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Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering

PRESENTED BY

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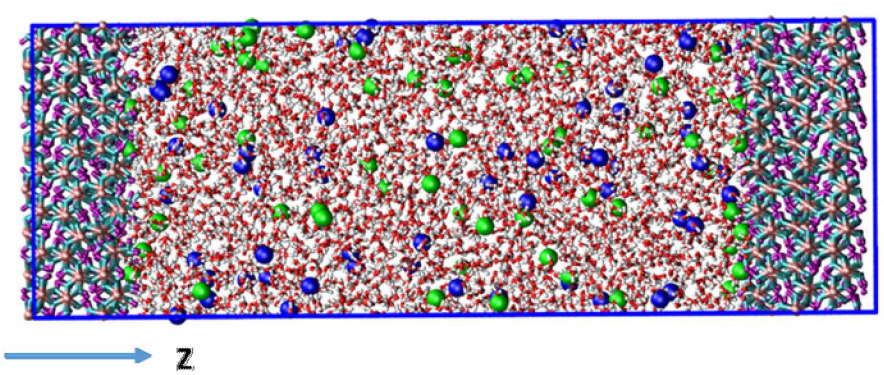
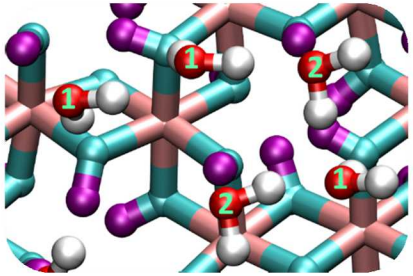
Objectives

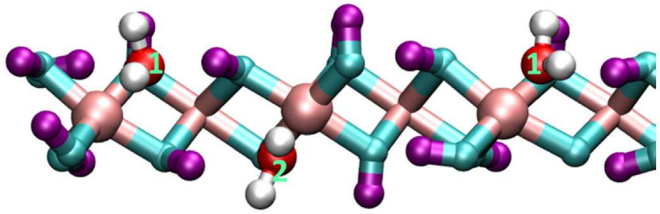
- To use molecular simulation to investigate ion diffusion and adsorption from aqueous solutions to minerals in increasing complex systems more representative of how mineral surfaces present themselves in a rock-like subsurface system.
- The model mineral used is gibbsite because it has properties similar to a clay mineral but does not include the additional complexity of an interlayer.
- Molecular simulations are performed for:
  - Water and ion adsorption to the basal (001) and edge (100) gibbsite surfaces
  - Water and ion adsorption to a gibbsite nanoparticle
  - Water adsorption to gibbsite nanoparticle aggregates that are created through de-watering and compaction

Adsorption on Gibbsite basal (001) and edge (100) surfaces



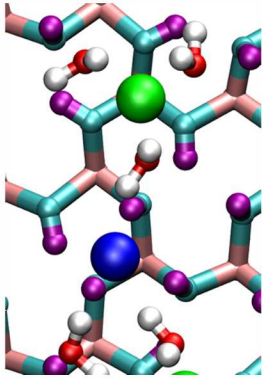


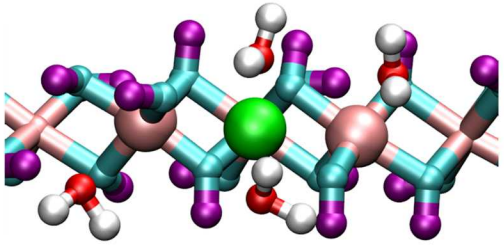
(001)



(100)

