SAND2015-6985C

Exceptional service in the national interest

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Methane hydrate formation in the presence of clay mineral surfaces

Stephanie Teich-McGoldrick, Margaret Gordon, Randall Cygan

Sandia National Laboratories, Albuquerque, NM

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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Exceptional service in the national interest

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The role of water models in the molecular-level structuring and dynamics at the surface of clay-minerals

Stephanie Teich-McGoldrick*, David Hart, Randall Cygan

Sandia National Laboratories, Albuquerque, NM

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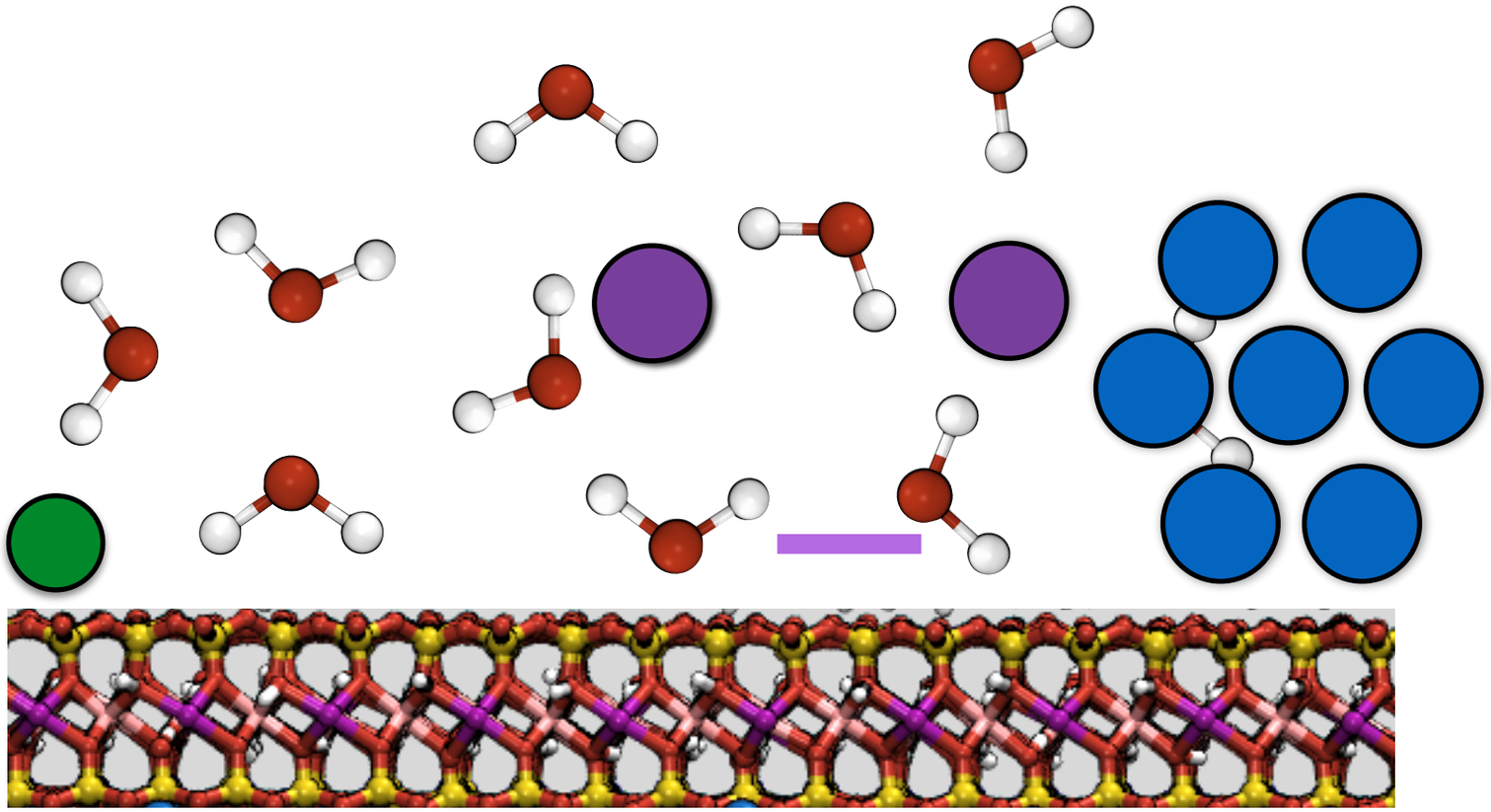
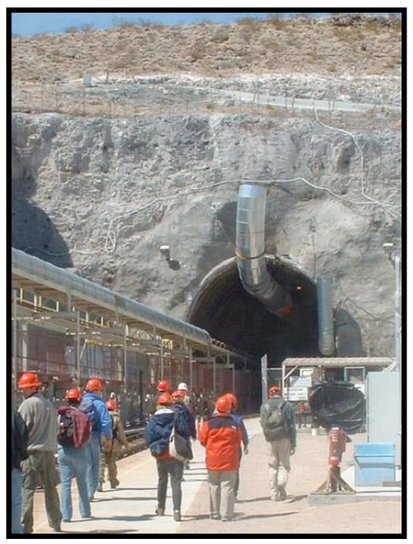
Critical geochemistry phenomenon occur at the clay-mineral interface

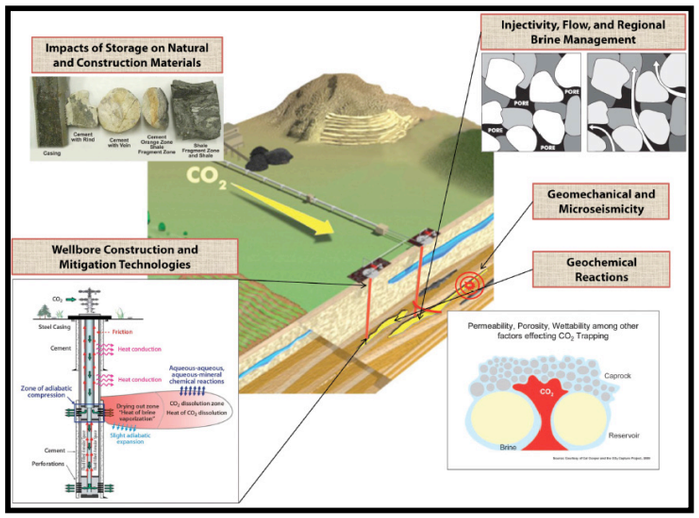


Engineered barriers



http://en.wikipedia.org/wiki/Yucca_Mountain_nuclear_waste_repository

Carbon sequstration



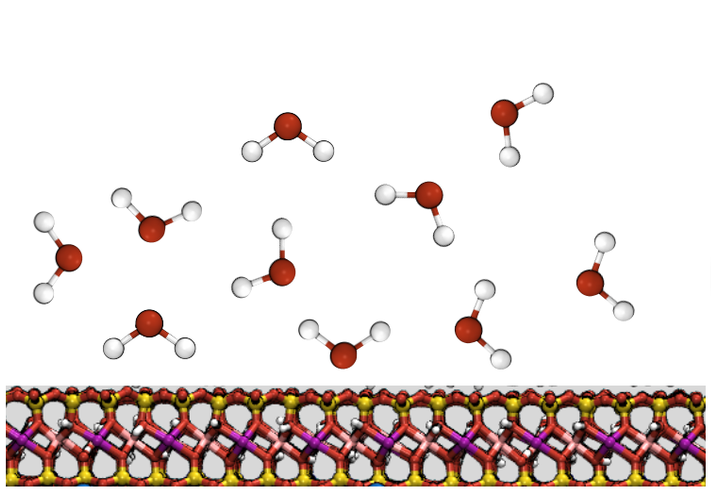
http://www.netl.doe.gov/technologies/carbon_seq/corerd/storage.html#geologic

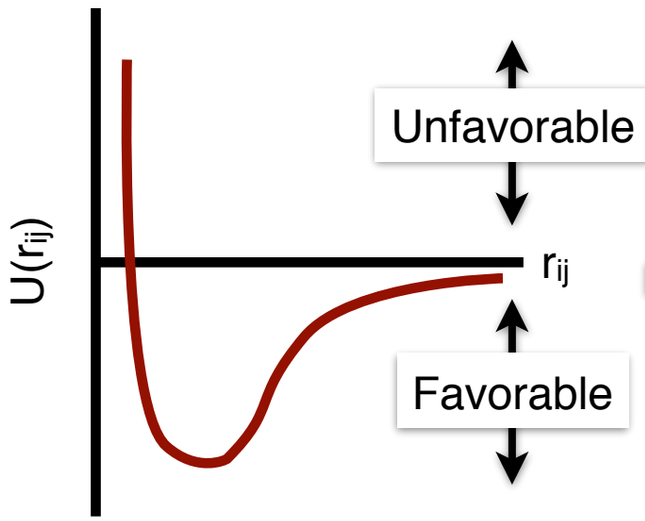
Contaminent transport

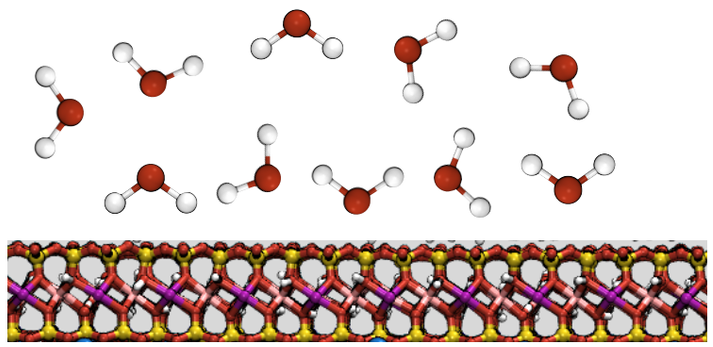
http://www.cnn.com/videos/us/2015/08/10/colorado-epa-chemical-spill-in-river-live-sater-nr.cnn

