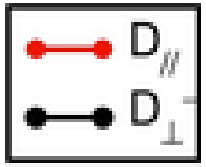


Diffusion parallel to the nanotube occurs via jump events

Water Diffusion Path Depends on Pore Size and Location

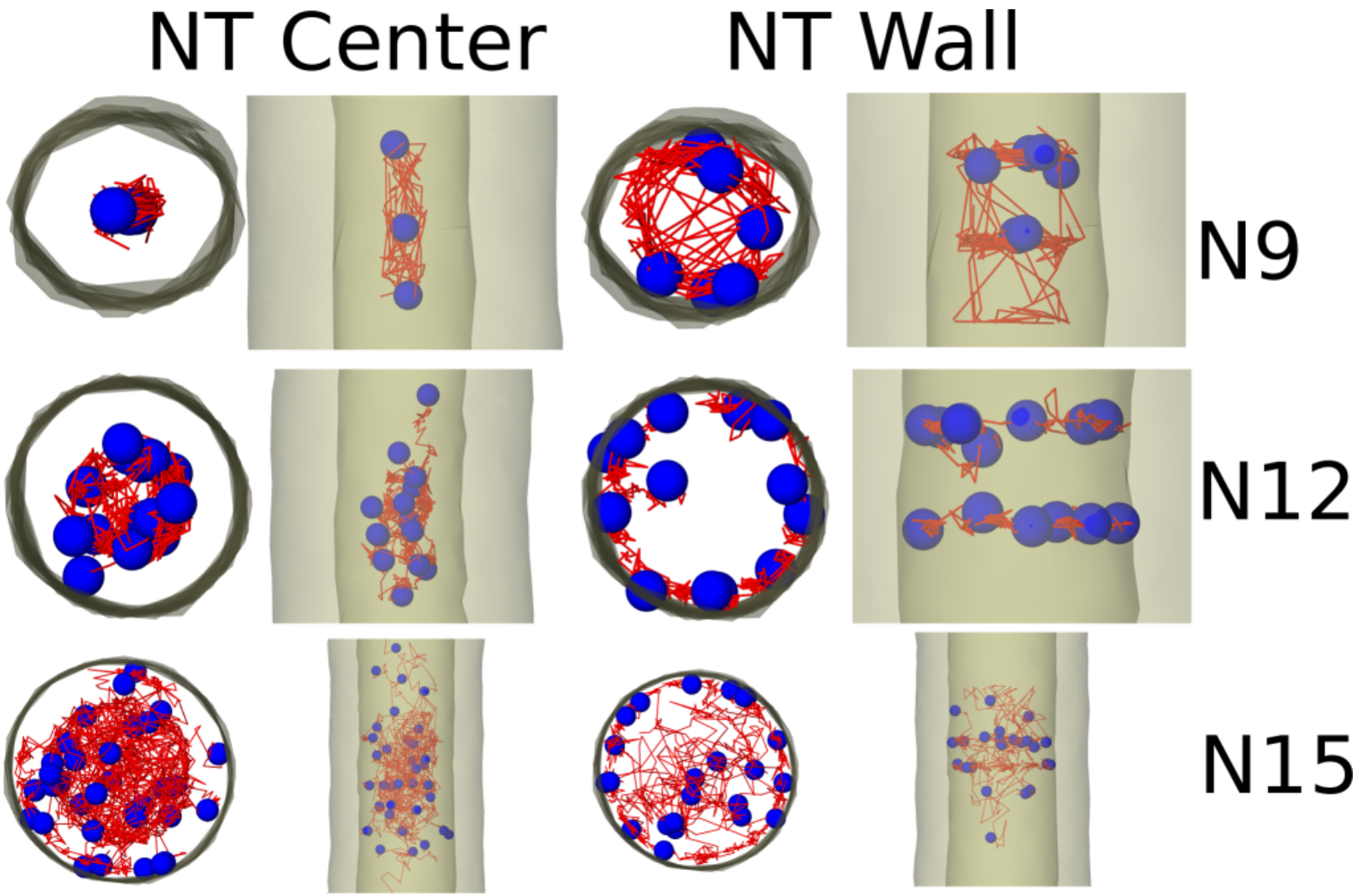
Water molecules at the $N = 9$ pore wall exhibit rapid diffusion along the pore wall (parallel).