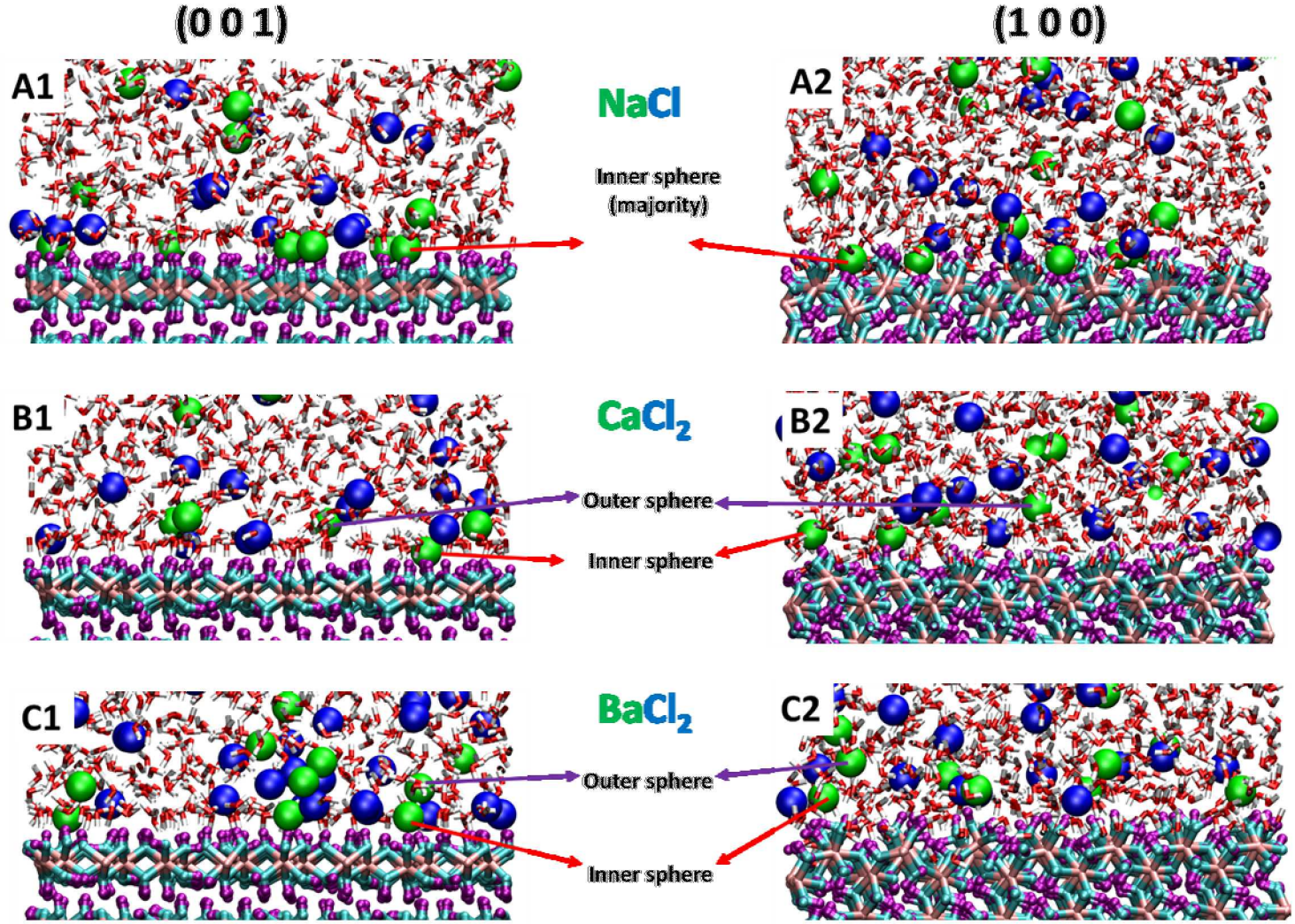
Water adsorption sites



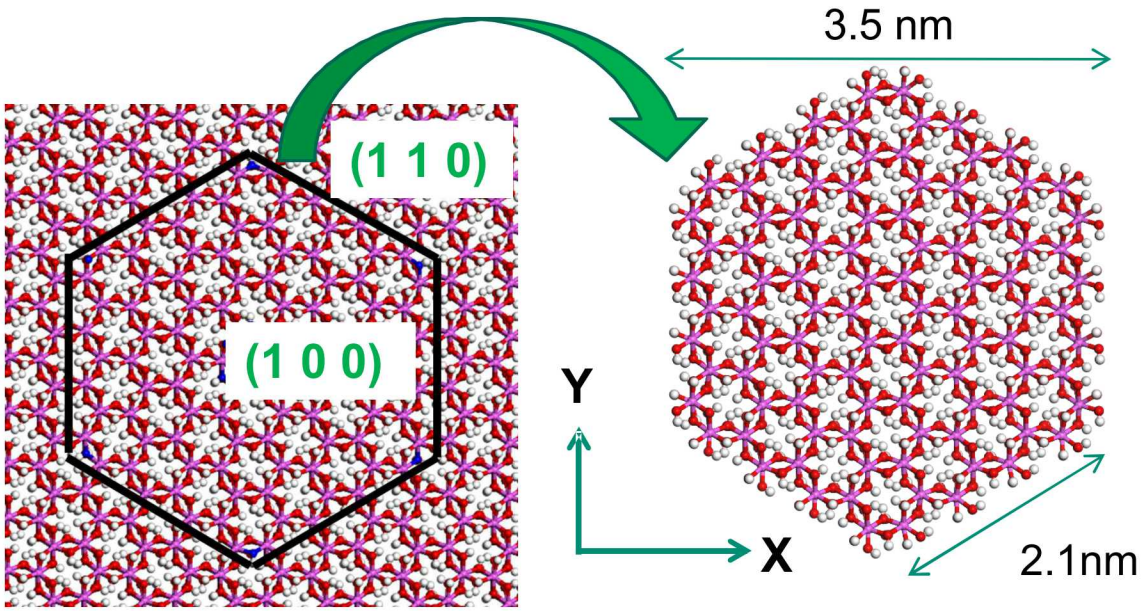


Ion adsorption sites

Cation Adsorption to Gibbsite Surfaces

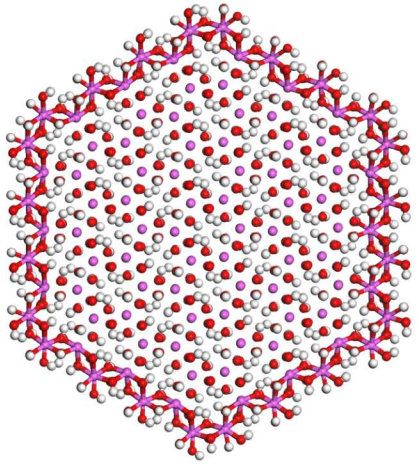


Gibbsite nanoparticle construction



Lateral dimension 2.1 – 3.5 nm
Particle thickness 3 layers (1.3 nm)