Molecular simulation can be used to study this phenomenon

t=0 → *Update particle velocities and coordinates* → *t=final*







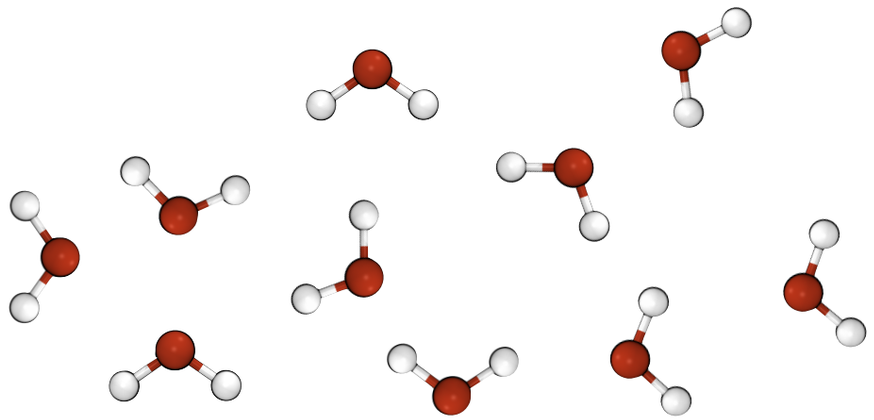
$$F = \frac{-\partial U}{\partial r} \qquad \frac{\partial^2 r}{\partial t^2} = \frac{1}{m}\frac{-\partial U}{\partial r}$$

$(r_{i,t},.....r_{N,t})$
$(v_{i,t},.....v_{N,t})$

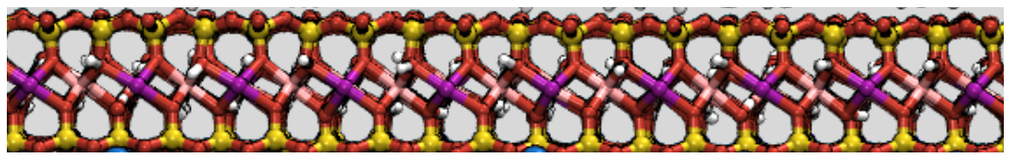
Force fields provide the description of atomic interactions

$U(r_{ij})$ {

SPC flexible



clayff force field



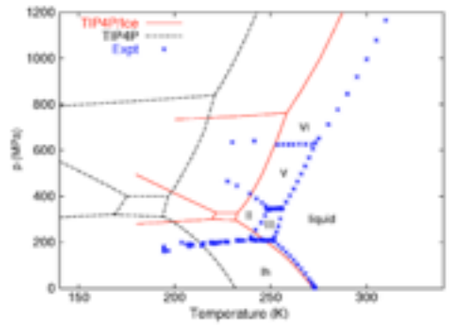
TIP3P - popular forcefield used often with biomolecules

TIP4P - four-site water model

TIP4P-Ice - captures liquid-solid phase boundary

SPC - computation speed-up over flexible force field

https://en.wikipedia.org/wiki/Biomolecule



J. Chem. Phys., Abascal et al.,2005

Two clays are chosen to study the effects of water model

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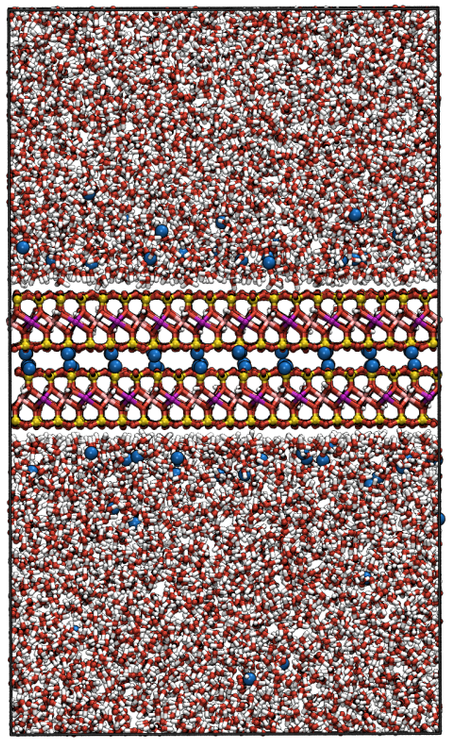
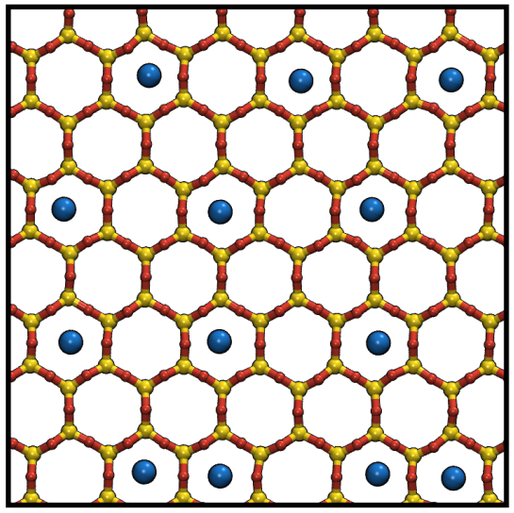
Montmorillonite

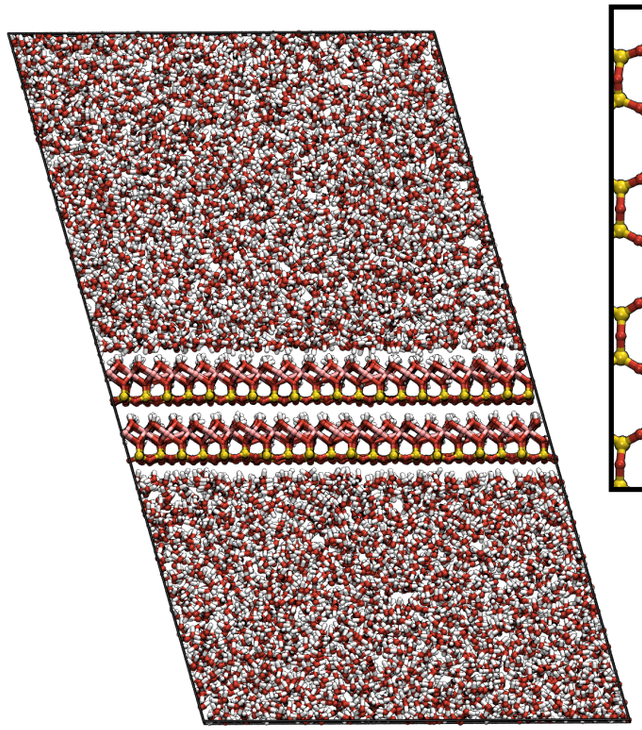
$NaSi_8Al_3MgO_{20}(OH)_4$
Layer charge 1e- in
10x6x2
5.16nm x 5.38nm x 1.87nm

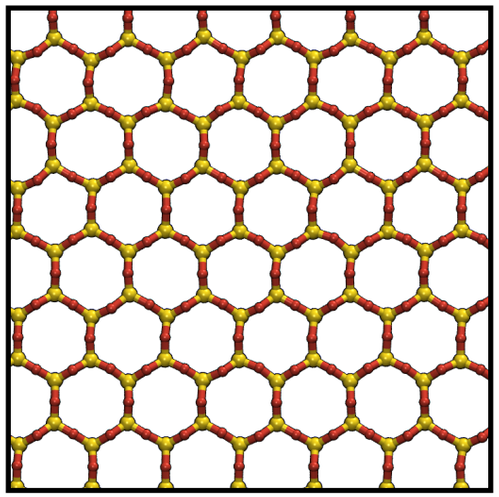


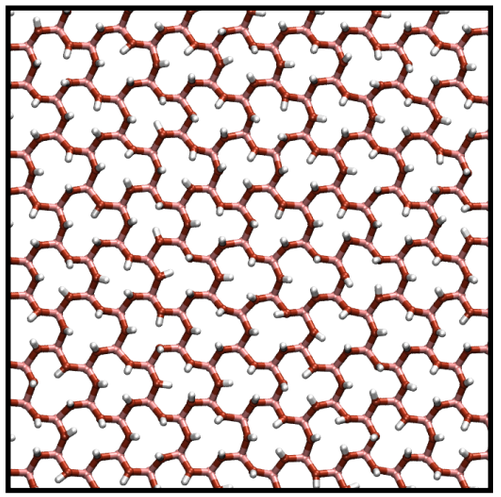


Kaolinite

$Al_2Si_2O_5(OH)_4$
No layer charge
10x6x2
5.15nm x 5.37nm x 1.43nm







Five water models are selected for investigation

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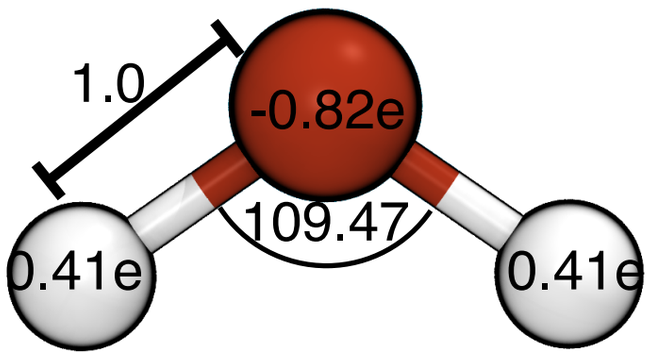
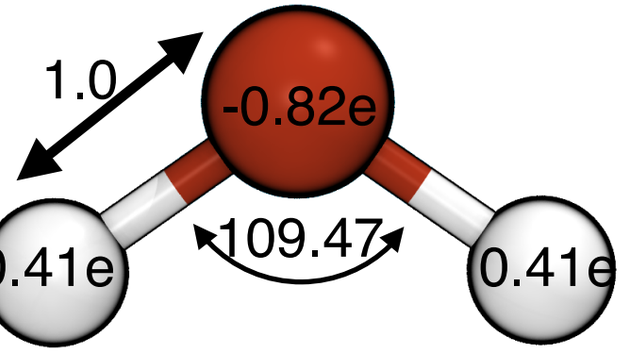
3-Site models

