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Sandia National Laboratories

Transport-mechanical-chemical coupling effects during clay dehydration

Tuan Ho, Carlos Jove-colon, Yifeng Wang, and Eric Coker

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U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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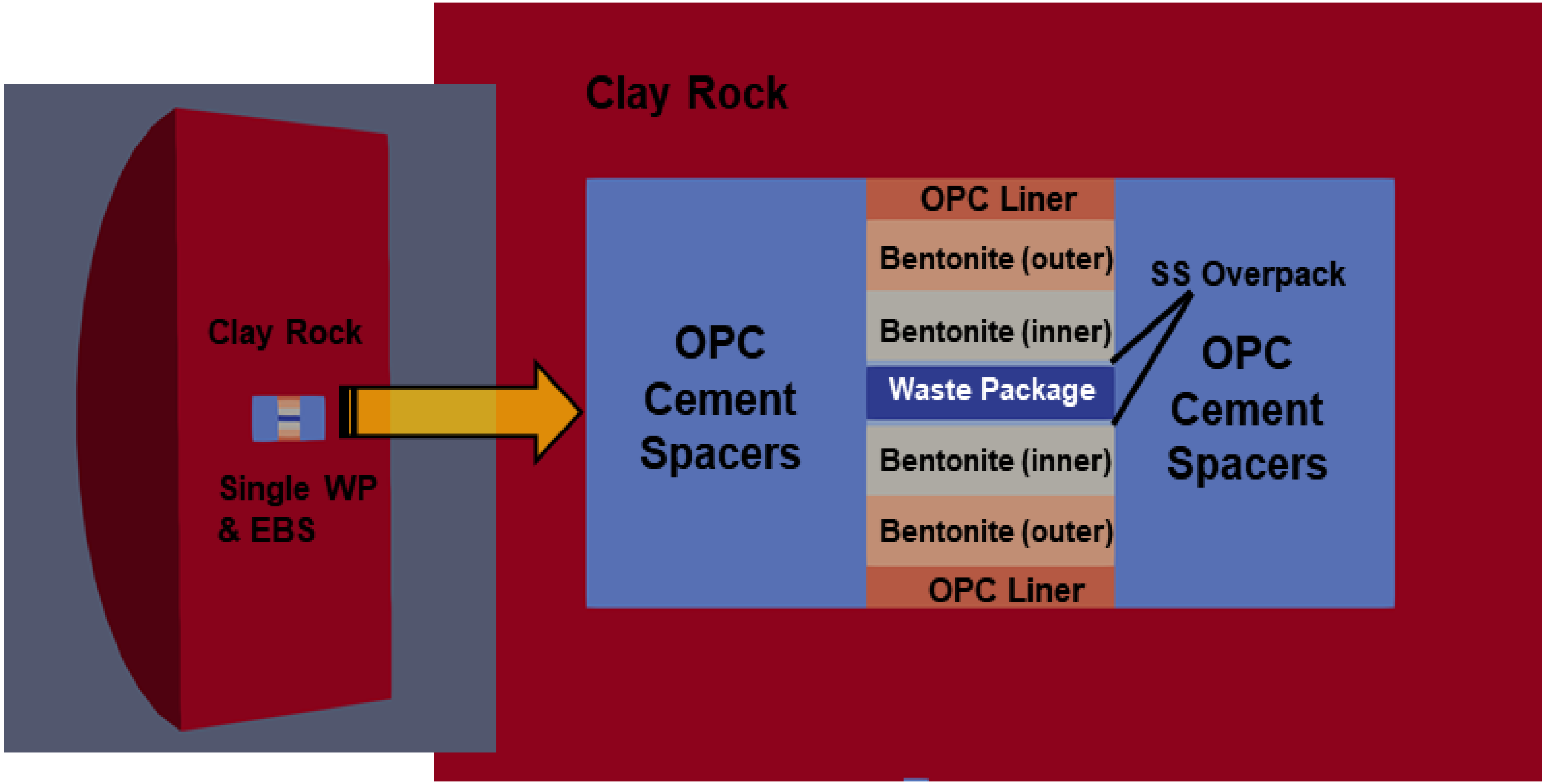
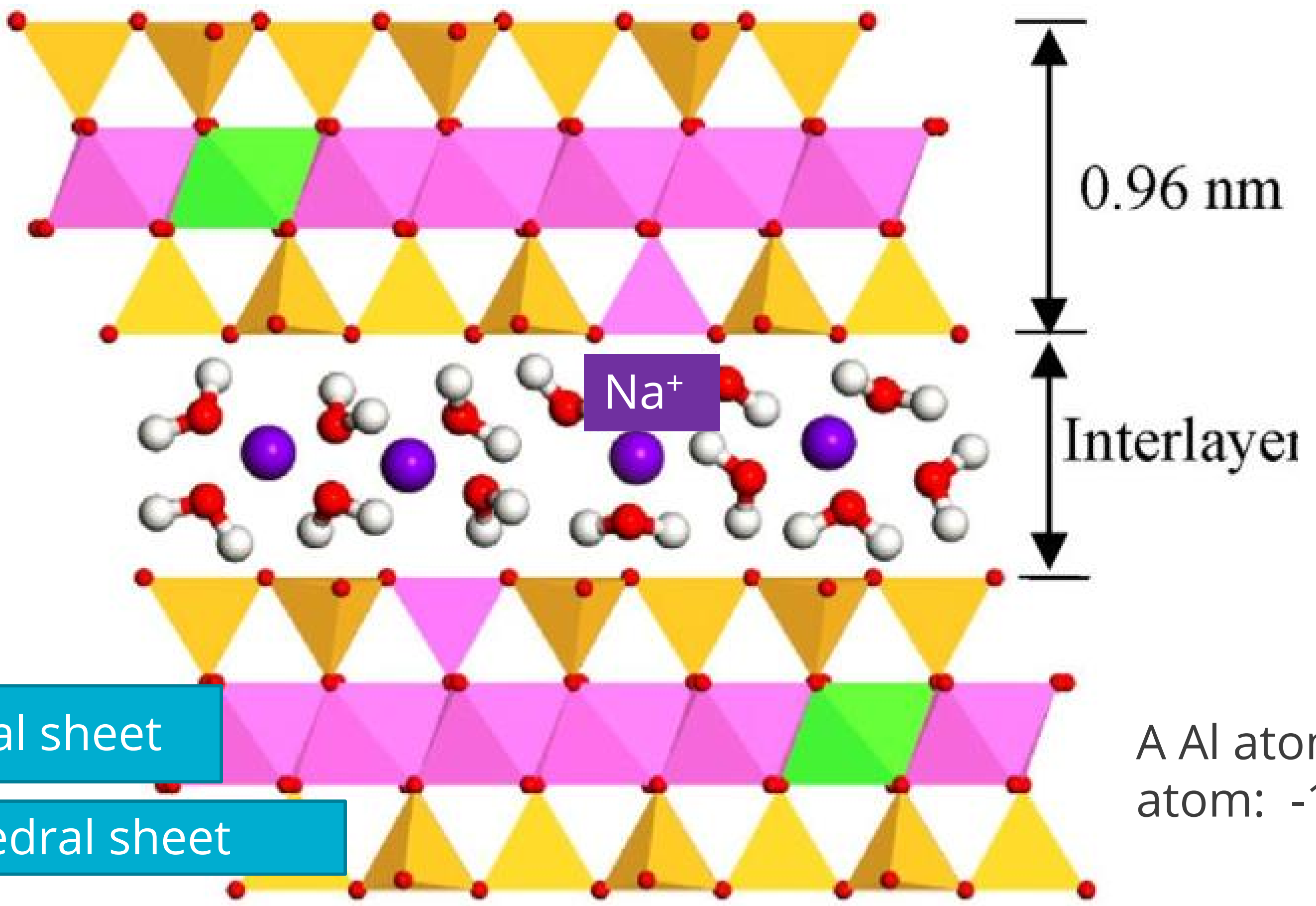
Introduction: engineered barrier system in a nuclear waste repository



Key benefits of bentonite:

- **Low hydraulic conductivity, and high self-sealing ability**
- **High retention capacity for radionuclides**

