SAND2019-3758C

Enhanced Ion Adsorption on Gibbsite Nanoparticles and the Formation of Gibbsite Nano-Aggregates from Simulated Compaction and Dewatering

PRESENTED BY

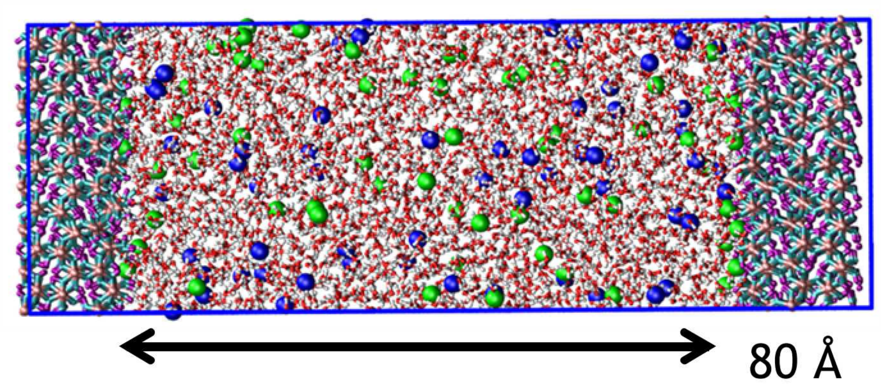
Louise J. Criscenti, Tuan A. Ho; Jeffery A. Greathouse; Yifeng Wang

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

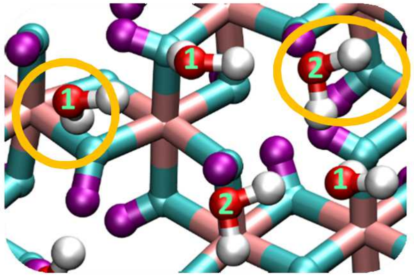
Introduction

- The objective is to use molecular simulation to investigate aqueous ion diffusion and adsorption to mineral surfaces in more complex systems more representative of compact soils and rocks.
- Gibbsite is used as a model mineral 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

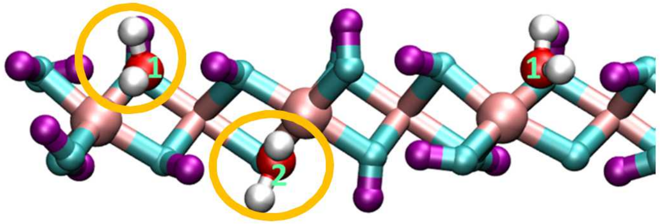
Adsorption on Gibbsite basal (001) and edge (100) surfaces



Al
O
H
O_w
H_w
Na
Cl

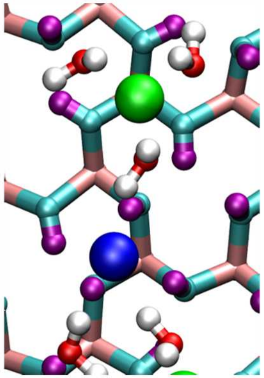


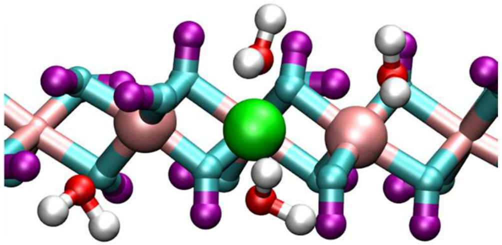
(001)



(100)