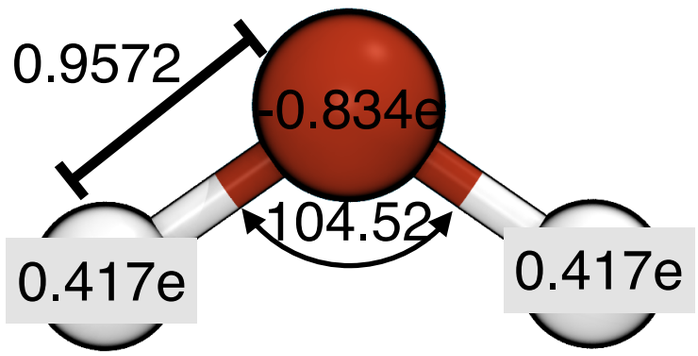
SPC



SPC Flexible

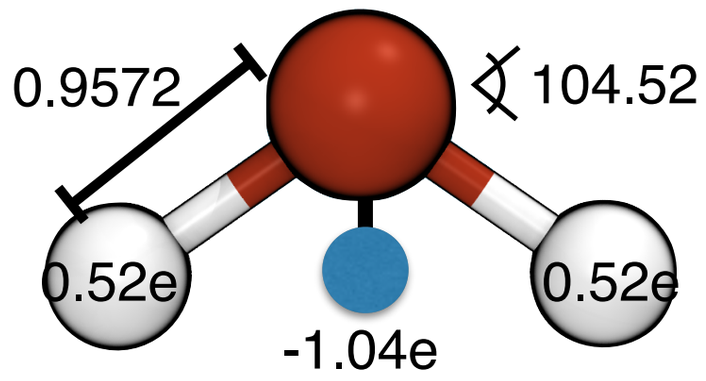


TIP3P

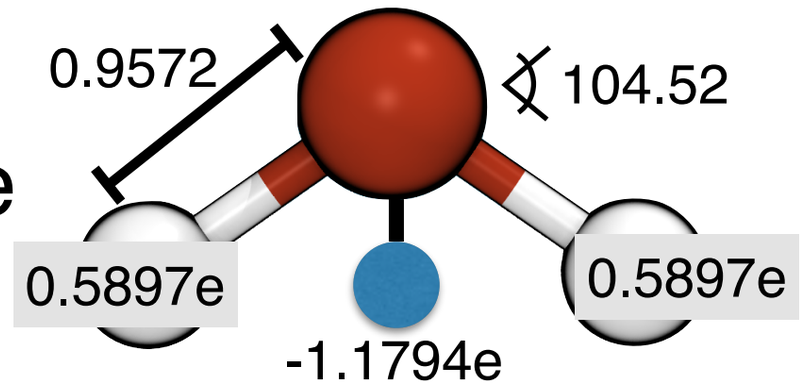


4-Site models

TIP4P



TIP4P-Ice

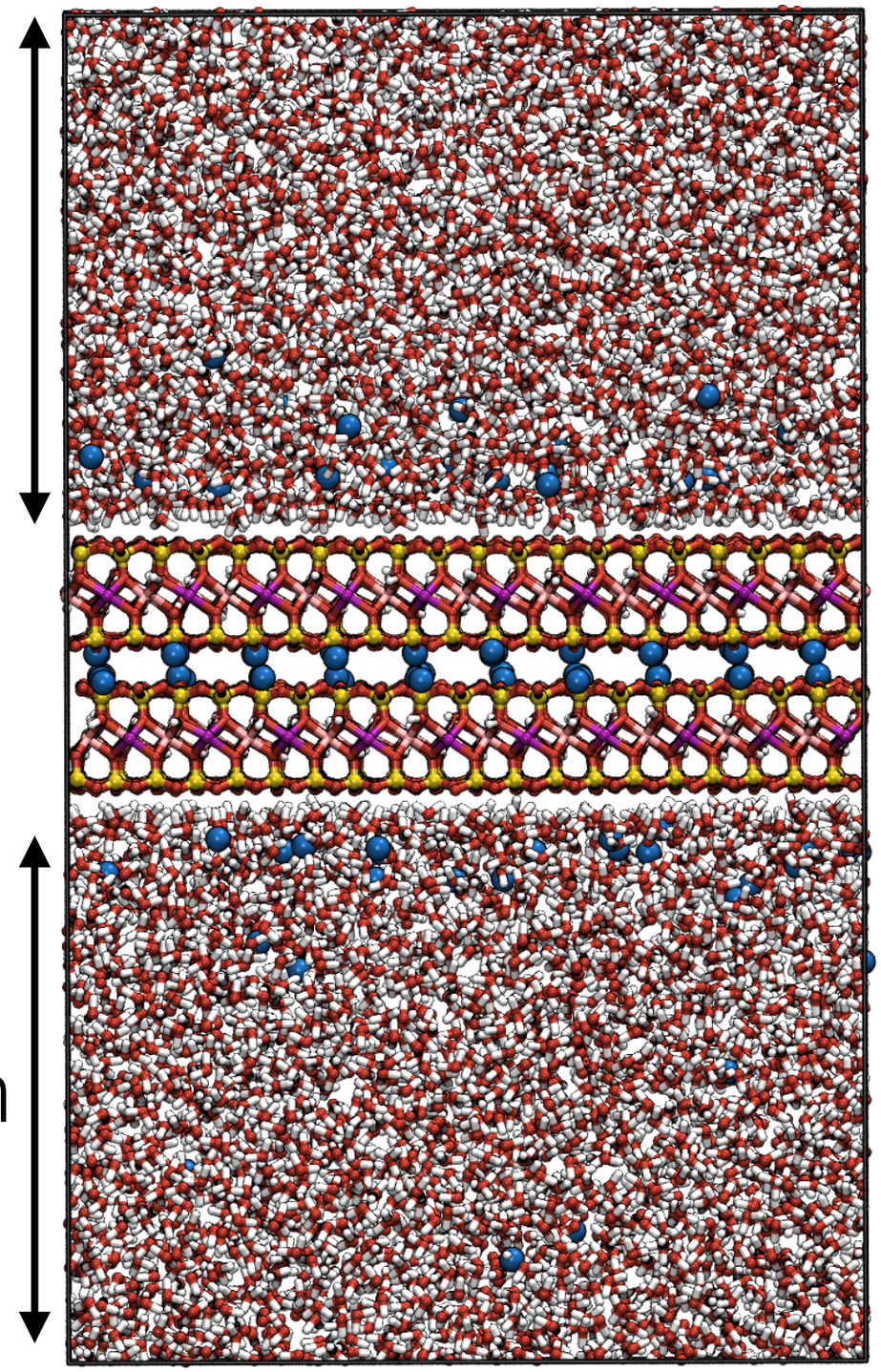


Molecular simulation can be used to study this phenomion

6400 water molecules
GROMACS simulation package
T = 300 K
P = 1 bar
2fs timestep for rigid waters
0.2fs timestep for flexible water

Systems equilibrate in *NPT* ensemble
Systems run in *NVT* ensemble
Structural properties
    10ns simulation
    Data collected every 5ps
Dynamic properties
    0.5ns simulations
    Data collected every 50fs

Clay hydroxyl bonds are held rigid with rigid water model



Hypothesis and data collected

Structural results will have similar for the three site models but potentially more structured for the higher charged 4 site models.

Rigid water models will have faster diffusion properties than flexible models.

Hydrophilic surfaces will be most impacted by choice of water model.

Structural data

- Water orientation on the surface
- 1D density profiles
- 2D density profiles

Dynamic data

- Diffusion coefficients as a function of distance from the surface

Structural data - water orientation on surface

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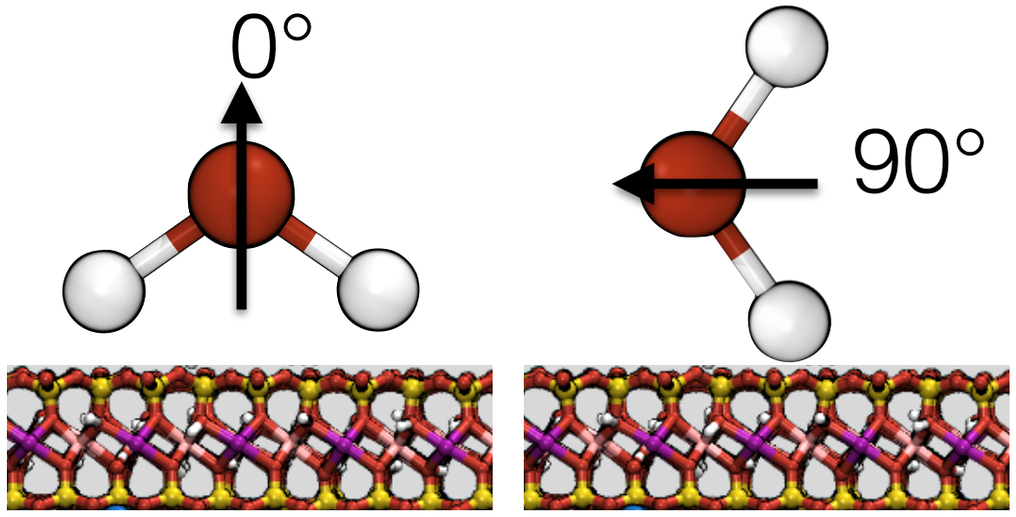
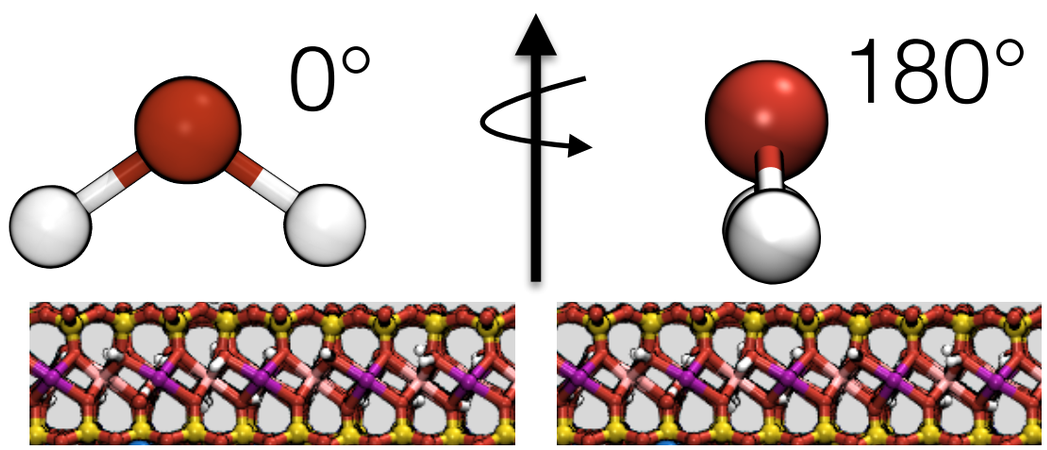
Rise from surface **θ**