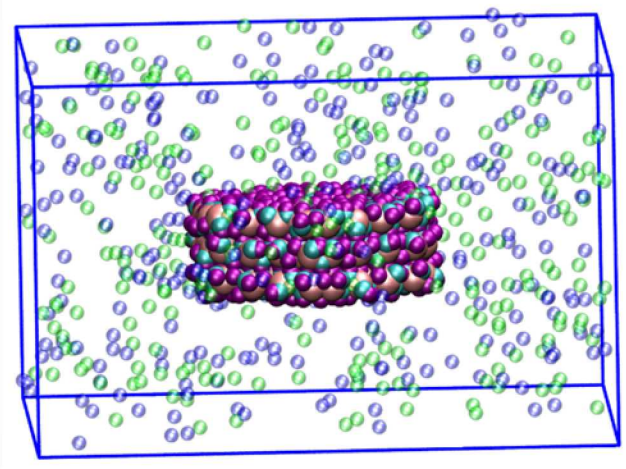
Exploit the hexagonal symmetry of bulk gibbsite



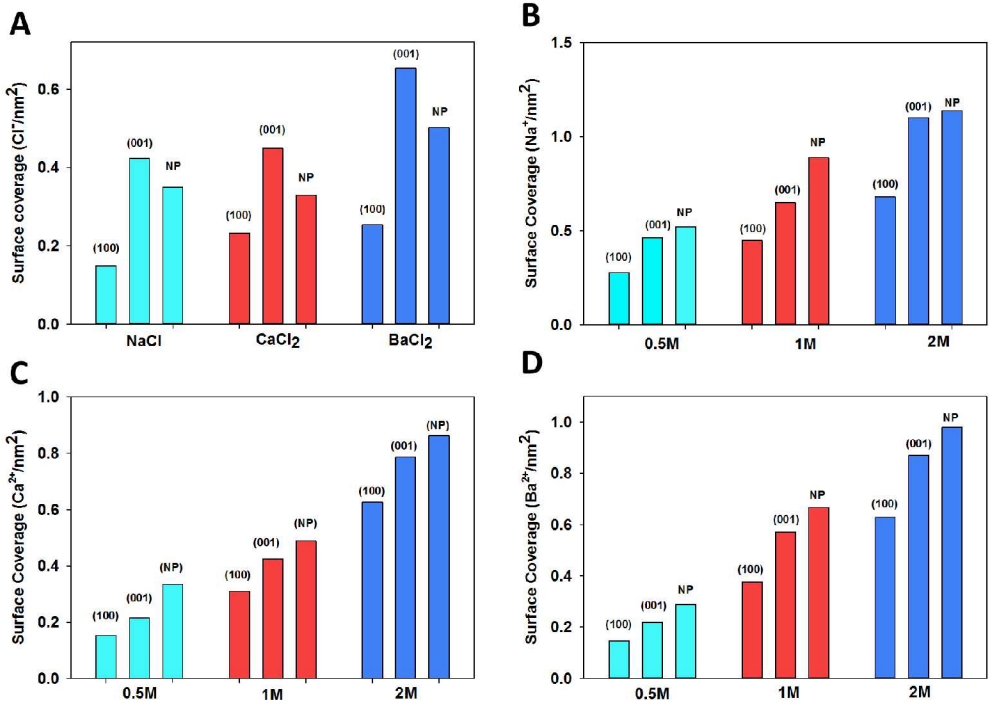
Molecular dynamics

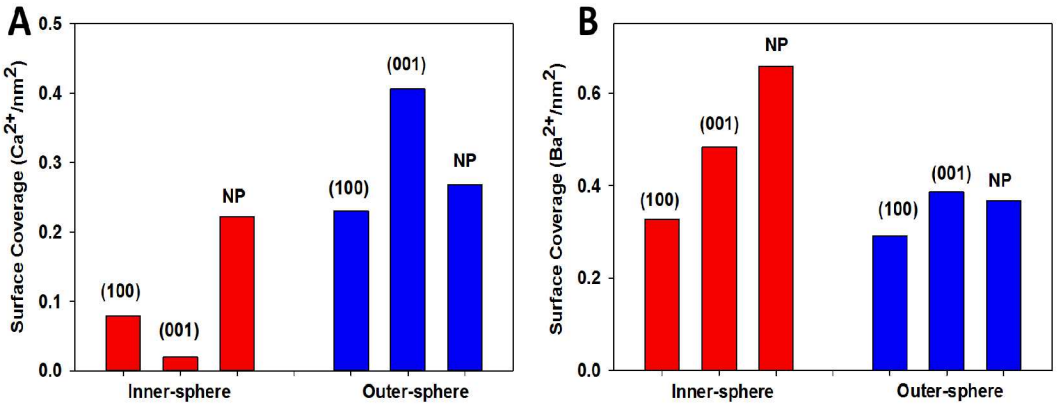
- LAMMPS code with ClayFF parameters.
- New Al-O-H angle bending term for stability of edge sites.
- Extra Al-O-Al term added for nanoparticle stability.