Water adsorption sites

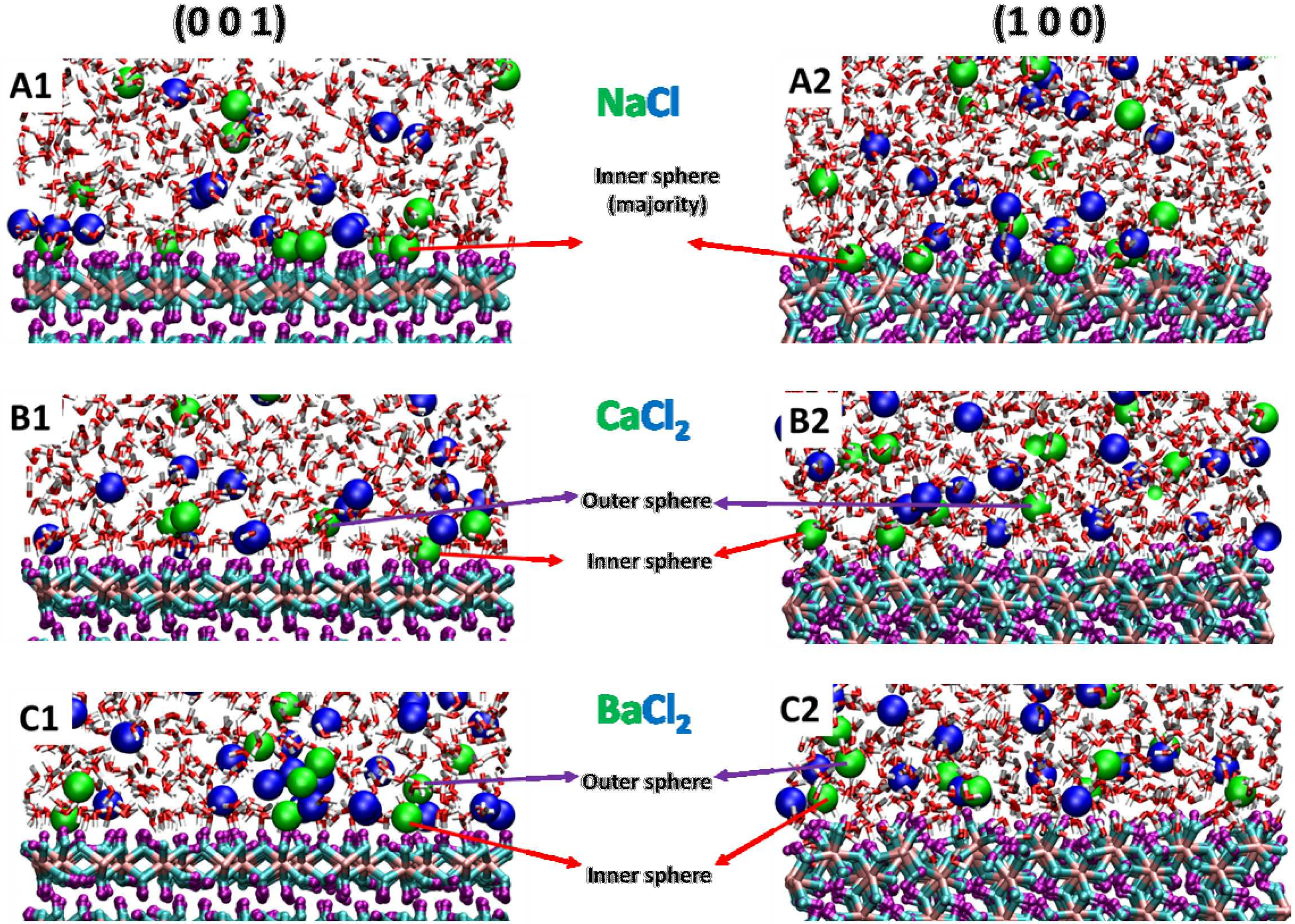




Ion adsorption sites

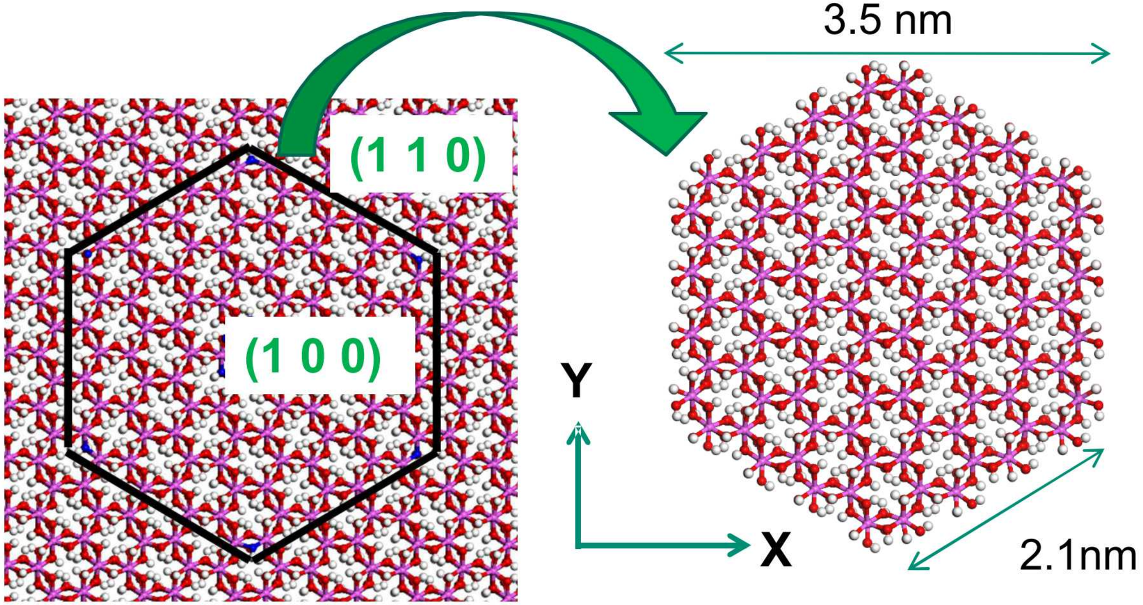
Ho, T.A., Greathouse, J.A., Lee, A.S. and Criscenti, L.J. (2018) Enhanced Ion Adsorption on Mineral Nanoparticles. Langmuir 34, 5926-5934.

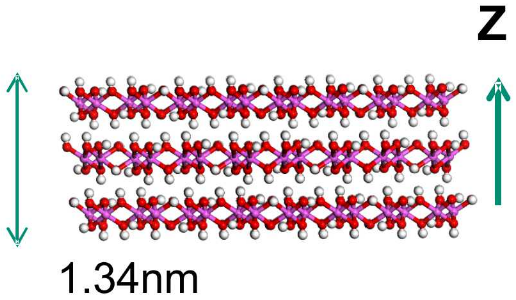
Cation Adsorption to Gibbsite Surfaces