Rotation on surface ϕ



Structural data - water orientation on surface

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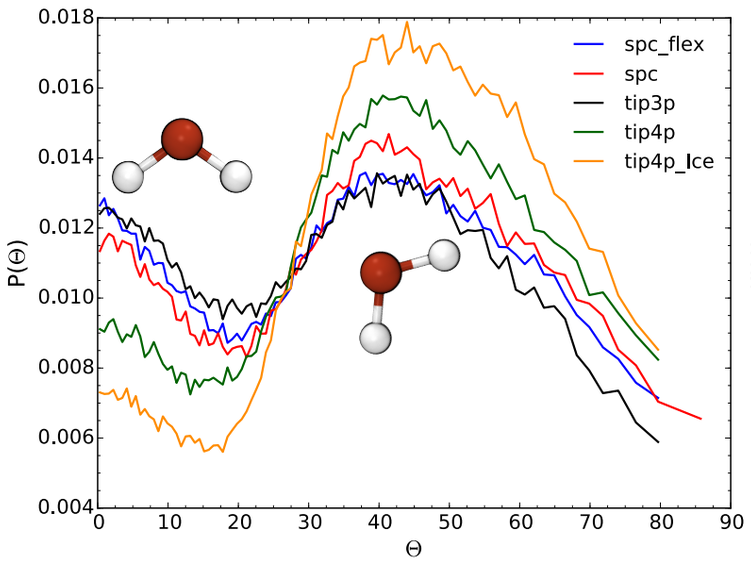
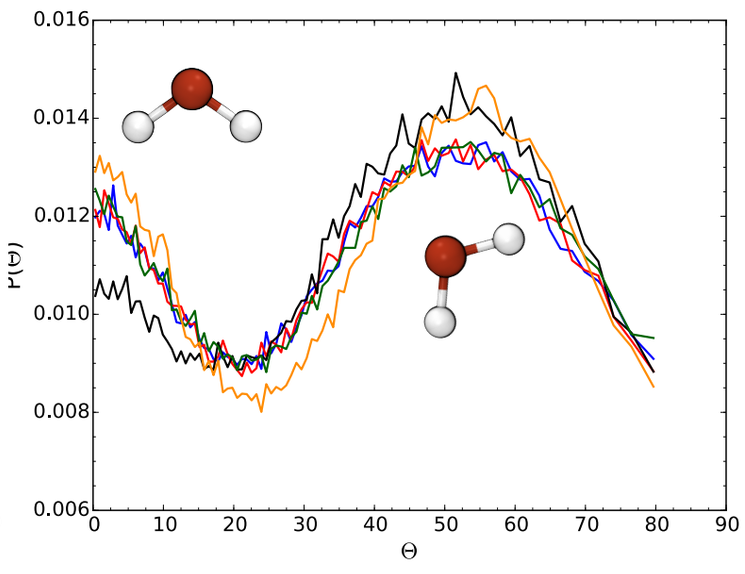
SPC | SPC - Flexible | Tip3p | Tip4p | Tip4p-Ice