Introduction: montmorillonite



d-spacing

Al-centered octahedral sheet

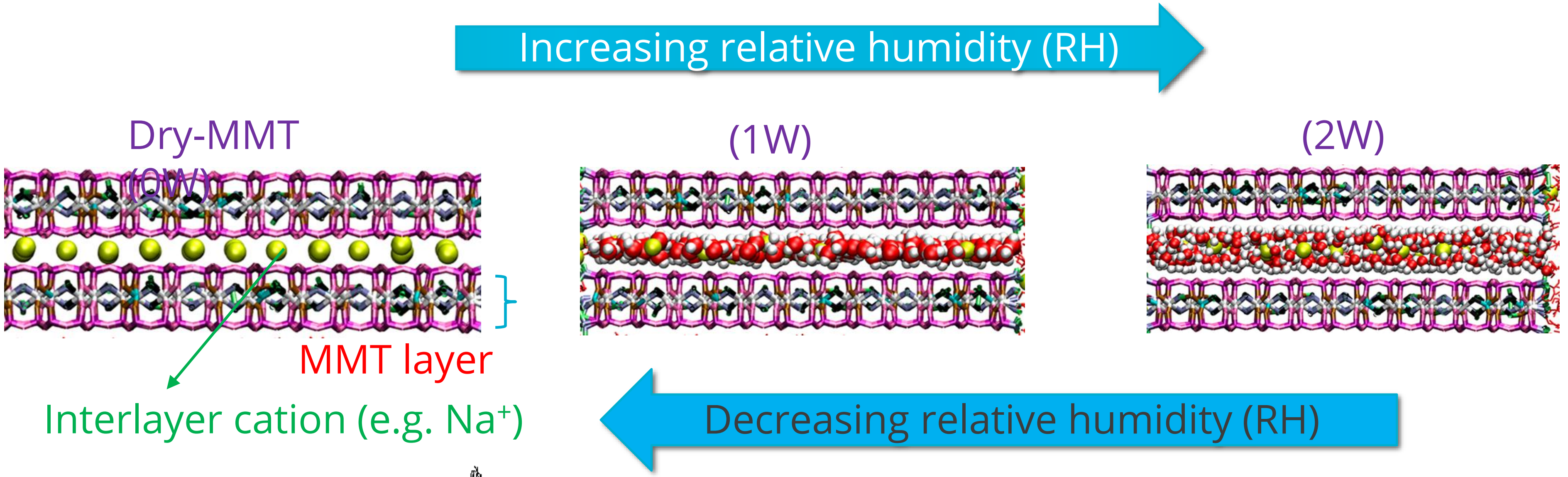
Si-centered tetrahedral sheet

A Al atom is replaced by a Mg atom: -1 charge

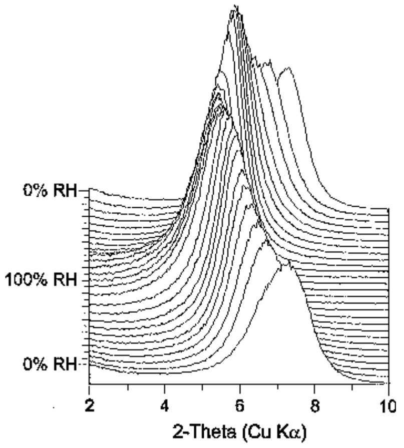
Applied Clay Science, 123, (2016), 239-258

Swelling/shrinking

Swelling/shrinking of montmorillonite (MMT) with increasing/decreasing relative humidity



XRD

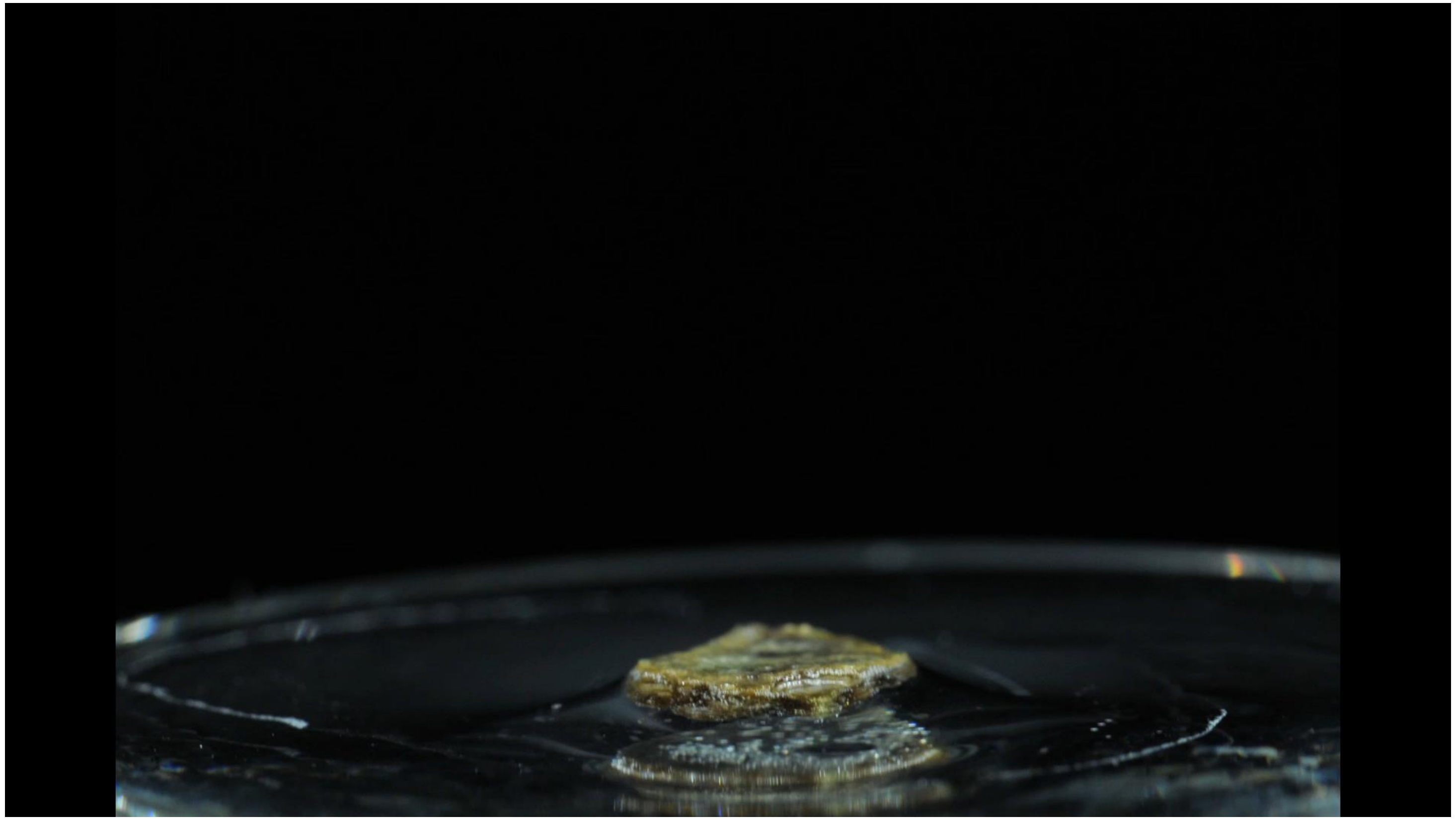


Chipera et al, *Advances in X-ray Analysis* 2019, *39*, 713-722.

Transport-mechanical-chemical coupling effects

Swelling

Transport-mechanical-chemical coupling effects

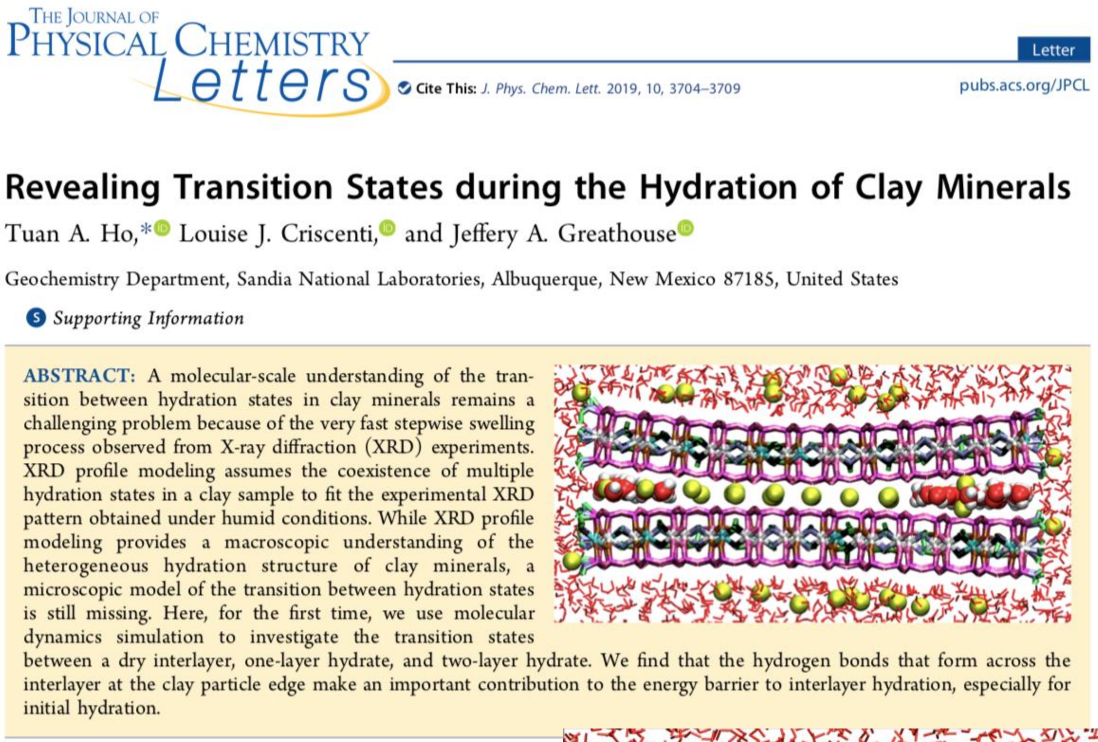


Vermiculite swelling in hydrogen peroxide

S. Hillier et al., Clay Minerals (2013) 48, 563

Hydration/dehydration

Hydration



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Letter

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Revealing Transition States during the Hydration of Clay Minerals

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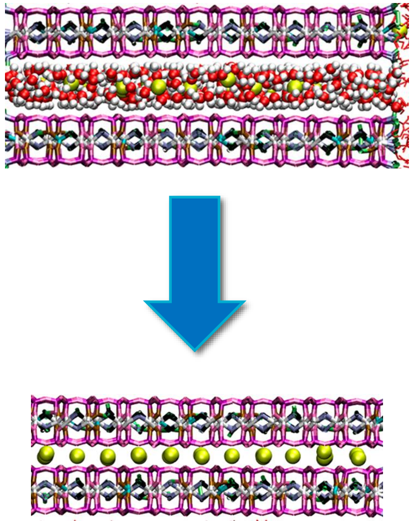
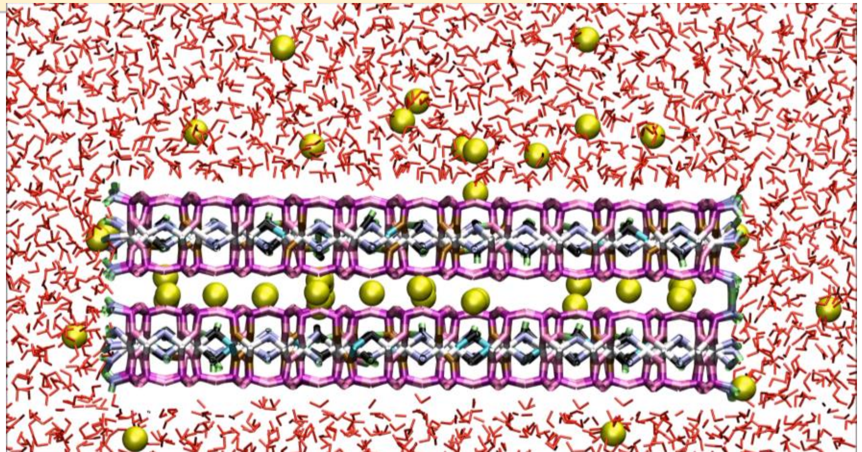
Supporting Information