Ho, T.A., Greathouse, J.A., Lee, A.S. and Criscenti, L.J. (2018) Enhanced Ion Adsorption on Mineral Nanoparticles. Langmuir 34, 5926-5934.

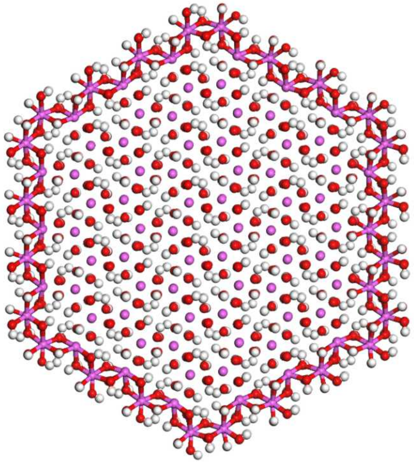
Gibbsite nanoparticle construction





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

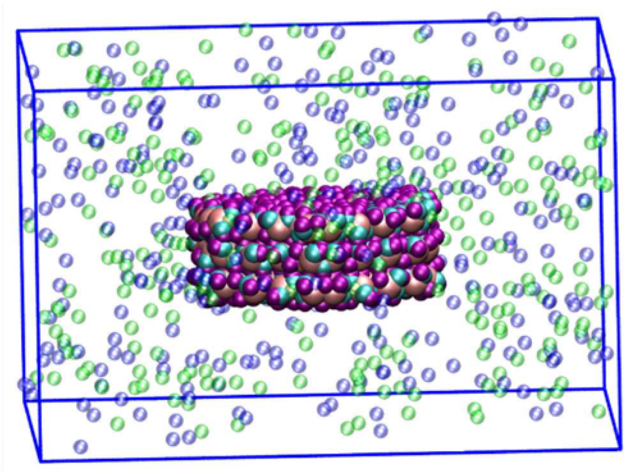
Exploit the hexagonal symmetry of bulk gibbsite