Rise

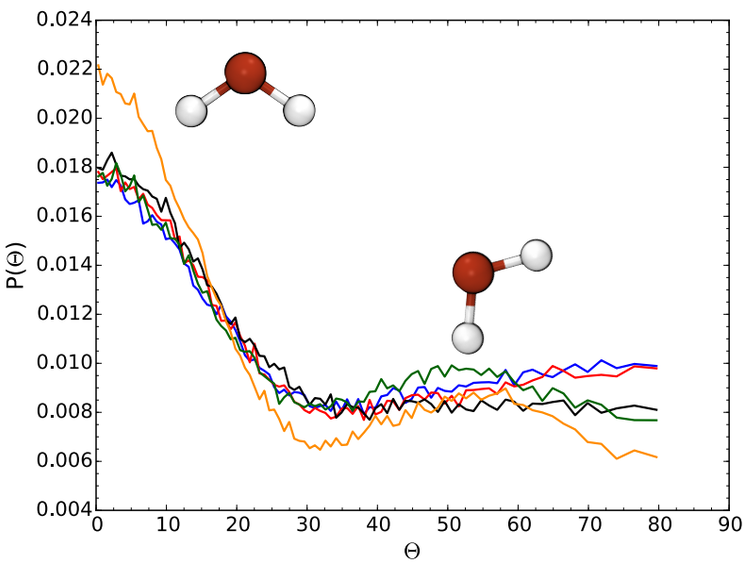
Montmorillonite



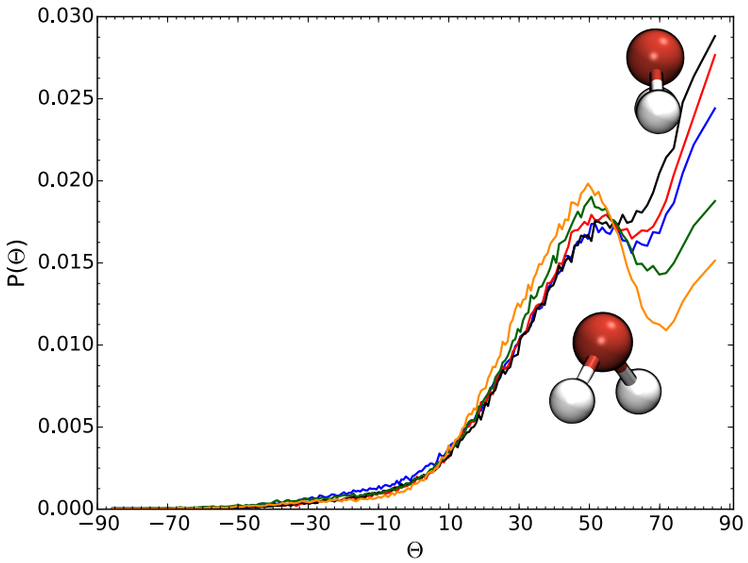
Kaolinite - siloxane

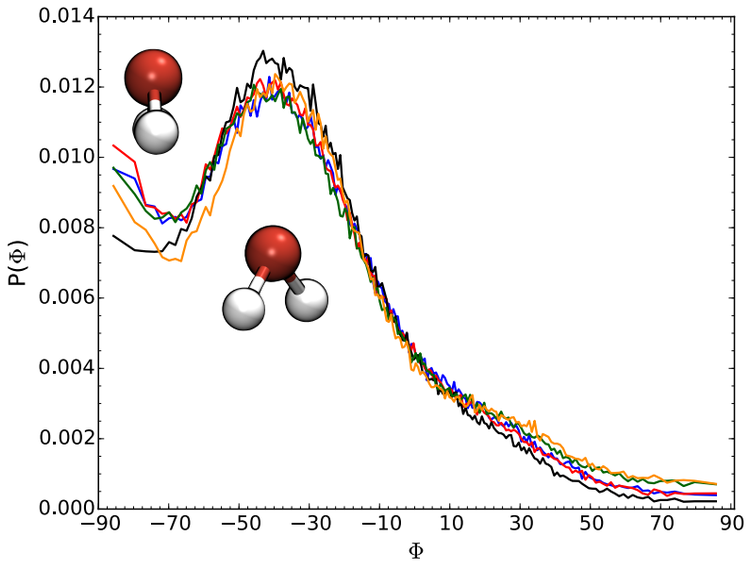


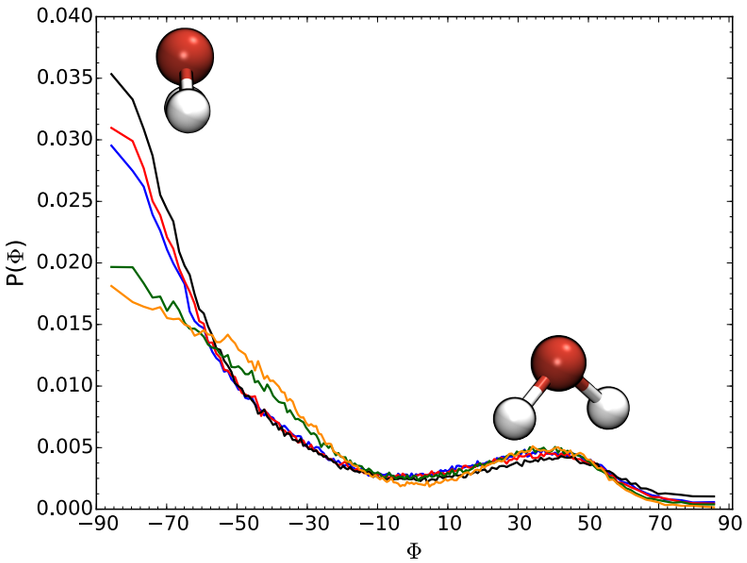
Kaolinite - gibbsite



Rotation



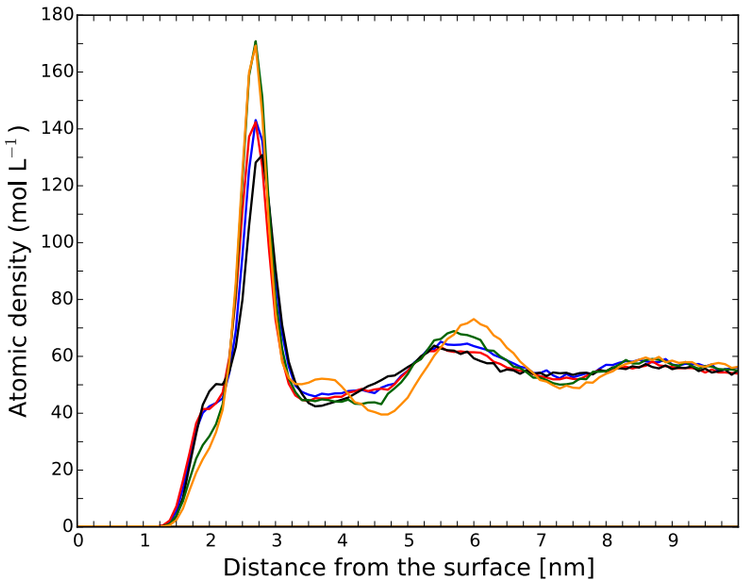




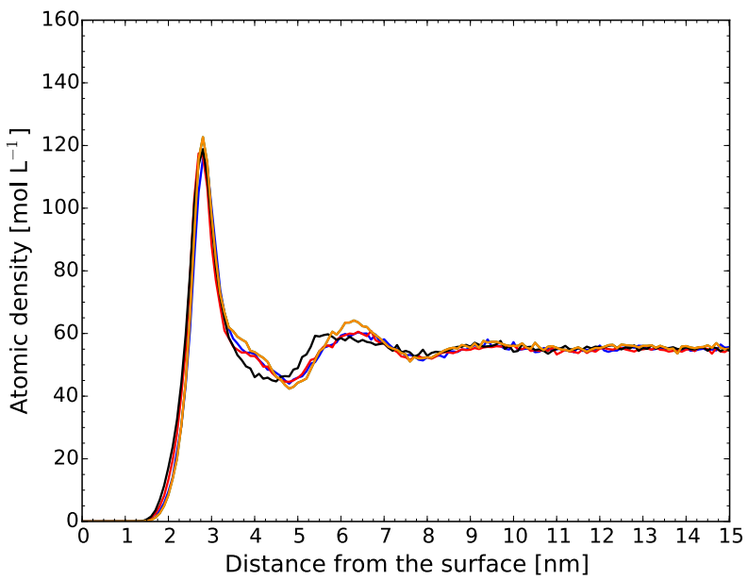
Structural data - 1D density profiles

SPC SPC - Flexible Tip3p Tip4p Tip4p-Ice

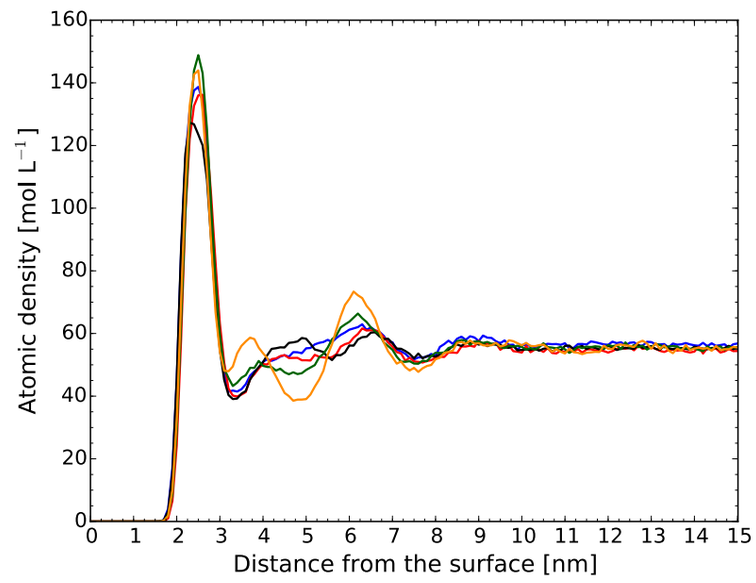
Montmorillonite



Kaolinite - siloxane



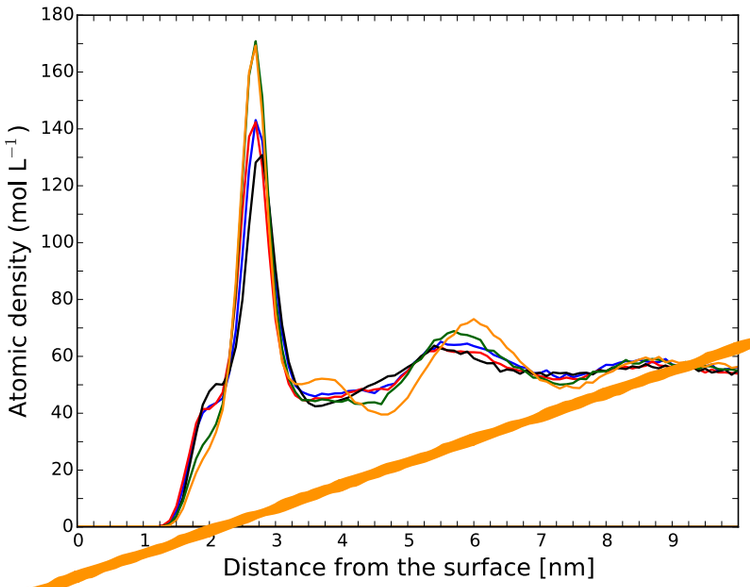
Kaolinite - gibbsite



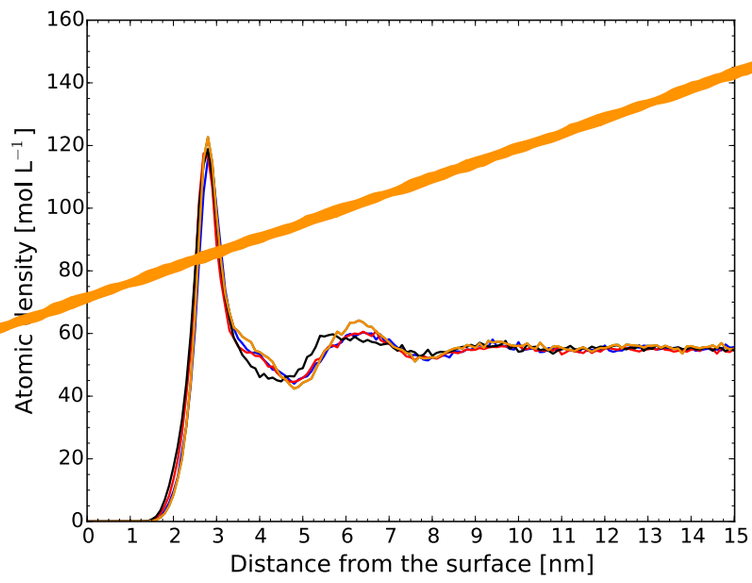
Structural data - 1D density profiles

SPC SPC - Flexible Tip3p Tip4p Tip4p-Ice