ABSTRACT: A molecular-scale understanding of the transition between hydration states in clay minerals remains a challenging problem because of the very fast stepwise swelling process observed from X-ray diffraction (XRD) experiments. XRD profile modeling assumes the coexistence of multiple hydration states in a clay sample to fit the experimental XRD pattern obtained under humid conditions. While XRD profile modeling provides a macroscopic understanding of the heterogeneous hydration structure of clay minerals, a microscopic model of the transition between hydration states is still missing. Here, for the first time, we use molecular dynamics simulation to investigate the transition states between a dry interlayer, one-layer hydrate, and two-layer hydrate. We find that the hydrogen bonds that form across the interlayer at the clay particle edge make an important contribution to the energy barrier to interlayer hydration, especially for initial hydration.

The focus of this talk: **dehydration**

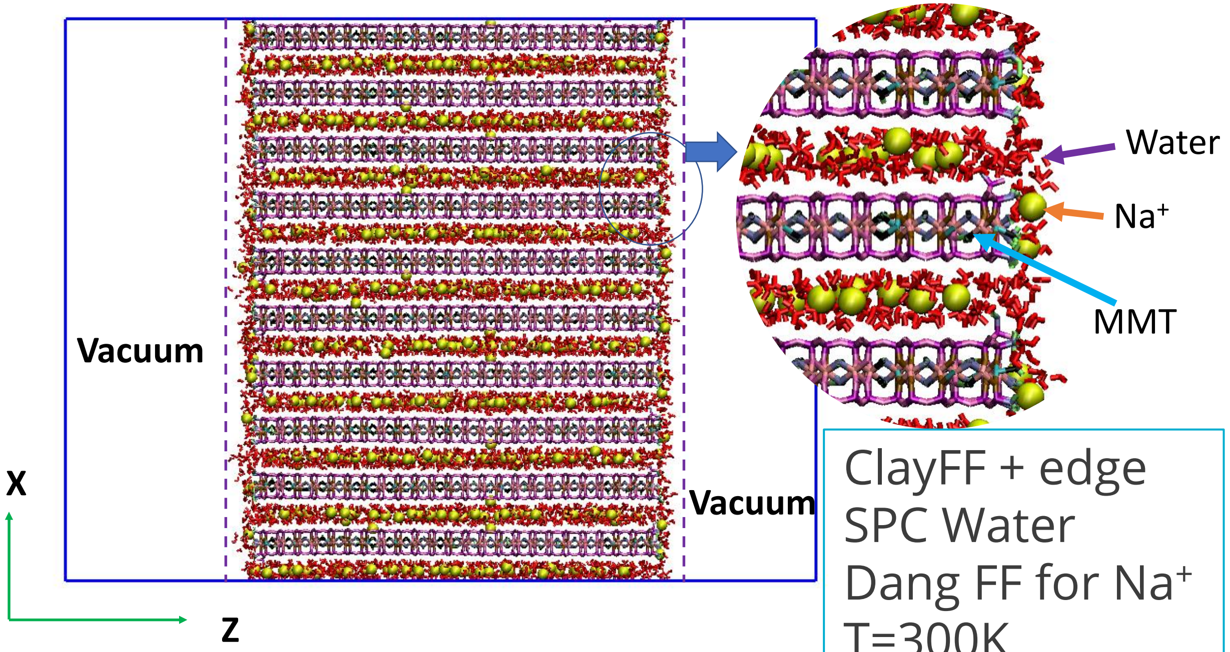


Structural-energetic relationship

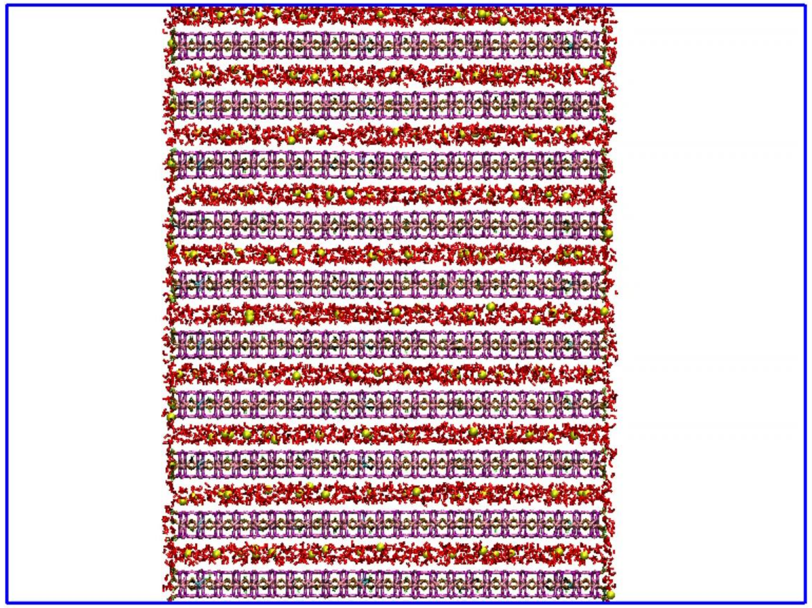


Method

Dehydration MD simulation



ClayFF + edge
SPC Water
Dang FF for Na^+
T=300K
P=1atm



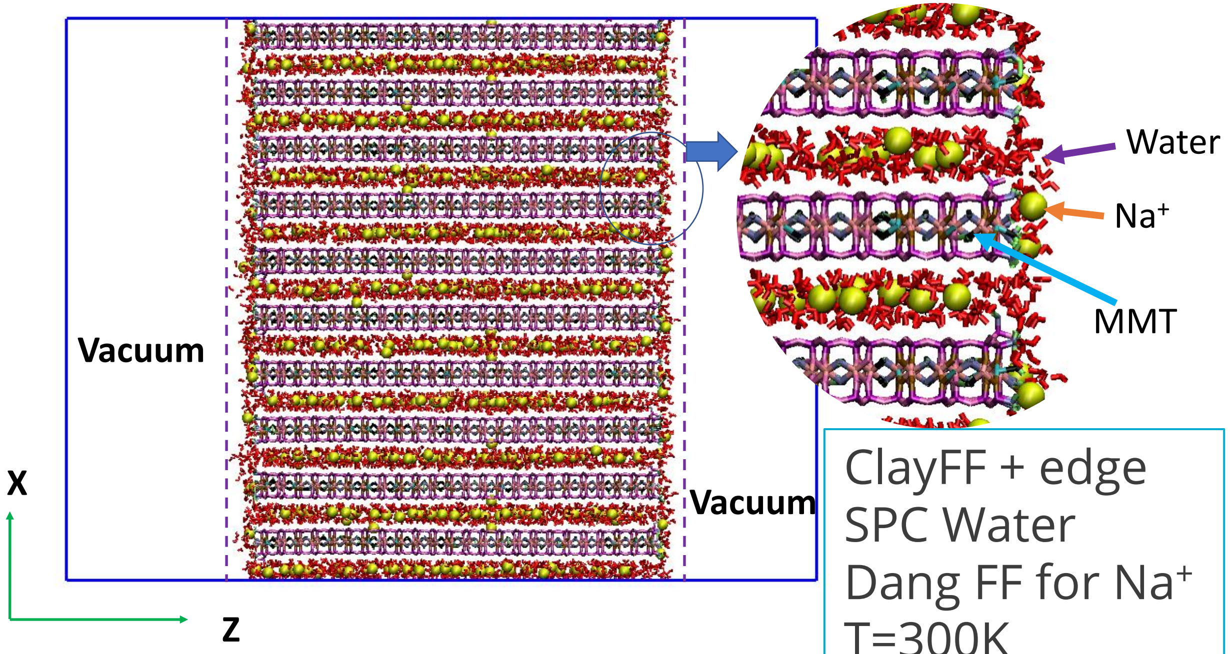
Unique features:

Remove water molecules that move to the vacuum region
Deform of materials in the X direction