Comparison of Adsorption on Gibbsite Nanoparticle vs. Surfaces

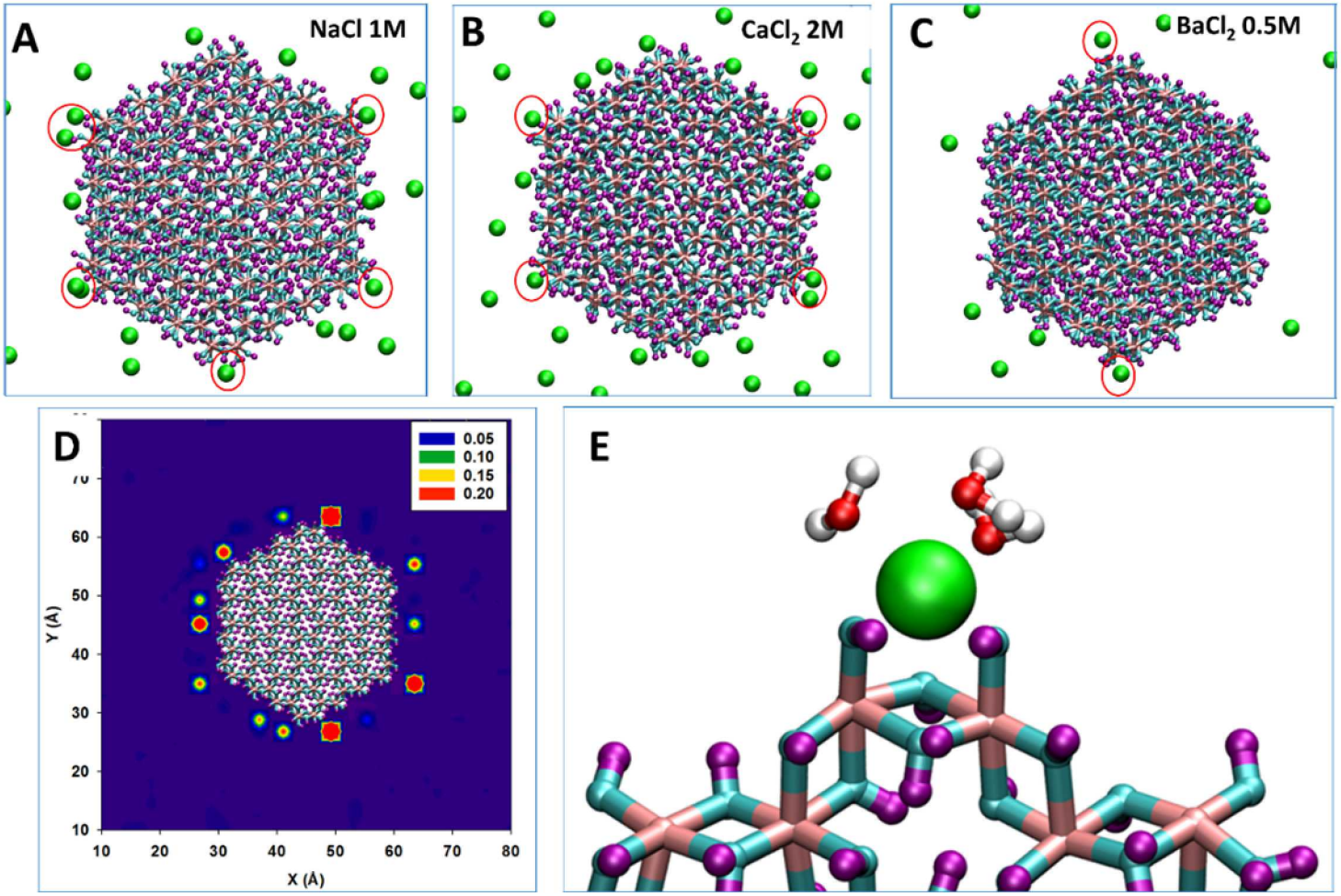


- Cl^- adsorption is not enhanced on NP
- Na^+, Ca^{2+}, and Ba^{2+} adsorption are enhanced on NP
- NPs exhibit higher concentrations of IS complexes