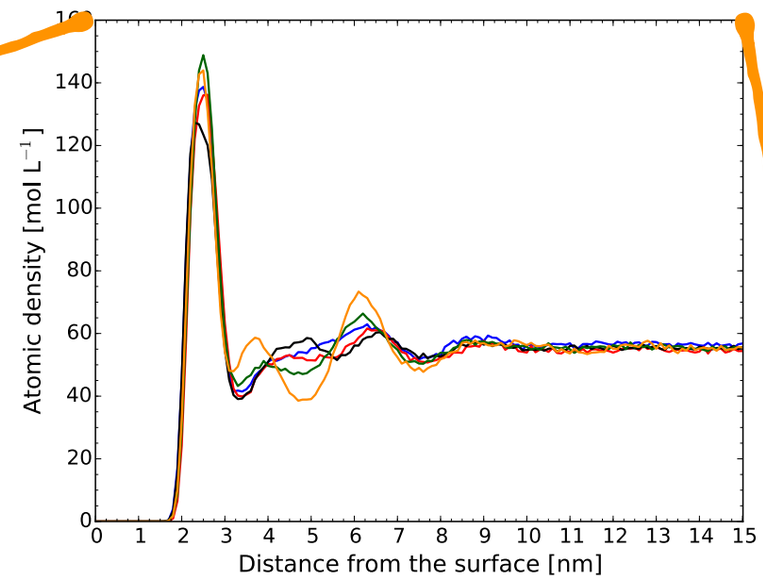
Montmorillonite



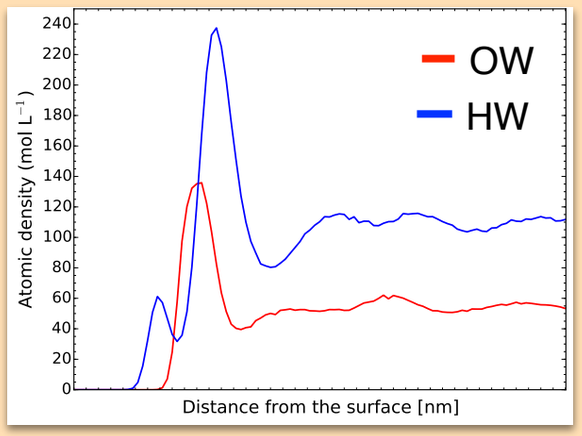
Kaolinite - siloxane



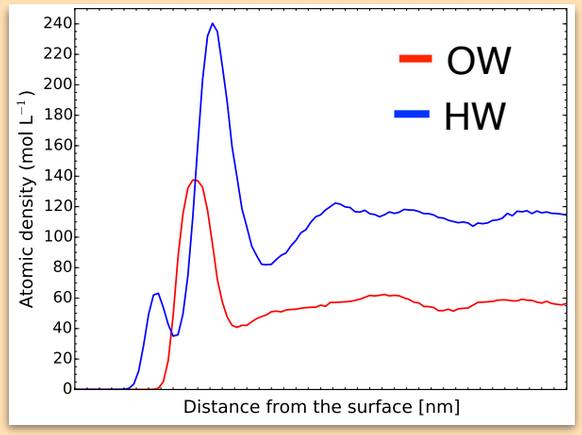
Kaolinite - gibbsite



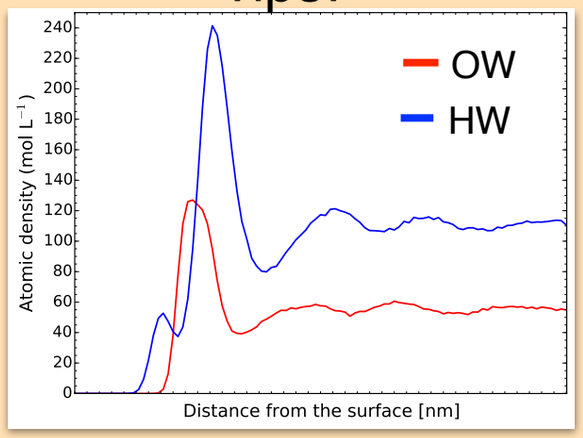
SPC



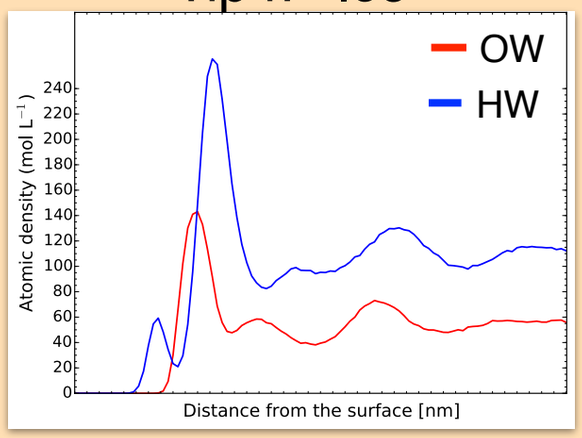
SPC - flexible



Tip3P



Tip4P-Ice



2D density profiles - projections on the xy plane

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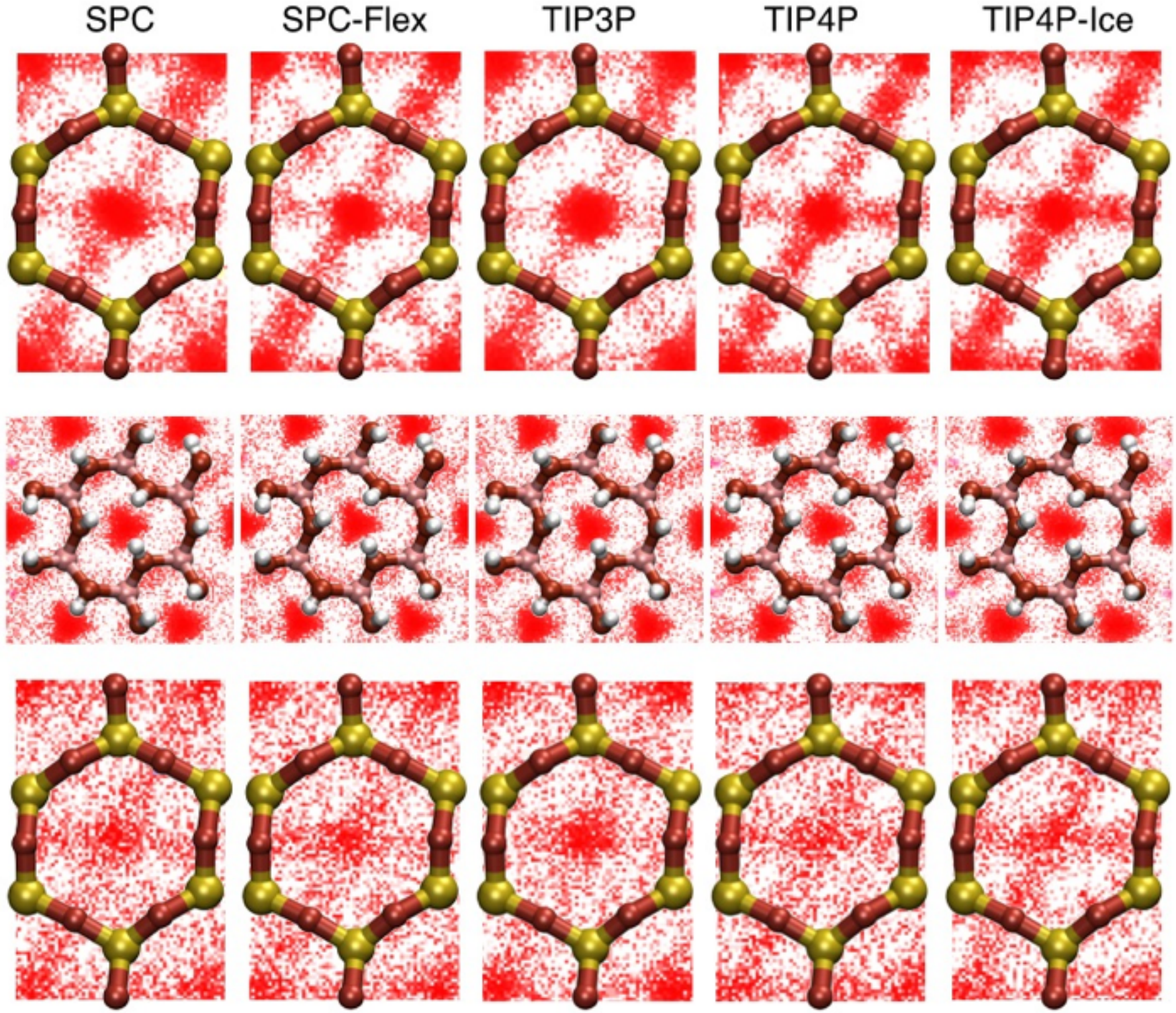
SPC | SPC-Flex | TIP3P | TIP4P | TIP4P-Ice

Montmorillonite

Kaolinite gibbsite

Kaolinite siloxane



2D density profiles - projections on the xy plane

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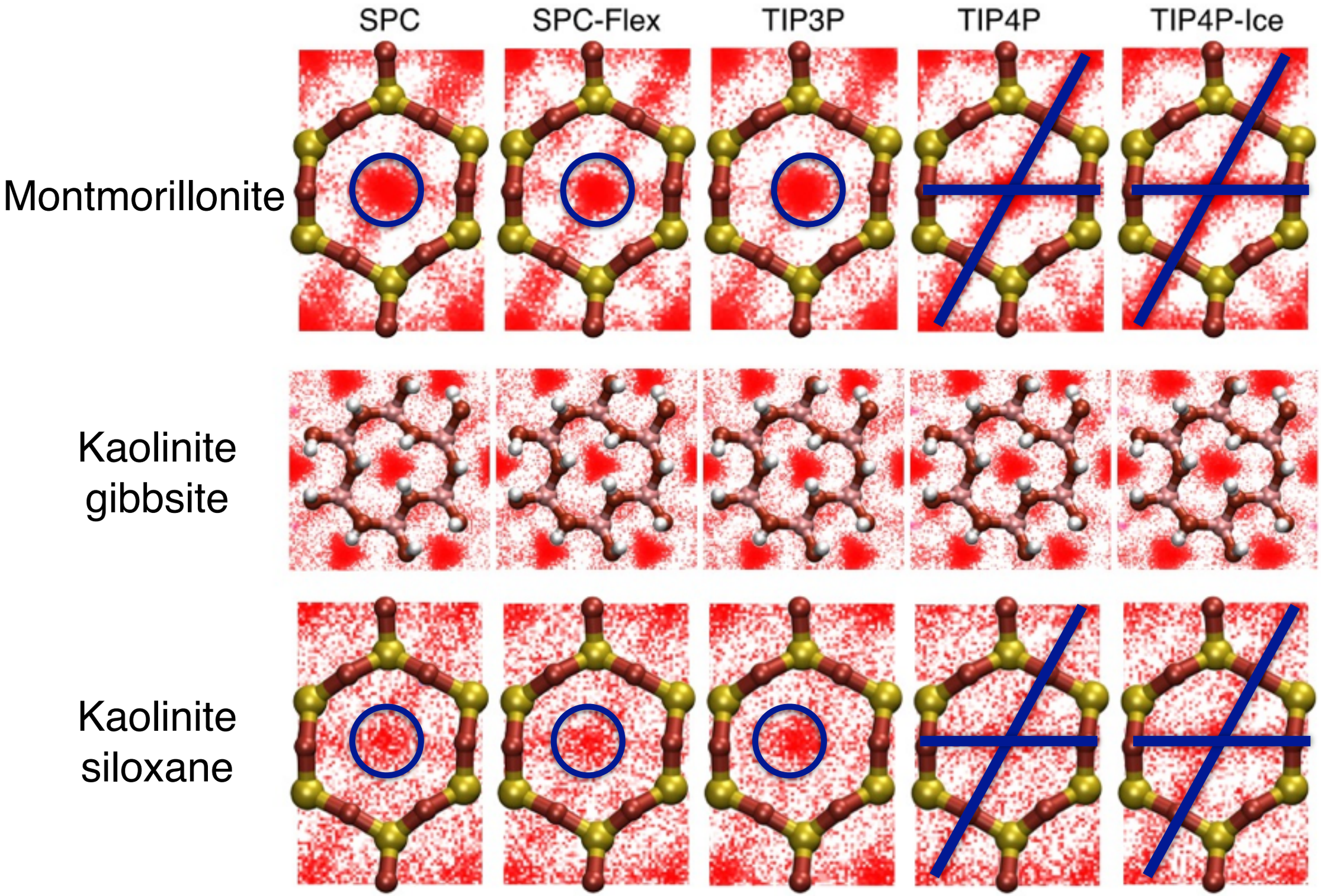