Simulate the transport, chemical, mechanical coupling effects

Method

Dehydration MD simulation



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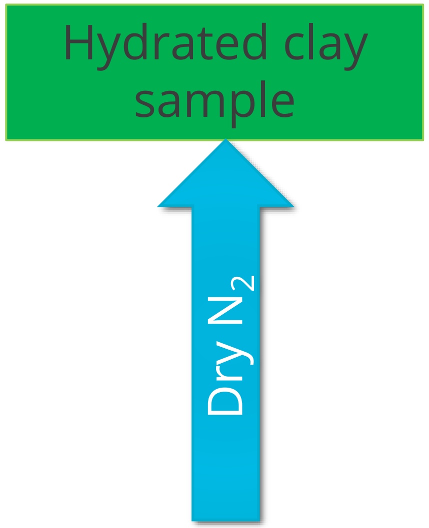
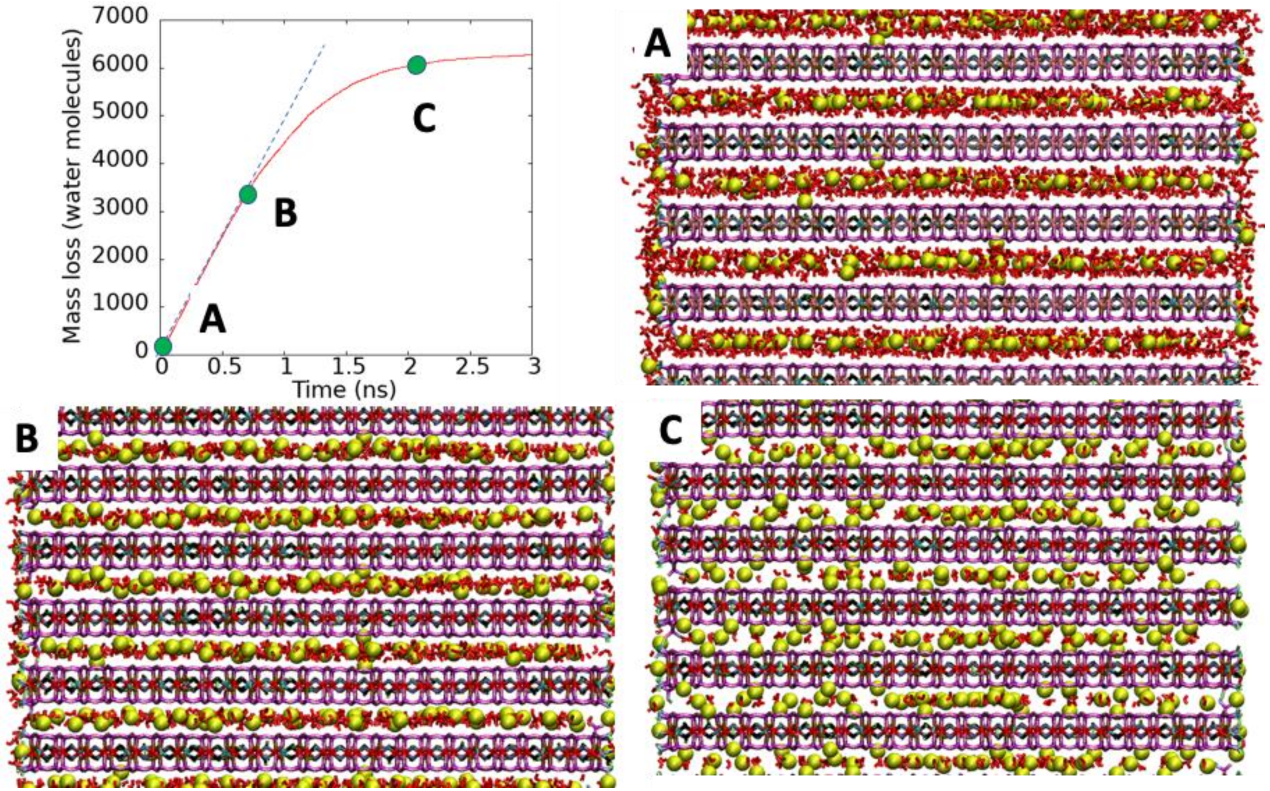
TGA/DSC/XRD experiment



Mass loss
In-situ XRD to monitor the d-spacing
Heat flow

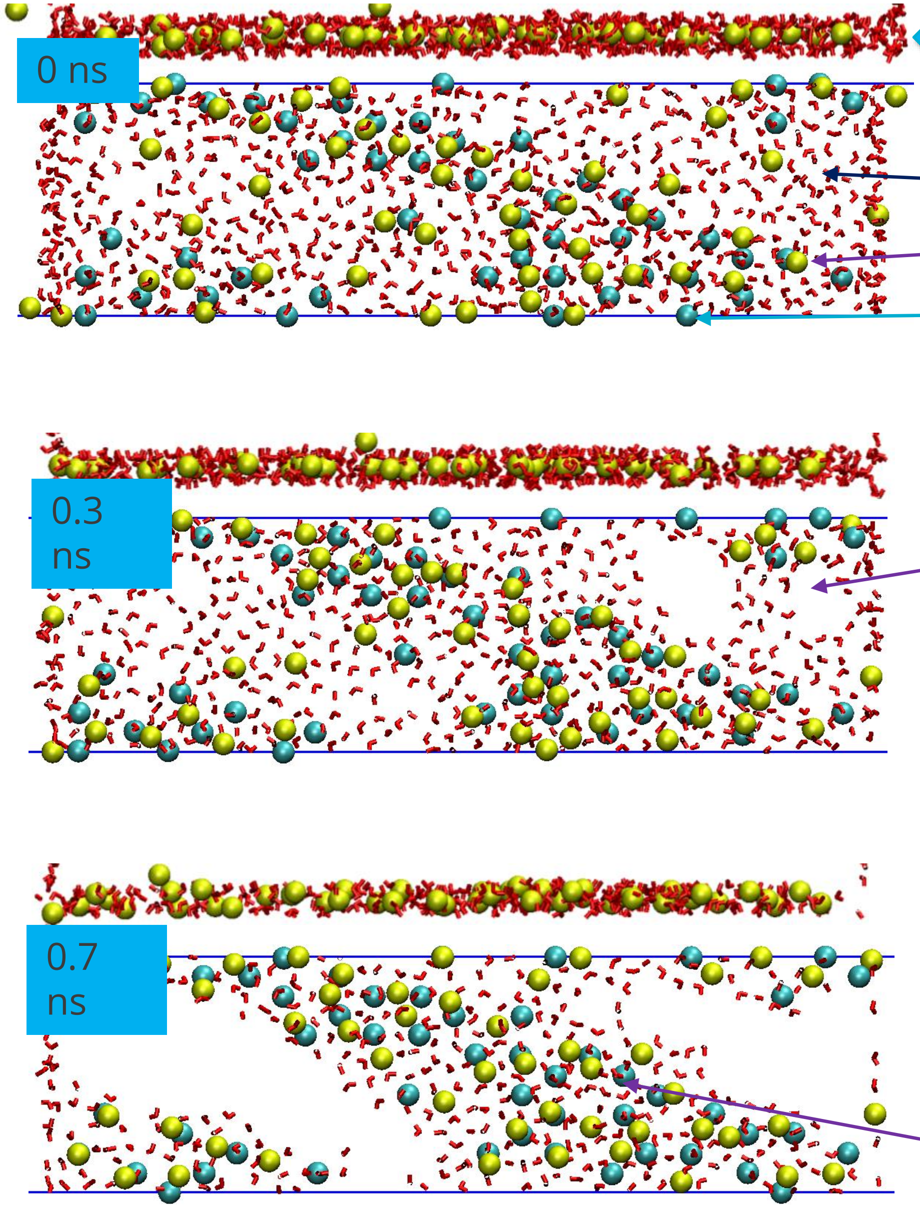
Mass loss

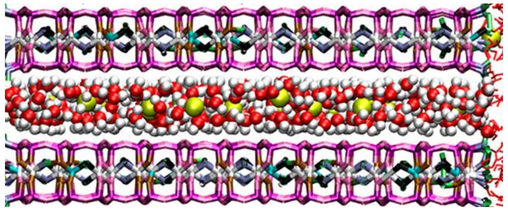
MD dehydration simulation for 2W state



Water transport in the early dehydration process is fast.
The whole process is controlled by the evaporation.

Transport pathway





Side view

Top view

Water (red)

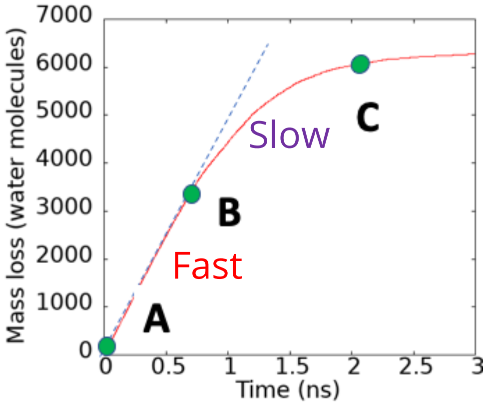
Na^+ (yellow)

Mg (cyan): substitute for Al in MMT layer

Mg:Al ratio of 0.75:3.25

Hydrophobic/ siloxane

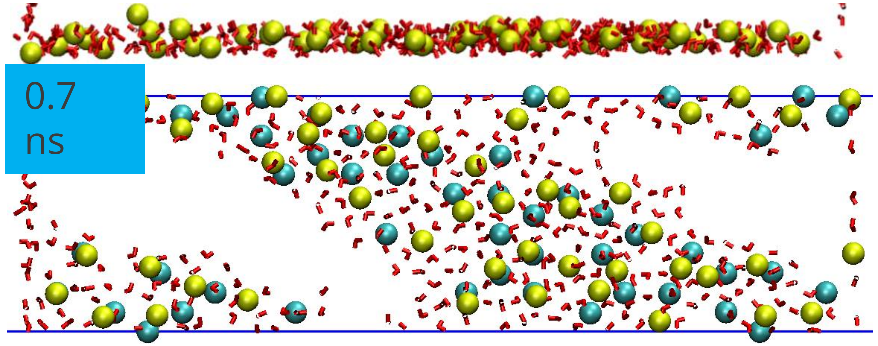
Water transport is fast near these sites