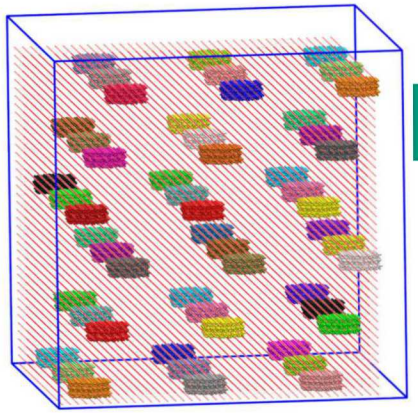




Cation Adsorption at Nanoparticle Corners

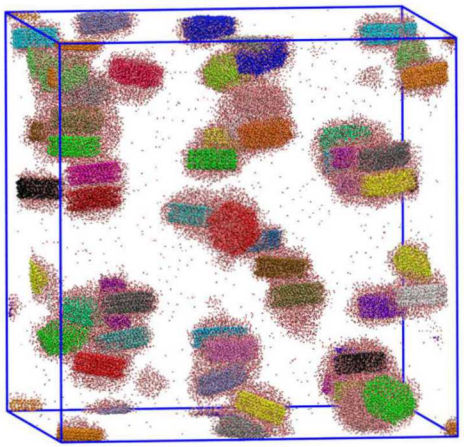


Gibbsite aggregation



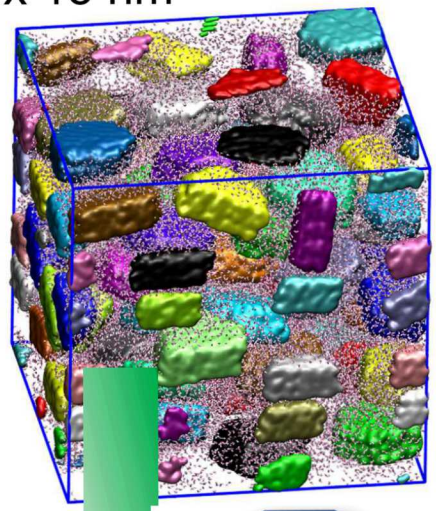
54 NPs, 55k H_2O
30 x 30 x 30 nm^3

NVT
0.3 ns
300 K



NPT
0.3 ns
300 K
100 MPa

Hydrated aggregate
15 x 15 x 15 nm^3



Effect of dewatering rate:

- Delete all water: "Fast"
- Delete 100 H2O/100 steps: "Intermediate"
- Delete 10 H2O/100 steps: "Slow"

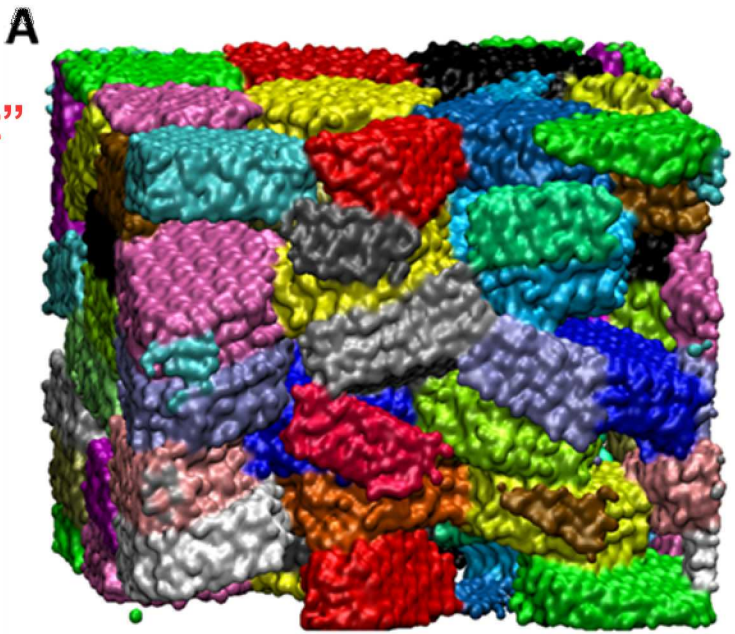
'Virtual' pump removes waters from a pre-defined region.

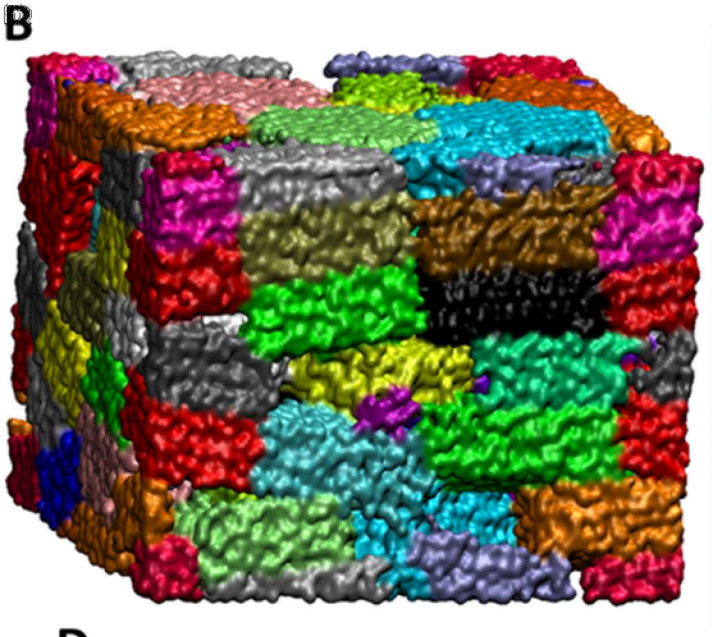
Effect of water content:

- 1 water layer around each particle: 1W (22.5 wt%)
- 2 water layers around each particle: 2W (37.2 wt%)
- Additional withdraw water from 2W: 2W_dewatering (6 wt%)
- Dry: 2W_dry