2D density profiles - projections on the xy plane

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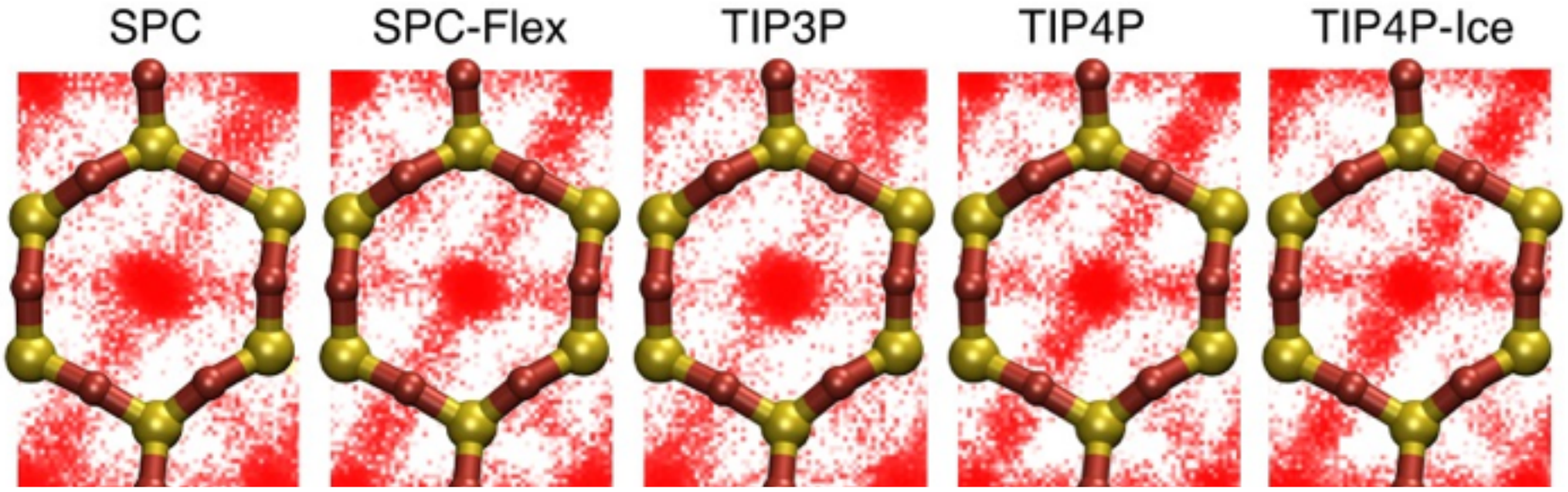
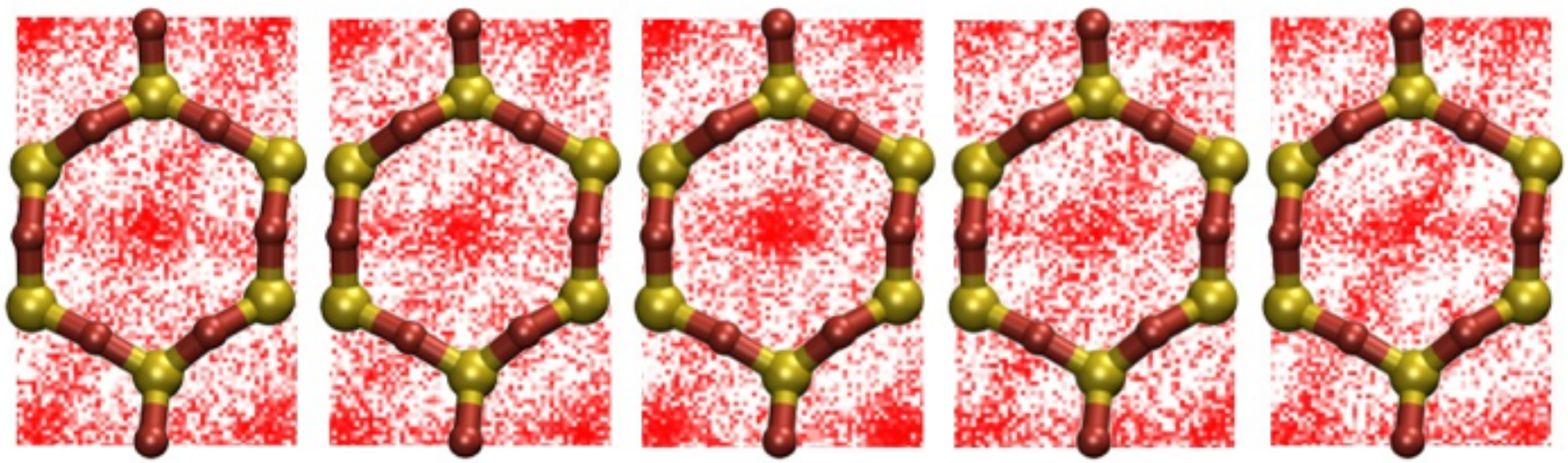


Montmorillonite

Siloxane rings of kaolinite show more diffuse water structuring

Kaolinite siloxane



2D density profiles - projections on the xz plane

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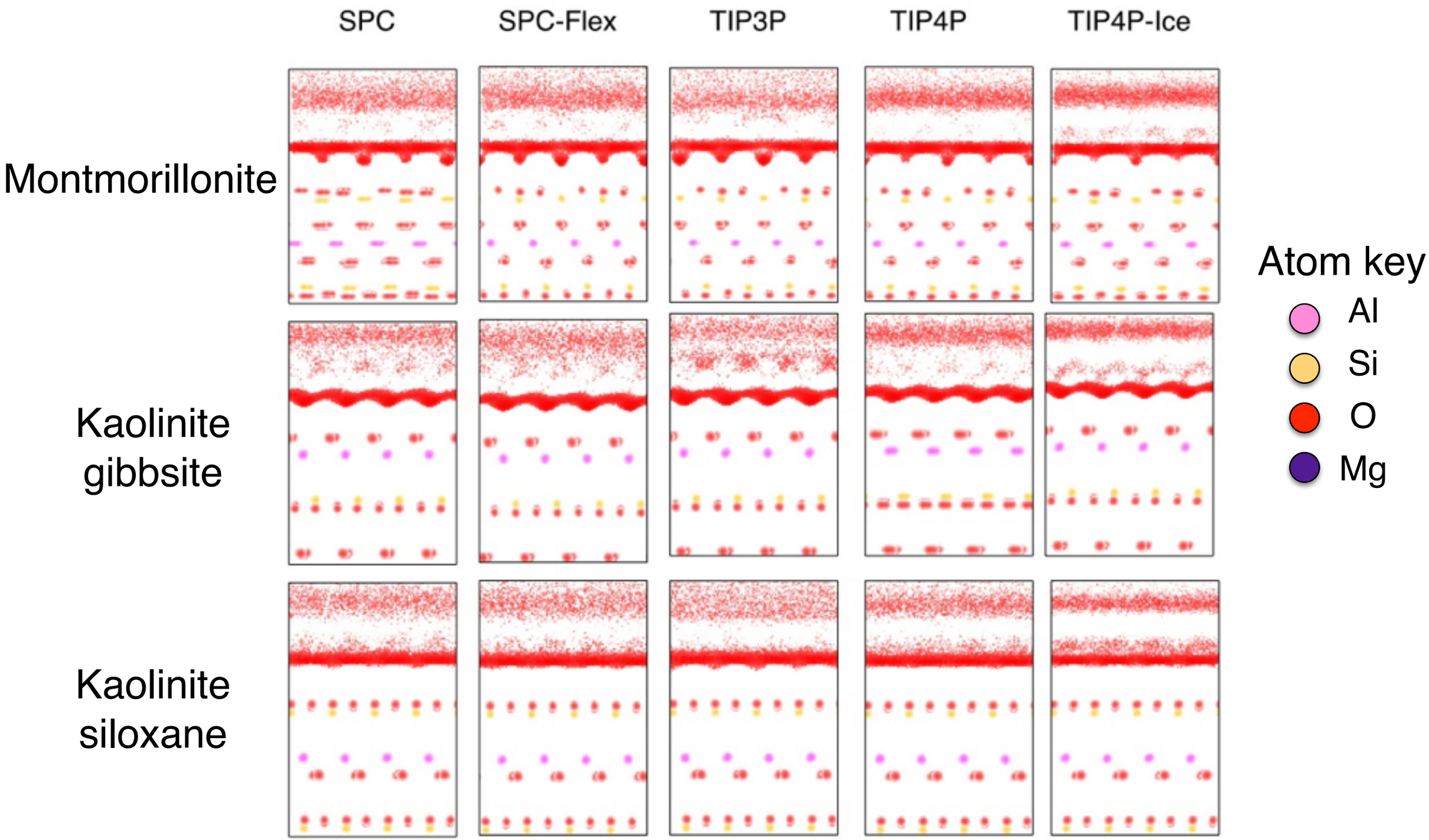