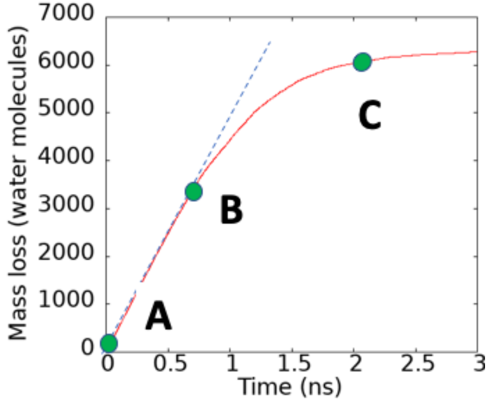


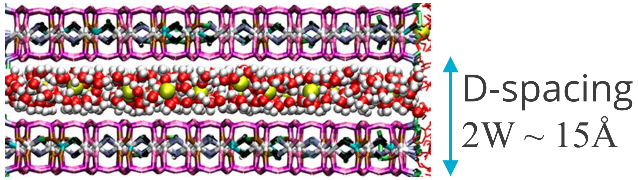
Hydrophilic/ Na+/metal substitution

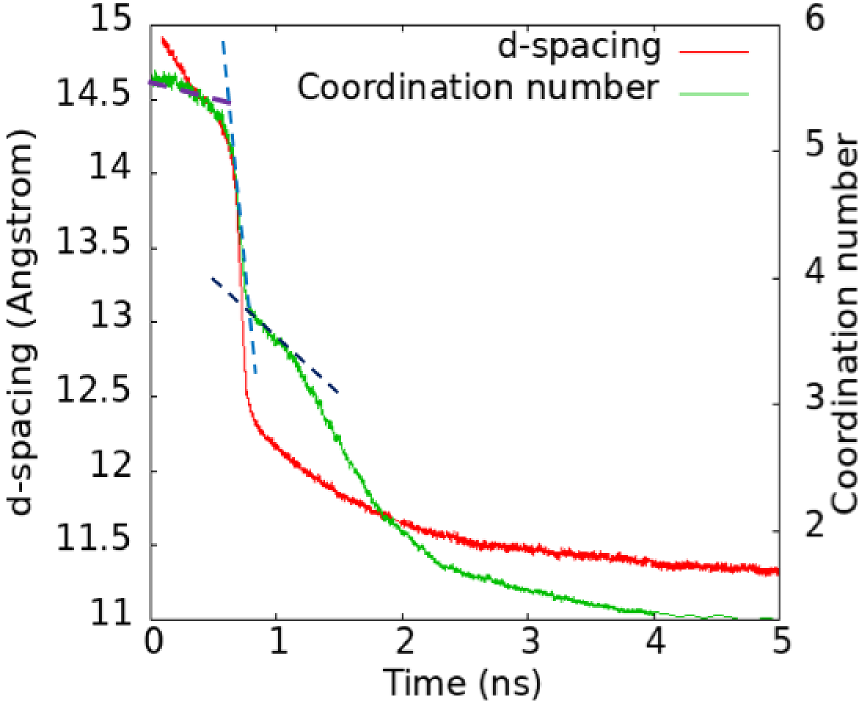
Water transport is slow near these sites

Transport-chemo-mechanical coupling effect



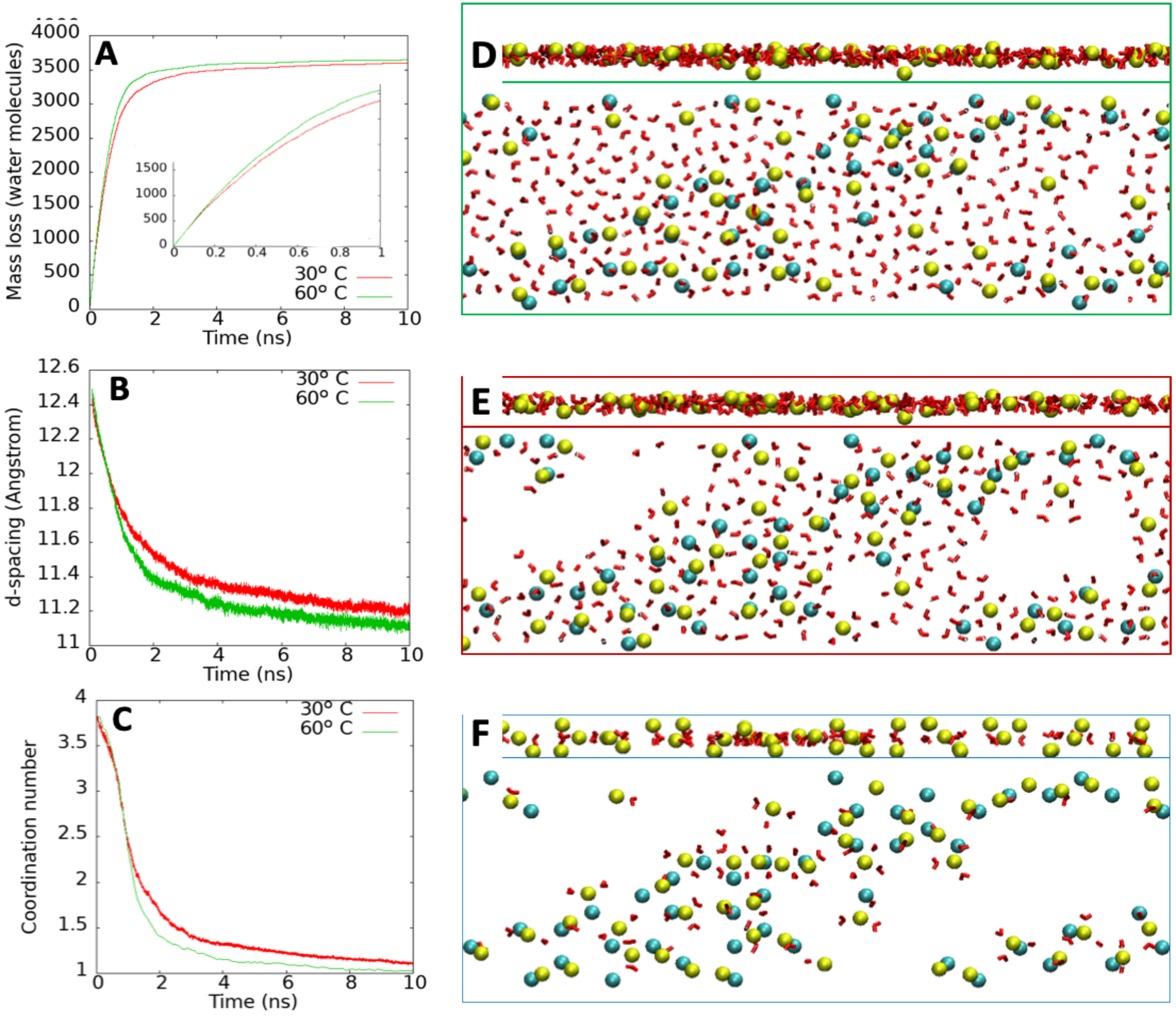






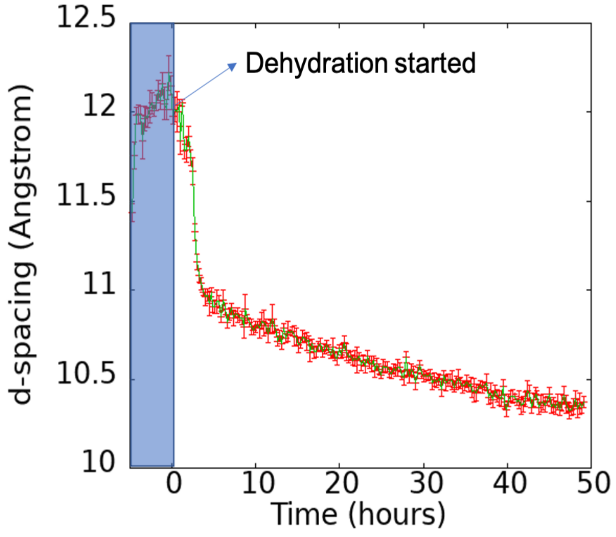
strong correlation between Na^{+} coordination number and d-spacing