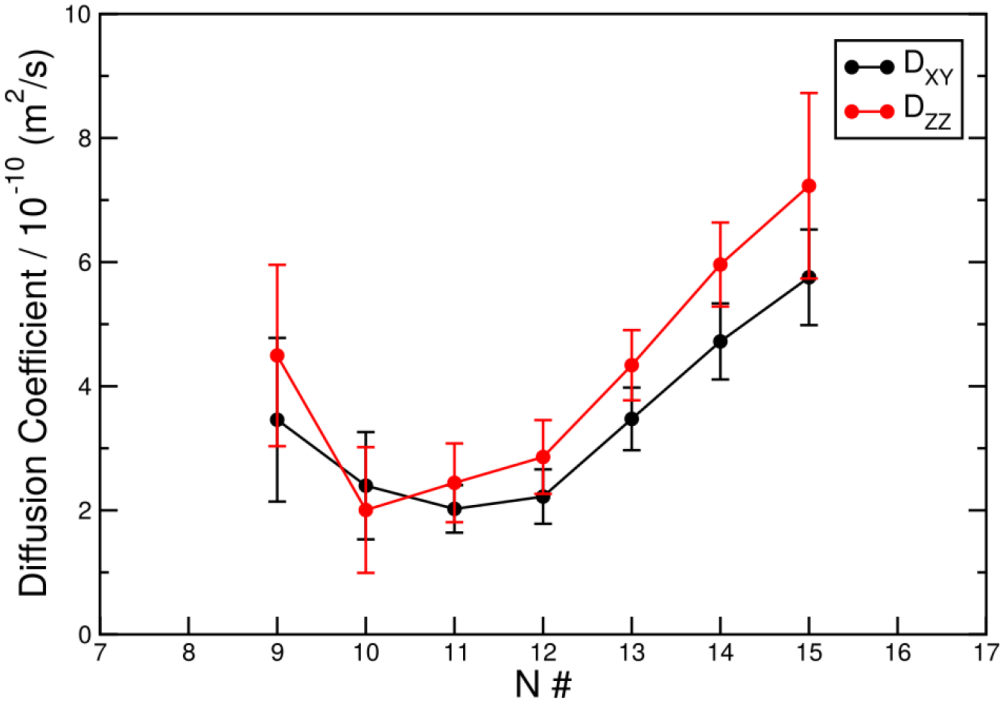
Parallel to pore wall

Perpendicular to pore wall

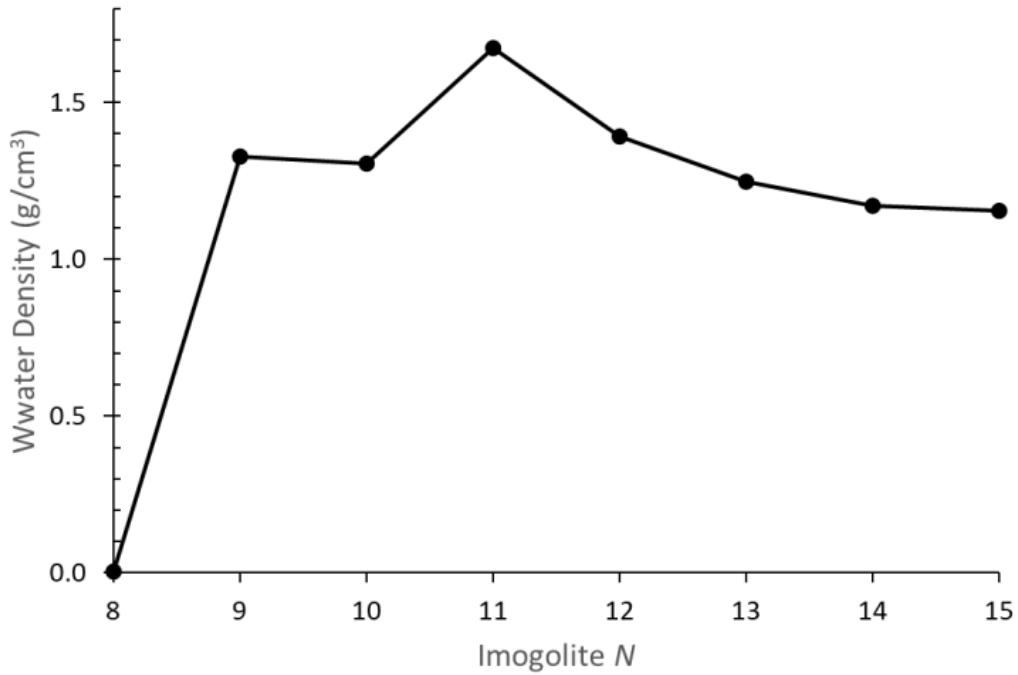


Diffusivity vs Pore Size

Water self-diffusion in imogolite pores
(L1 and L2 layers combined).