Molecular simulation can be used to study this phenomion

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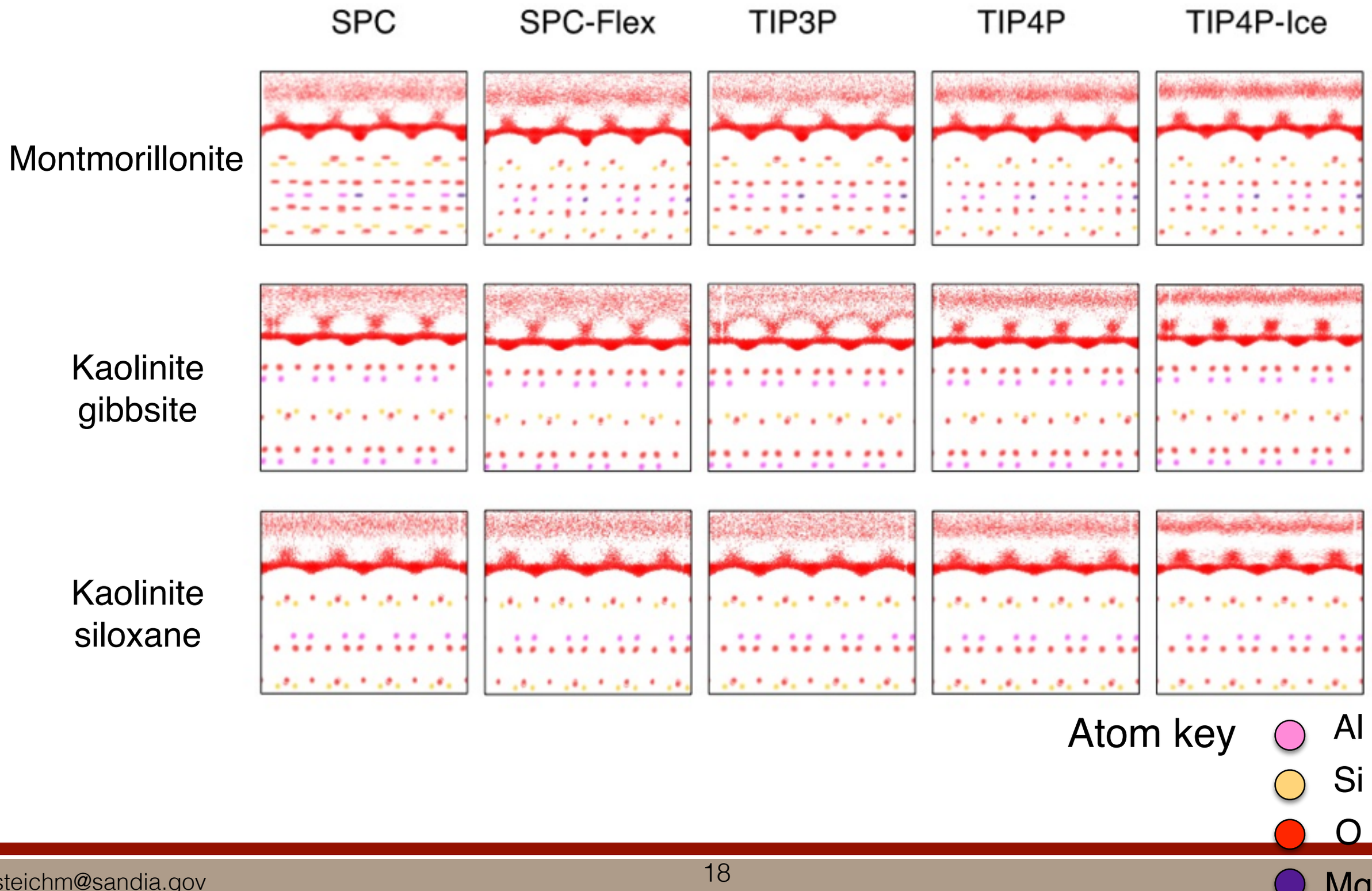

Diffusion coefficients are calculated based on MSD peaks

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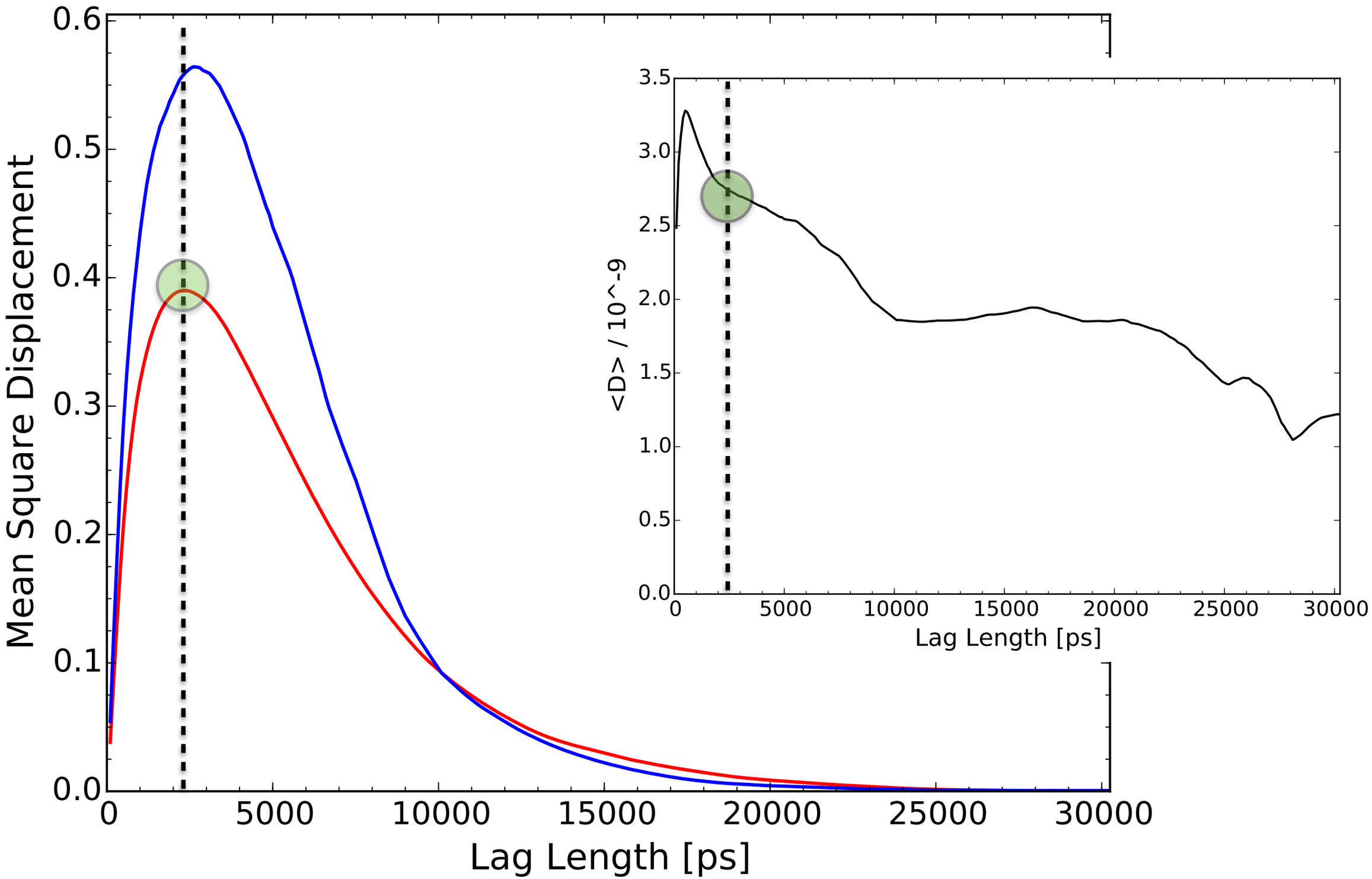
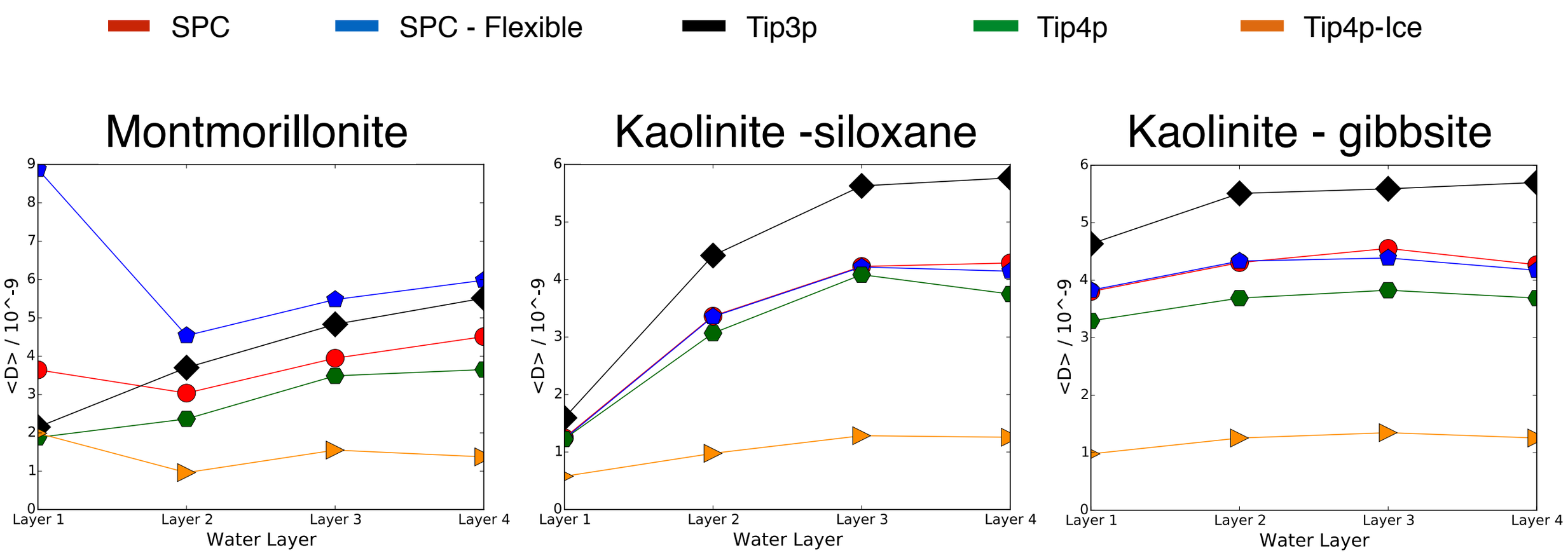


Dynamic properties - diffusion coefficients



Conclusions

Original hypothesis

- *Structural results will have similar for the three site models but potentially more structured for the higher charged 4 site models.* ★
- *Rigid water models will have faster diffusion properties than flexible models.* ★
- *Hydrophilic surfaces will be most impacted by choice of water model.* ★

Additional comments

- Overall, water models behave similarly when studying interfacial properties using the clayff force field
- The Tip4P-Ice model shows the most structure in the first and second water layers

Acknowledgements and thank you

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Sodium ion 1d density profiles (montmorillonite)