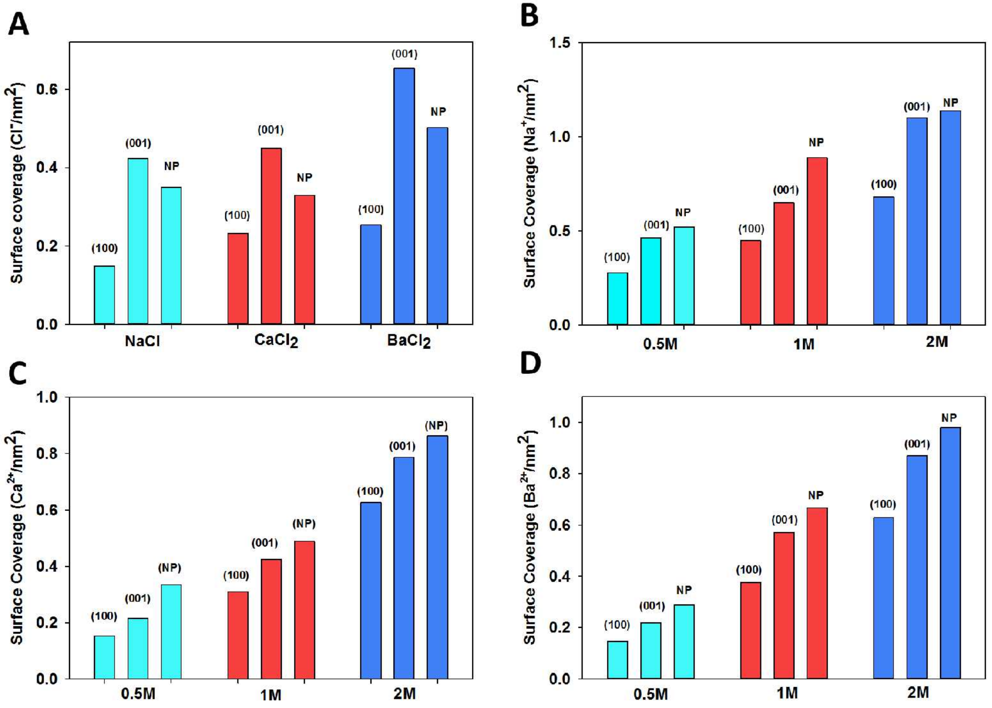


Molecular dynamics

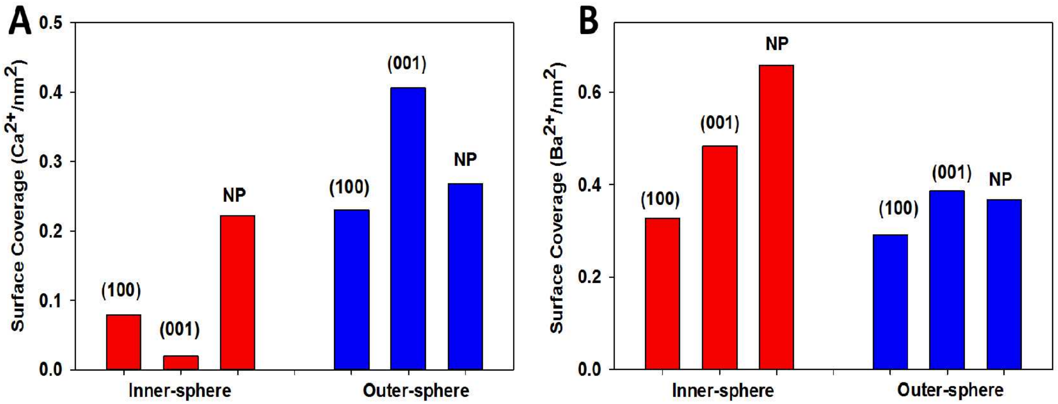
- **LAMMPS code with ClayFF parameters.**
- **New Al-O-H angle bending term for stability of edge sites.**
- **Extra Al-O-Al term added for nanoparticle stability.**