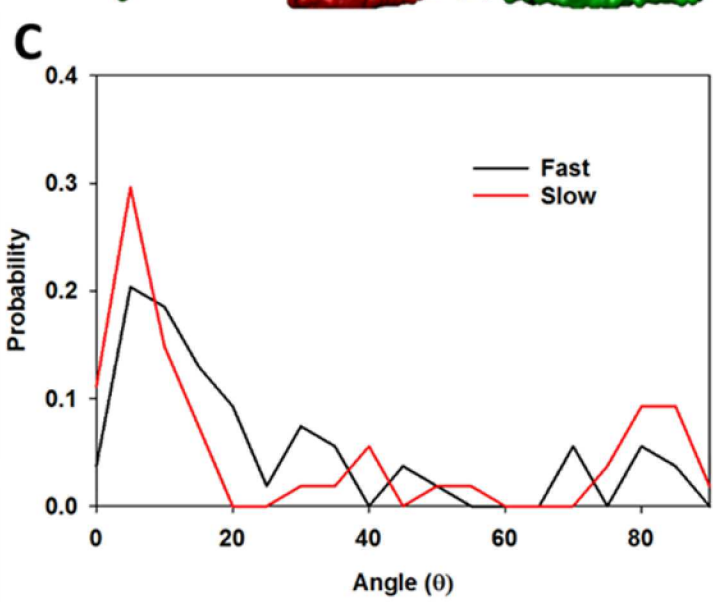
Stacking of nanoparticles

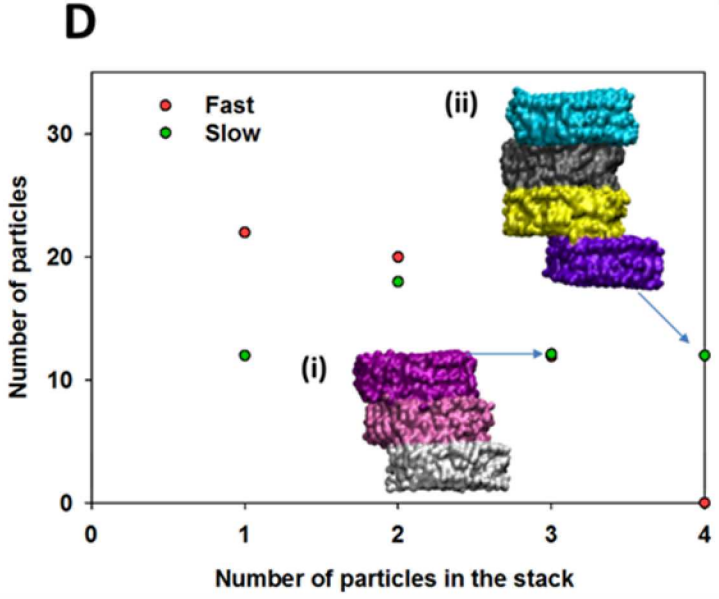
"Fast"





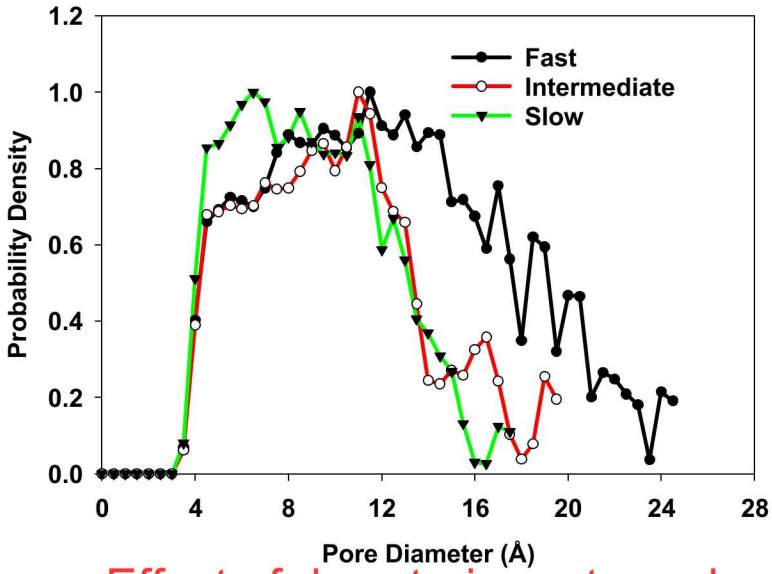
"Slow"