Dehydration simulation for 1W state

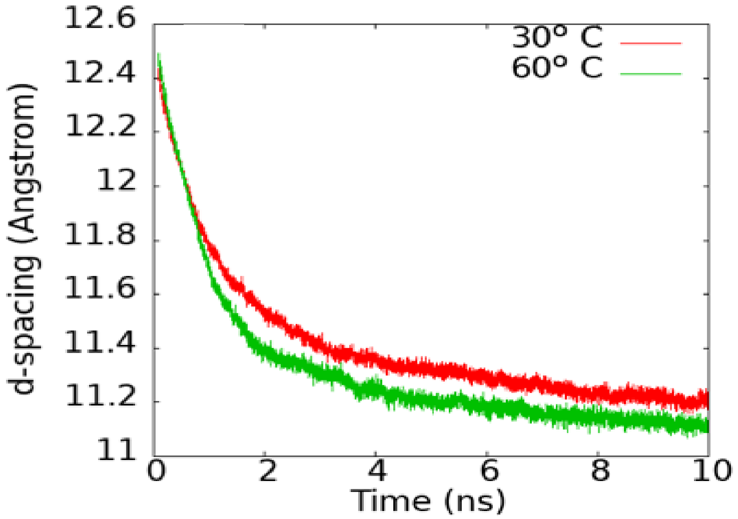


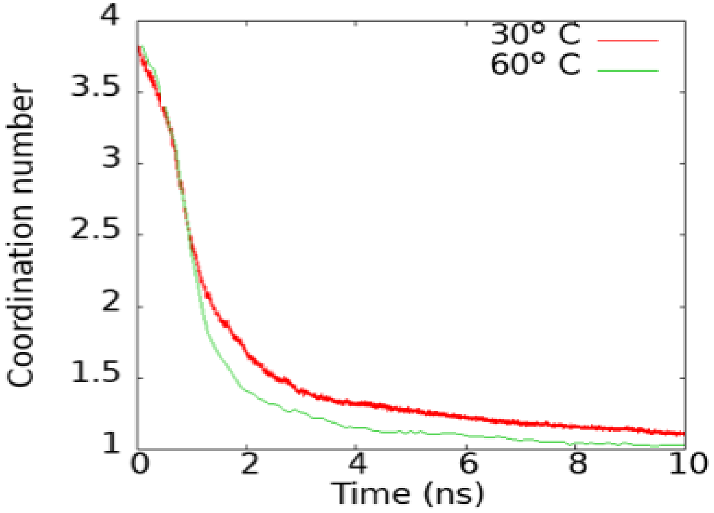
Dehydration simulation for 1W state

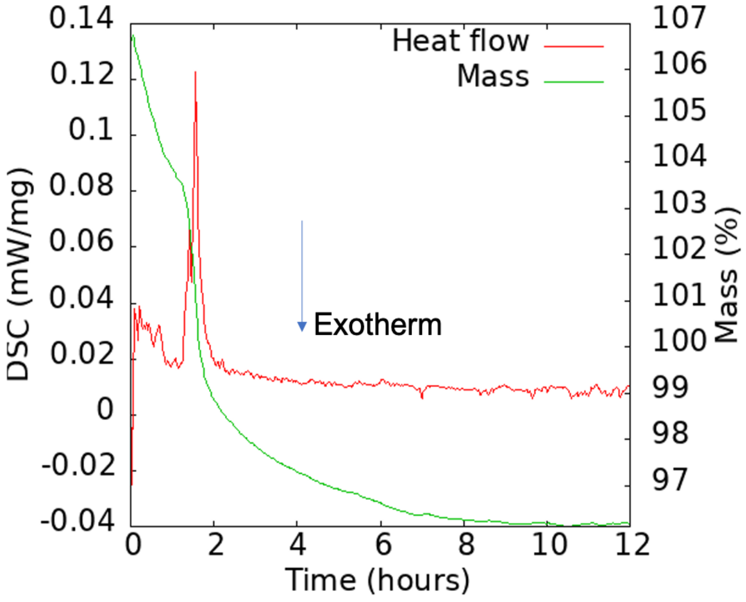
Experimental results



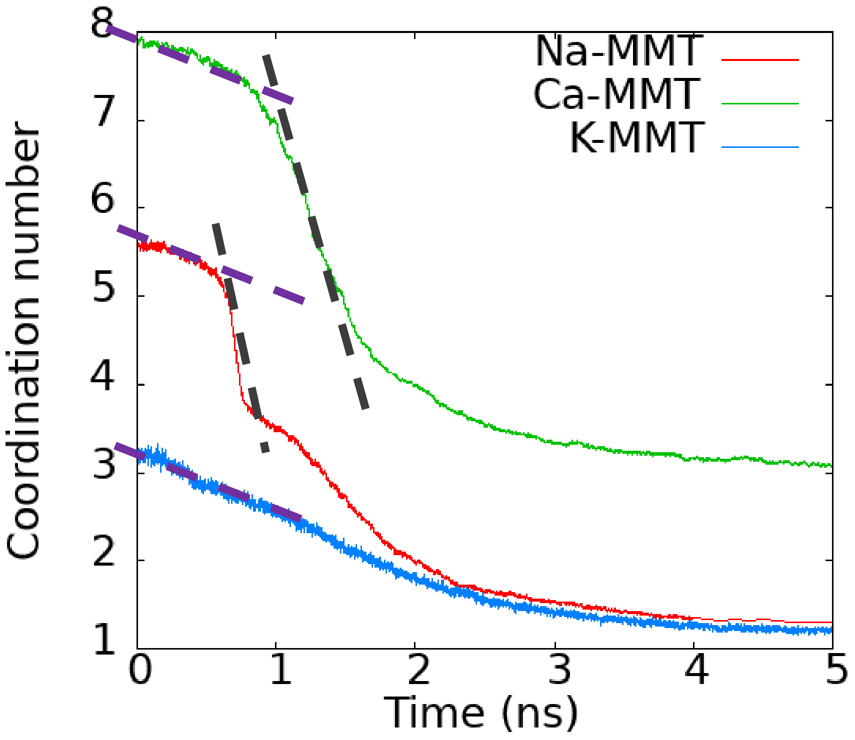
MD results

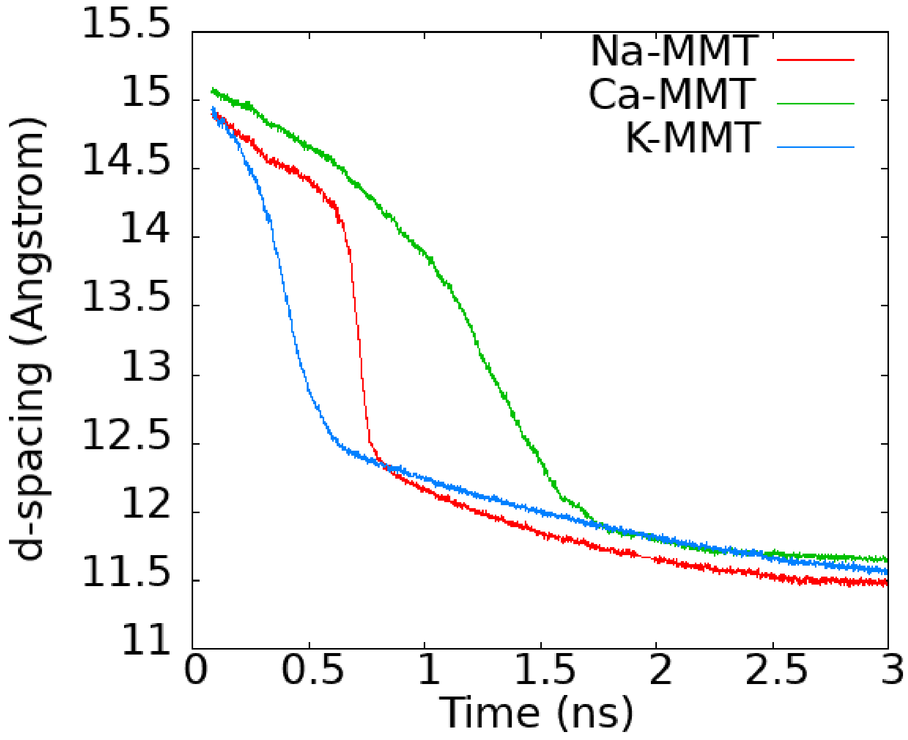




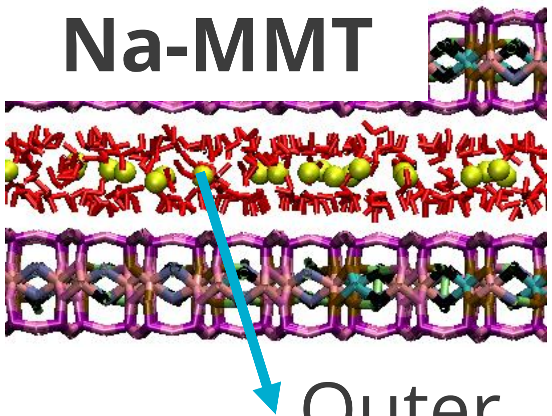


Effect of cations

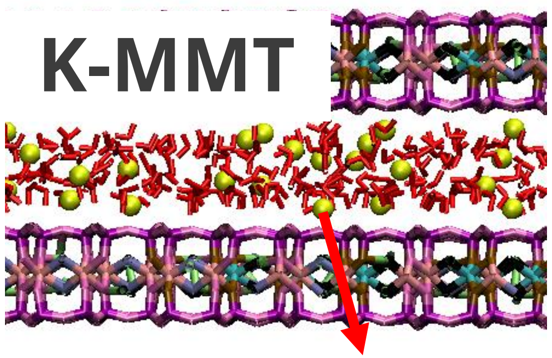




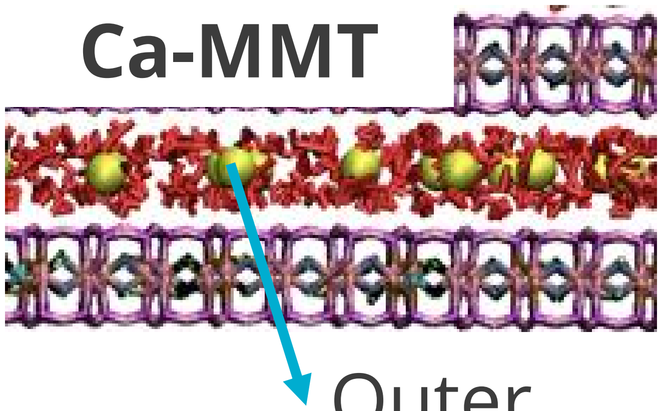
Higher abundance of water molecules in the hydration shell leads to a slower decrease in d-spacing