Comparison of Adsorption on Gibbsite Nanoparticle vs. Surfaces



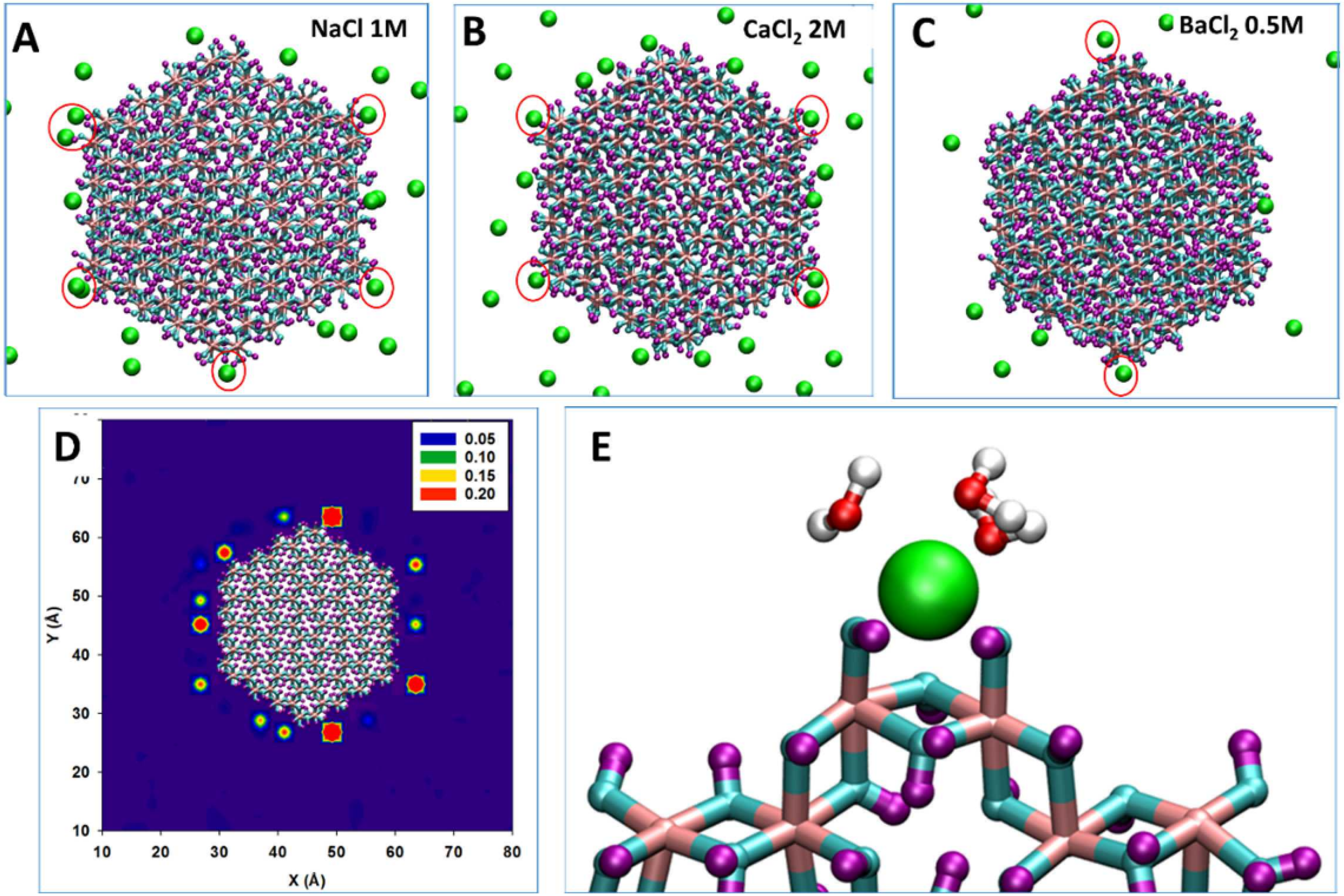


- Cl^- adsorption is not enhanced on NP
- Na^+, Ca^{2+}, and Ba^{2+} adsorption are enhanced on NP
- NPs exhibit higher concentrations of IS complexes



Ho, T.A., Greathouse, J.A., Lee, A.S. and Criscenti, L.J. (2018) Enhanced Ion Adsorption on Mineral Nanoparticles. Langmuir 34, 5926-5934.