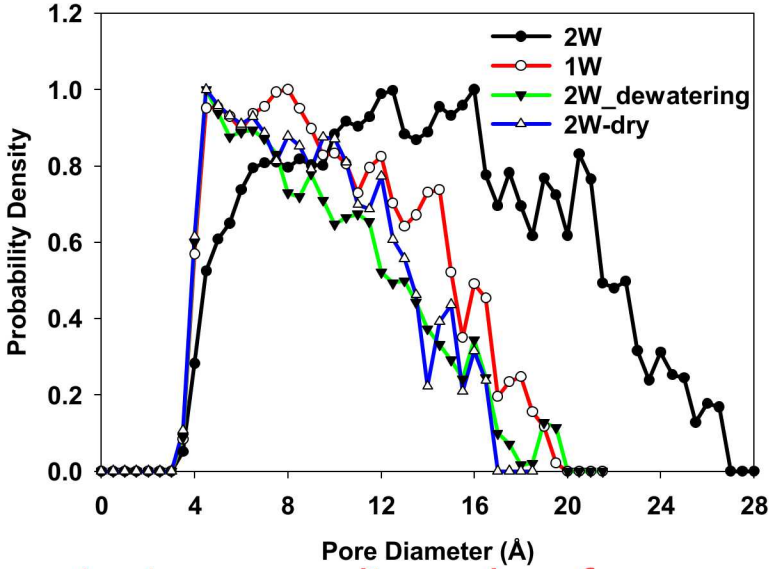


Pore properties

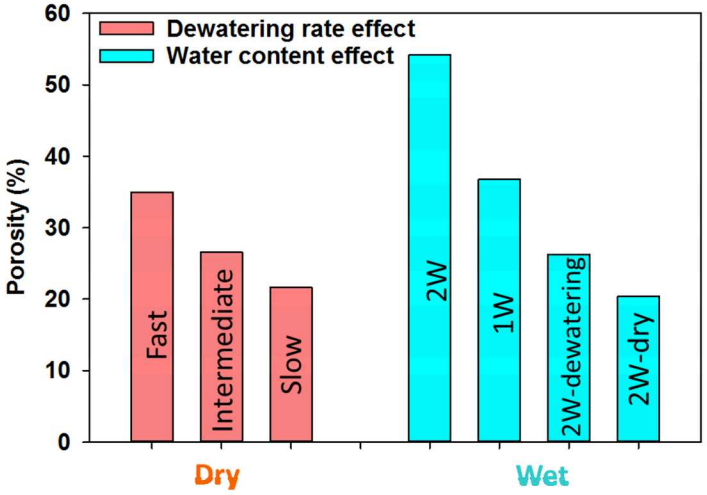
Effect of dewatering on PSD

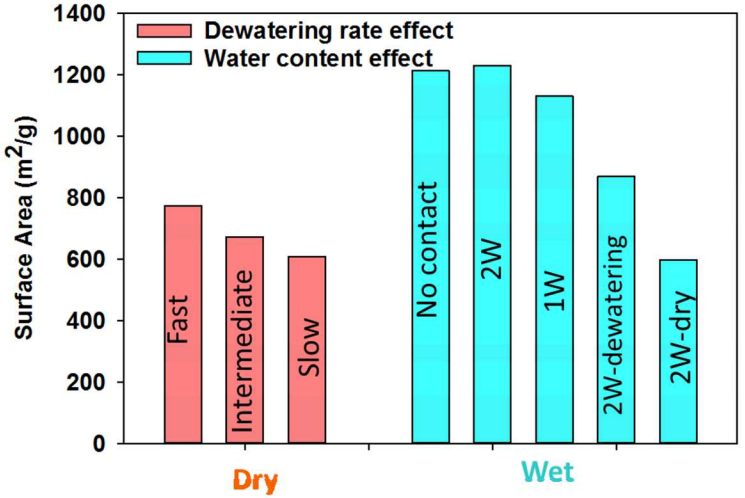


Effect of water content on PSD



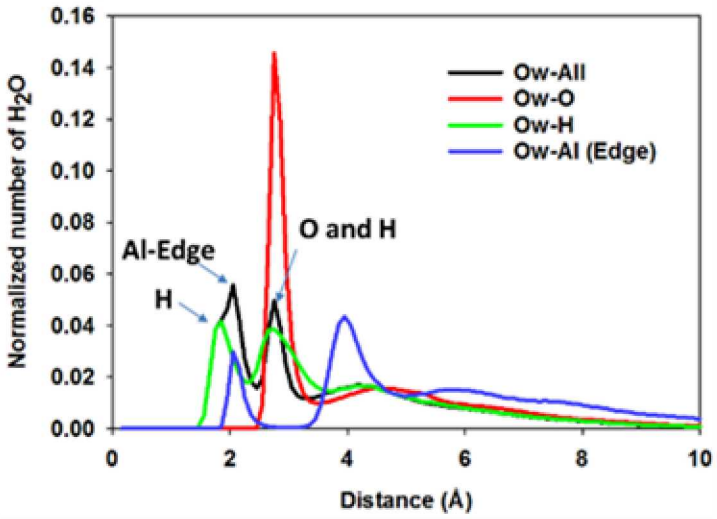
Effect of dewatering rate and water content on porosity and surface area

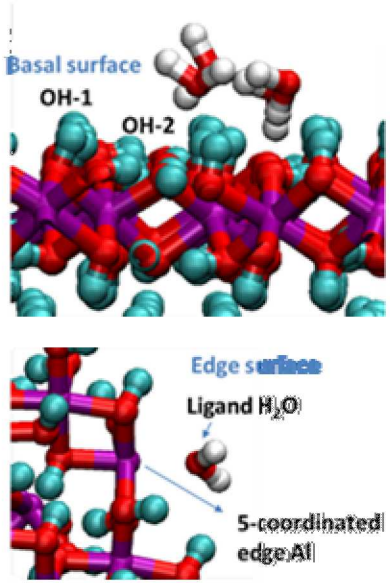




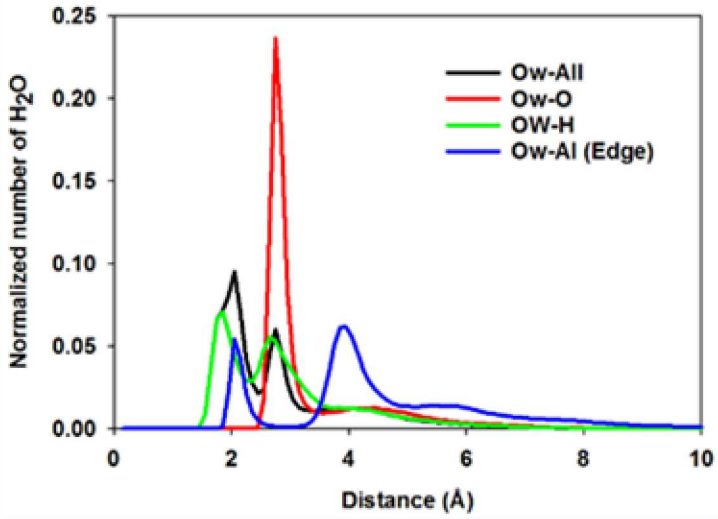
Water structure: 1D atomic density profiles

2W water content (37 wt%)





1W water content (22 wt%)



Distinct peaks due to water at basal vs edge surfaces.