Outer sphere

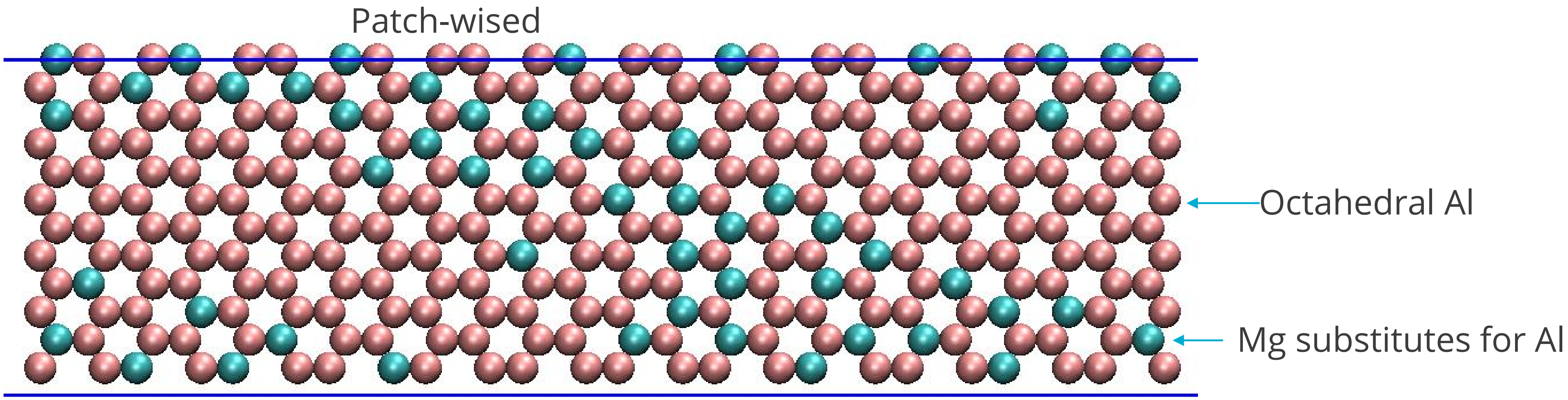


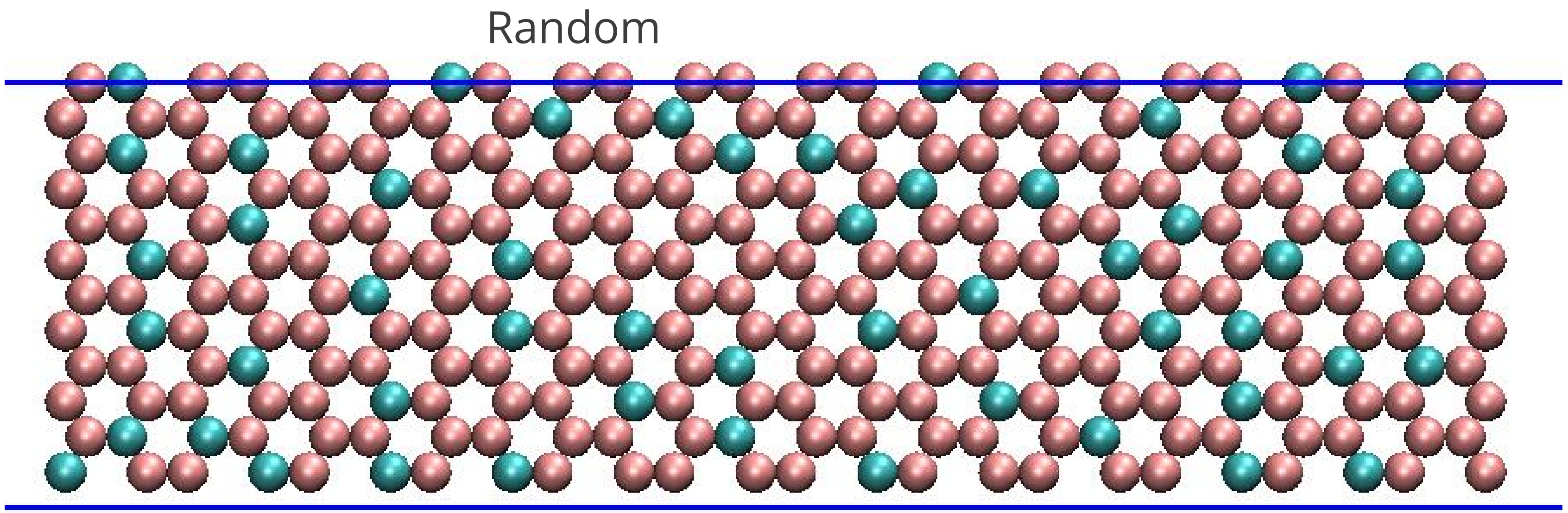
Inner sphere



Outer sphere

Effect of layer charge distribution





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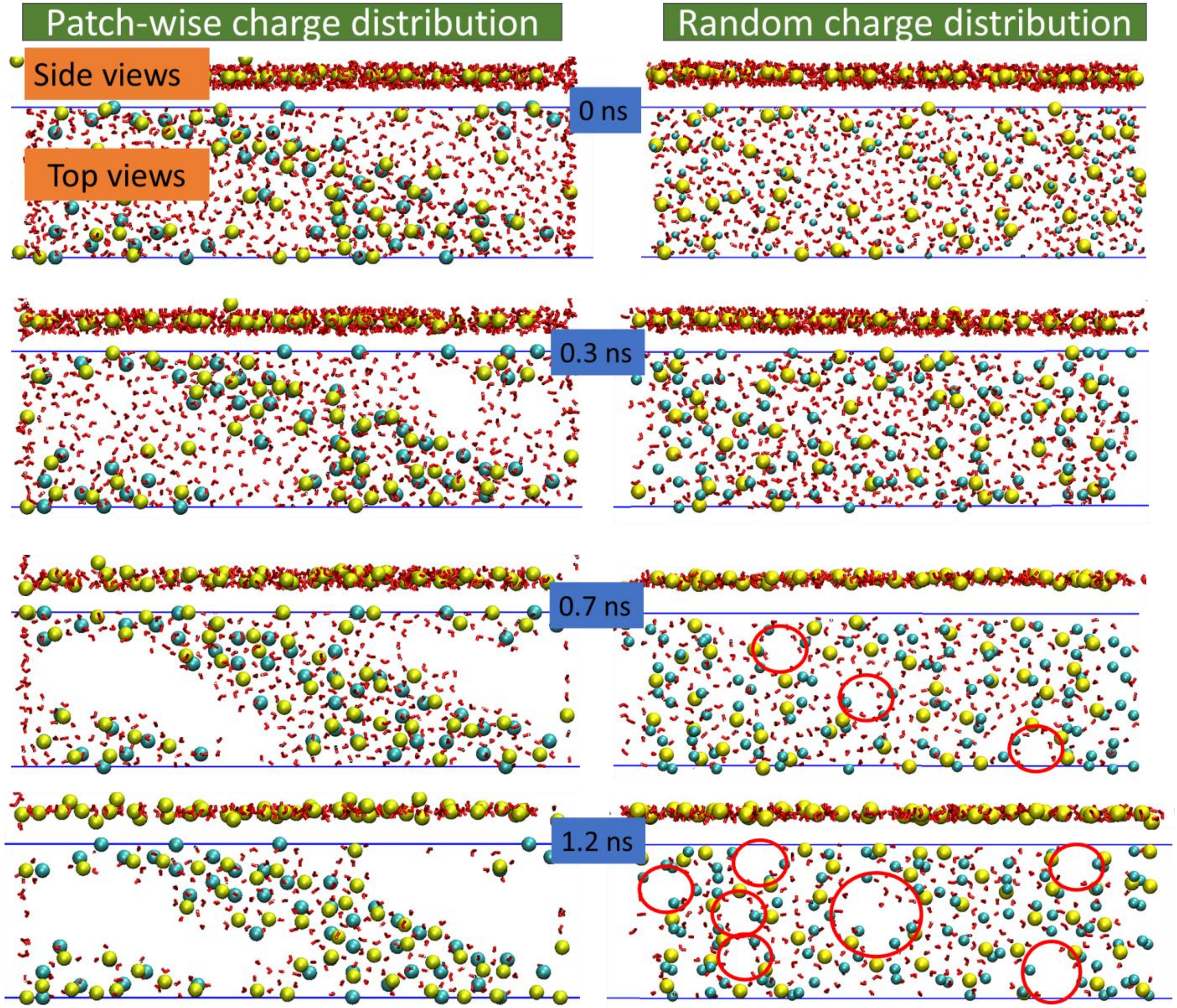