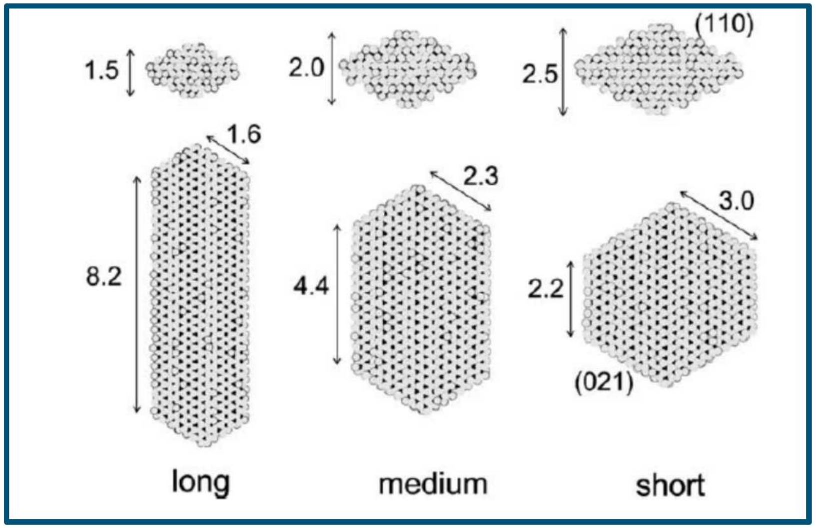
Cation Adsorption at Nanoparticle Corners



Ho, T.A., Greathouse, J.A., Lee, A.S. and Criscenti, L.J. (2018) Enhanced Ion Adsorption on Mineral Nanoparticles. Langmuir 34, 5926-5934.

Other Studies Showing Importance of Edge and Corner Site Importance to Adsorption/Reactivity

Rustad and Felmy (2005) The influence of edge sites on the development of surface charge on goethite nanoparticles: A molecular dynamics investigation. GCA, 69, 1405-1411

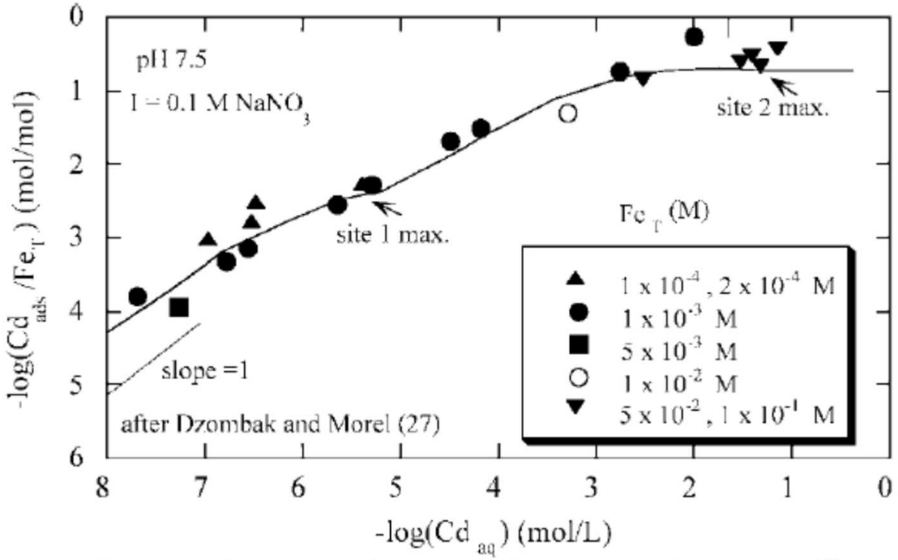


Large-scale molecular simulation of proton accumulations were carried out on

- (110) and (021) slabs immersed in aqueous solution
- a series of model goethite nanoparticles of dimension 2 to 8 nm with systematically varying acicularity and (110)/(021) surface areas.