Water density



- Opposite trends in *D* and water density.
- Minimum in *D* occurs for *N* = 10-12 (minimum-energy structures).
- During synthesis, diameter may be controlled by solvent diffusion (changing imogolite precursor and solvent).

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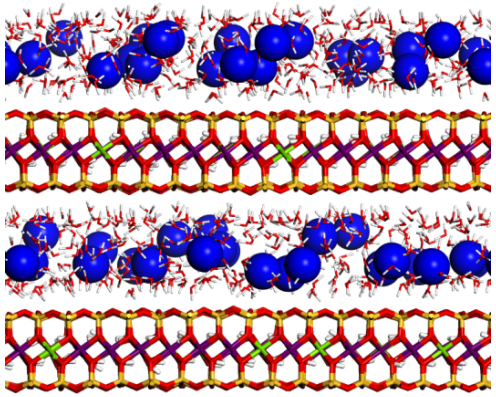
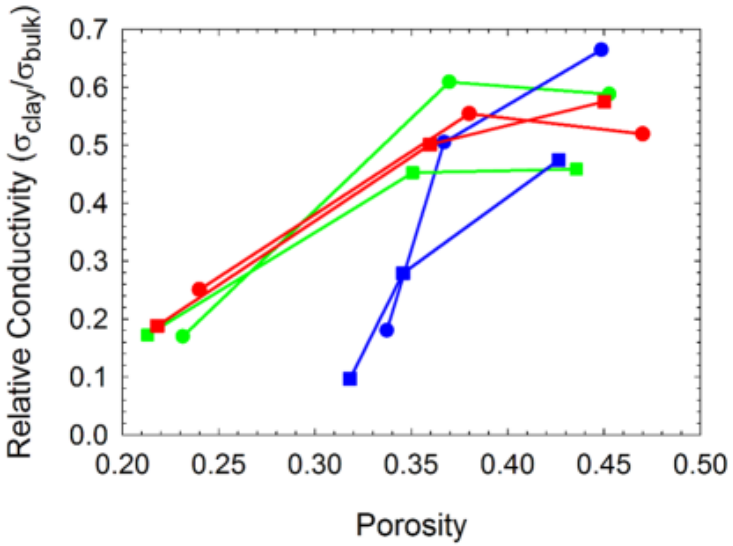
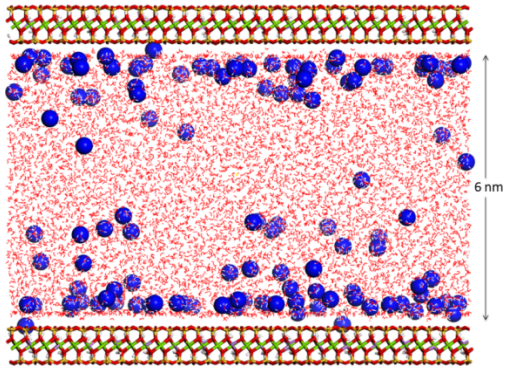
Summary

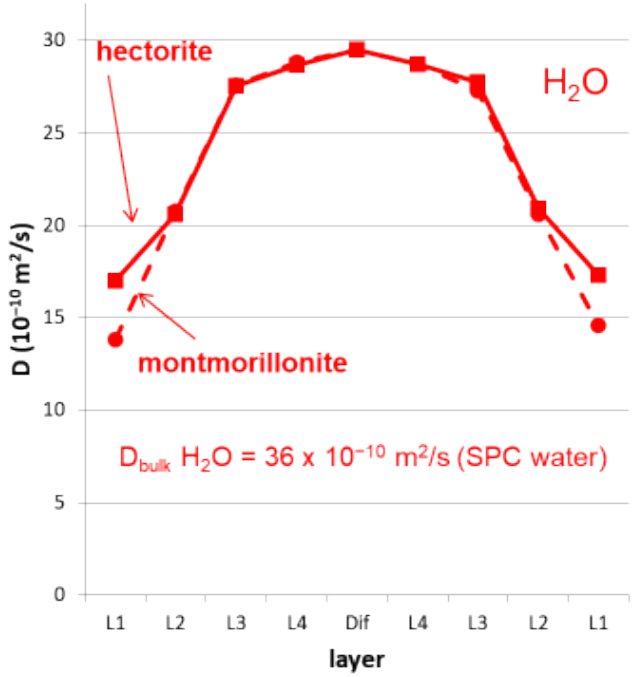
Clay Interlayers





Clay Nanopores





Imogolite Nanotubes