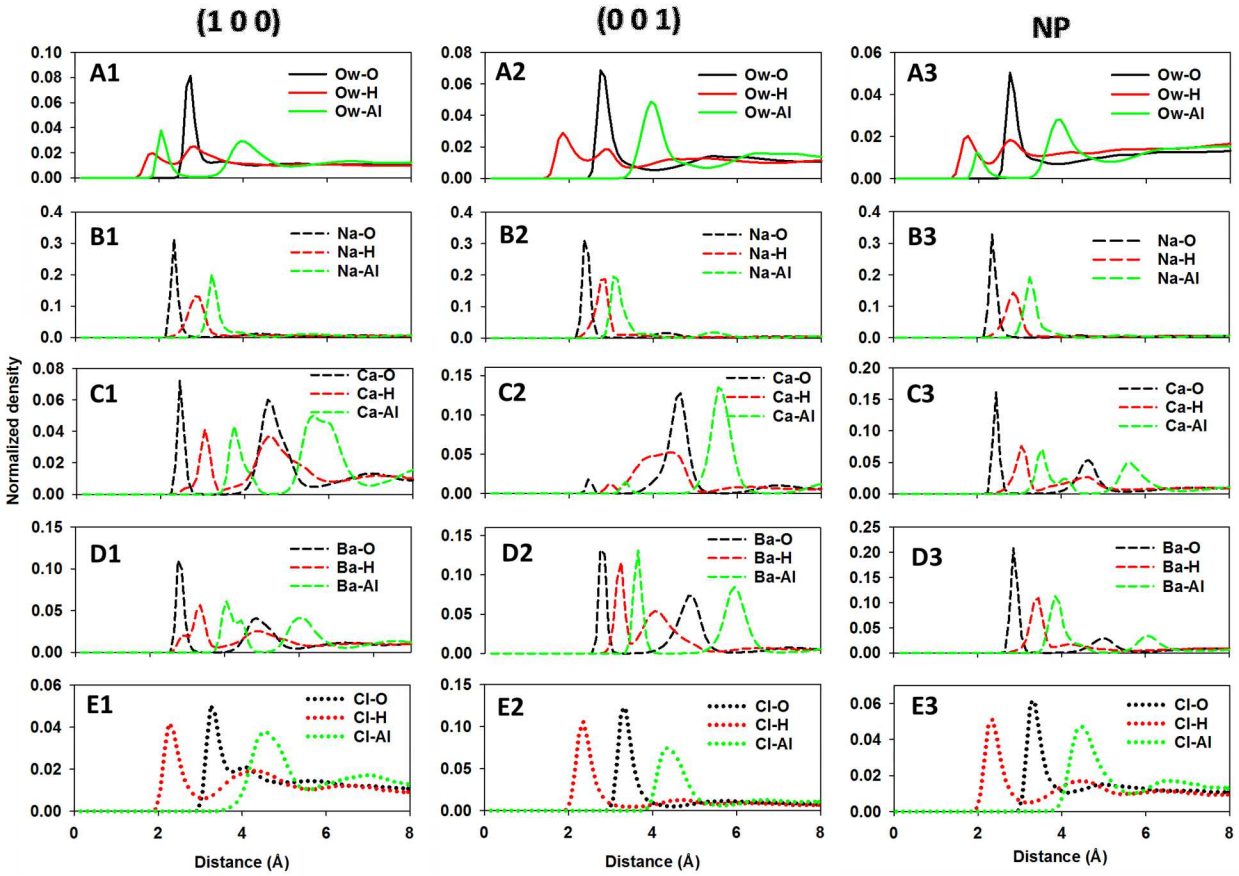
Water structure at nanoparticle surfaces qualitatively the same regardless of water content.

- < 5 Å from surface: similar water coordination environments.
- > 5 Å from surface: pore water seen up to 10 Å from surface.

Conclusions

- The percent cation adsorption as inner-sphere complexes depends on the gibbsite surface.
- For all cations, surface coverages are higher on the basal surface than the edge surface.
- For all cations, surface coverages are highest for the nanoparticle, due to the significant number of inner-sphere cations found at nanoparticle corners.
- Slow dewatering creates more compact aggregates that fast dewatering.
- The amount of water present in the aggregates strongly affects the particle-particle interactions and the aggregate structure

Extra Slide


(1 0 0)
(0 0 1)
NP
A1
A2
A3
B1
B2
B3
C1
C2
C3
D1
D2
D3
E1
E2
E3
Ow-O
Ow-H
Ow-Al
Na-O
Na-H
Na-Al
Ca-O
Ca-H
Ca-Al
Ba-O
Ba-H
Ba-Al
Cl-O
Cl-H
Cl-Al
Normalized density
Distance (Å)