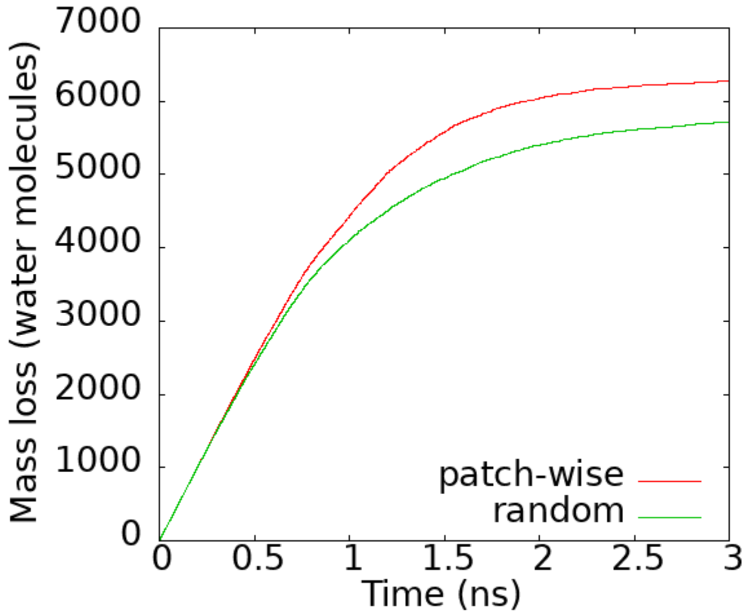

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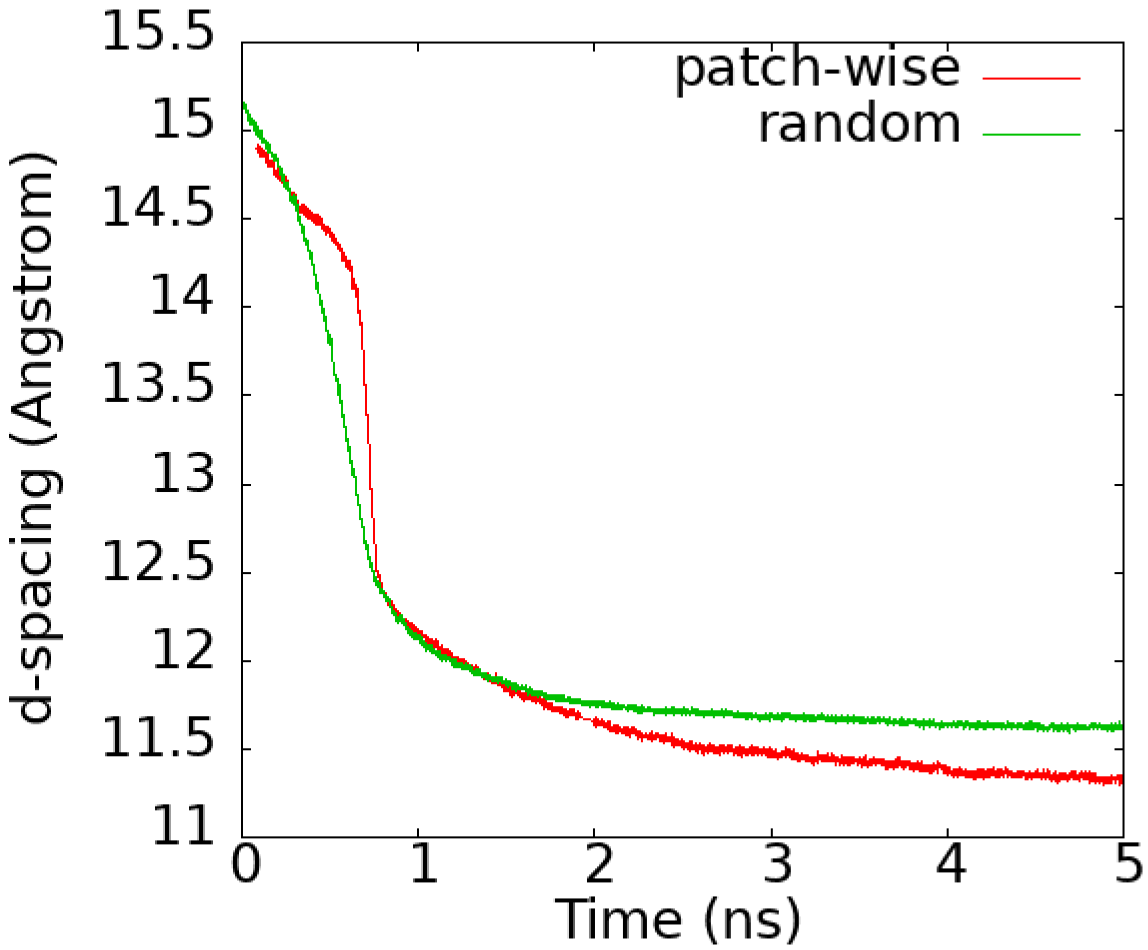
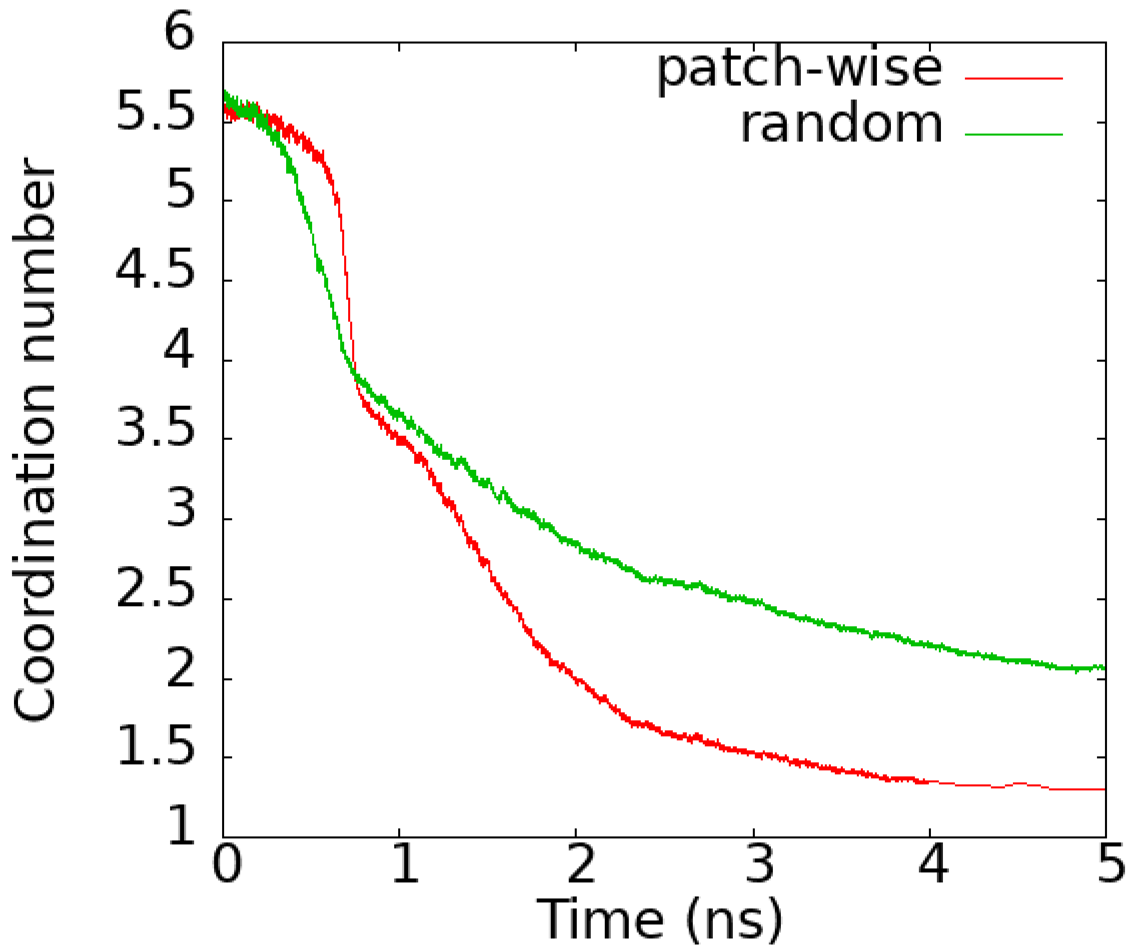
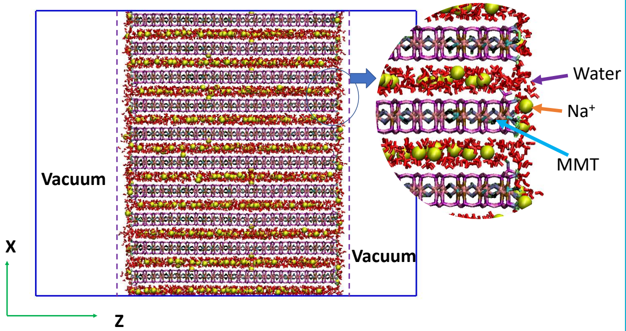
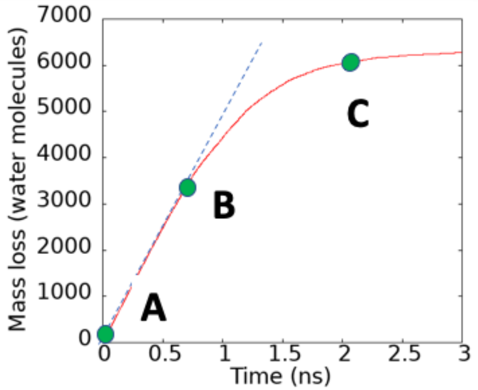


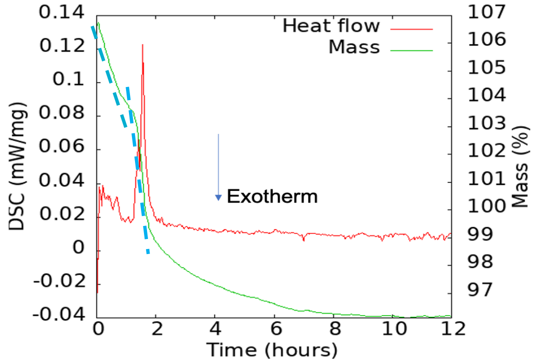


Conclusions



TGA/DSC





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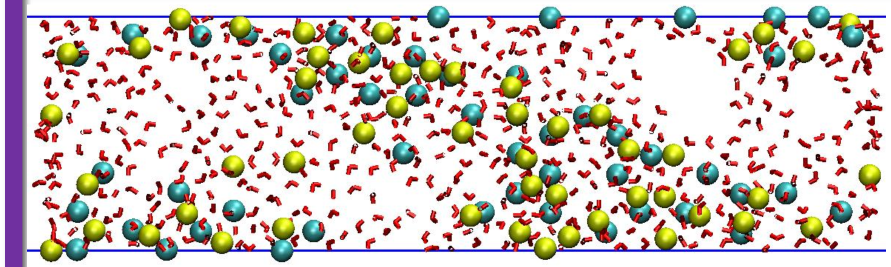
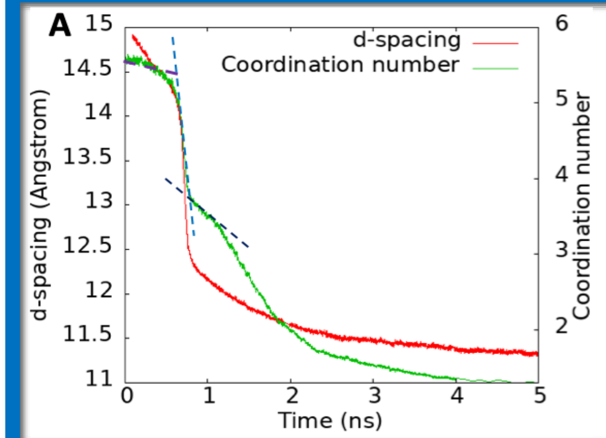


Water transport is

fast near hydrophobic/ siloxane sites

slow near hydrophilic/metal substitutions sites



Chemo-mechanical coupling effect

Thank you!

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