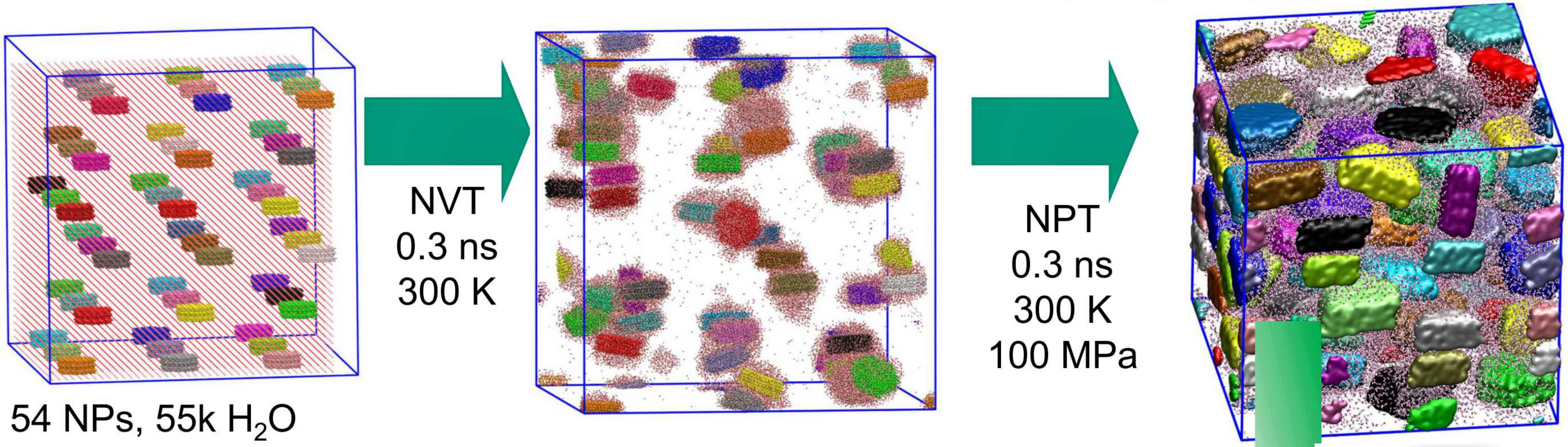
- Particulate systems show a preferential accumulation of protons at acute (110)-(110) intersections. More H_2O accessible.
- Charge accumulates preferentially in this region because excess proton charge at an asperity is more effectively solvated than at a flat interface.

Surface Complexation Models



- Two-site isotherm has a slope of 1.0 at log (Cd^{2+})(mol/L)<-6.5 corresponding to the filling of the high-energy site 1 (maximum occupancy 0.005 mol/mol Fe).
- For -5.5 < log $(Cd^{2+}aq)$ (mol/L) < -3.0, corresponds to filling of the low-energy site 2 (maximum occupancy 0.2 mol/mol of Fe).
- The very low abundance of the “high energy” sites has been attributed to the role of lattice defects, crystal edges, dislocations or surface sites on the smallest crystallographic faces. (Robertson & Leckie, 1998, Misra, 1968; Catts and Langmuir, 1986; Spadini et al., 1994).

Gibbsite aggregation

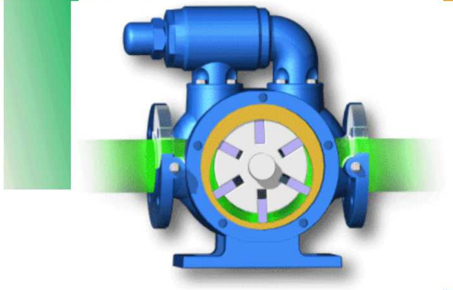


54 NPs, 55k H_2O
30 x 30 x 30 nm^3

NVT
0.3 ns
300 K

NPT
0.3 ns
300 K
100 MPa

Hydrated aggregate
15 x 15 x 15 nm^3



‘Virtual’ pump removes waters from a pre-defined region.

Effect of dewatering rate:

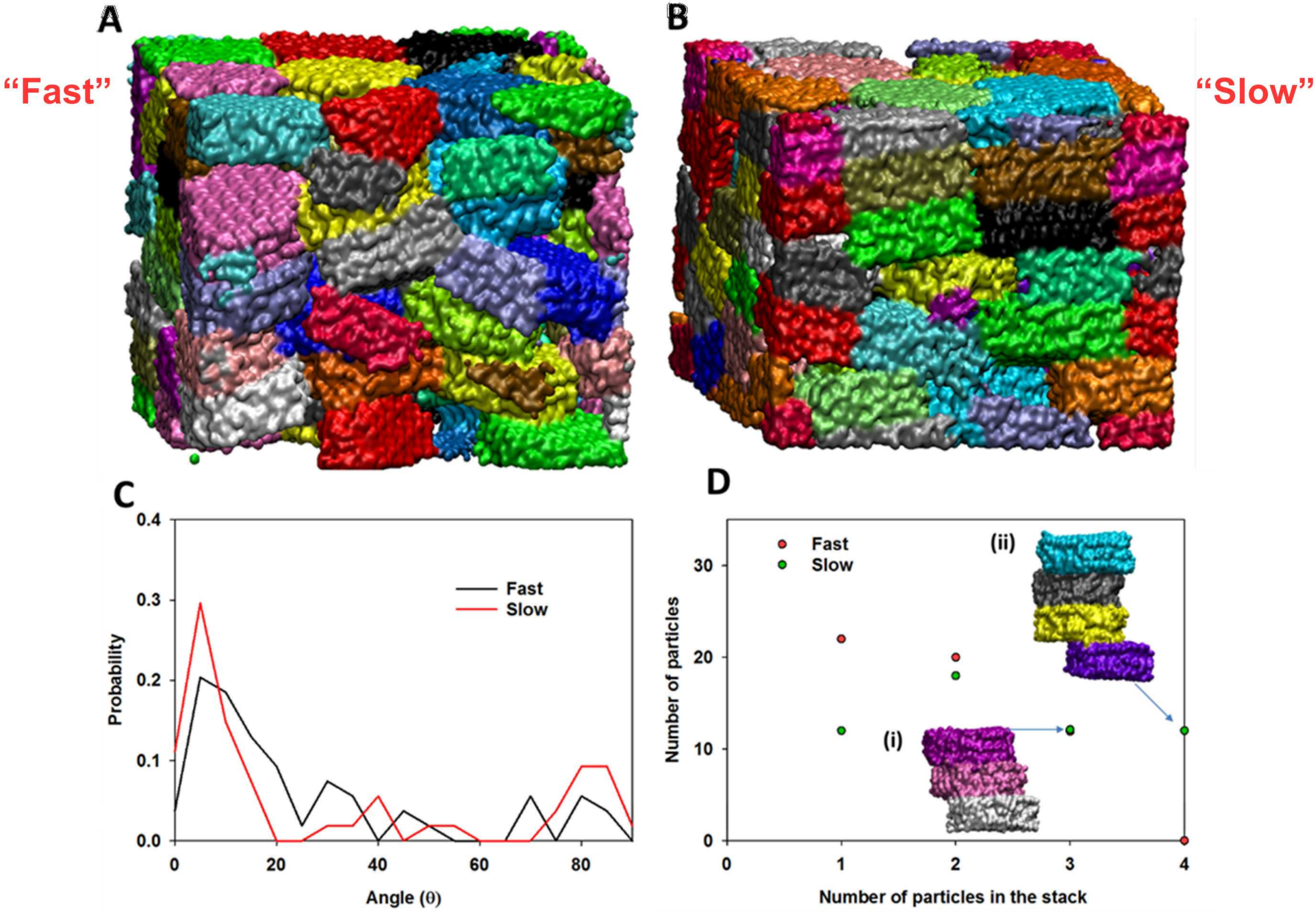
- **Delete all water: “Fast”**
- **Delete 100 H2O/100 steps: “Intermediate”**
- **Delete 10 H2O/100 steps: “Slow”**

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**

Ho, T.A., Greathouse, J.A., Wang, Y. and Criscenti, L.J. (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. Scientific Reports 7:15286

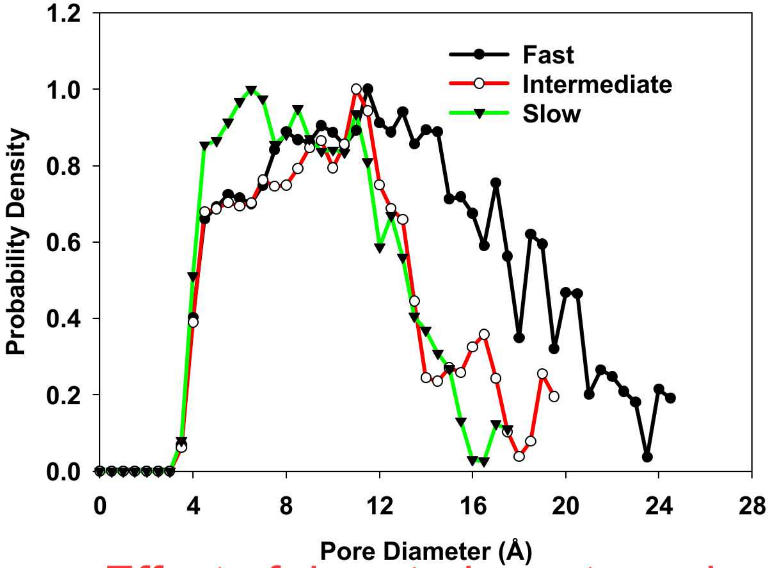
Stacking of nanoparticles



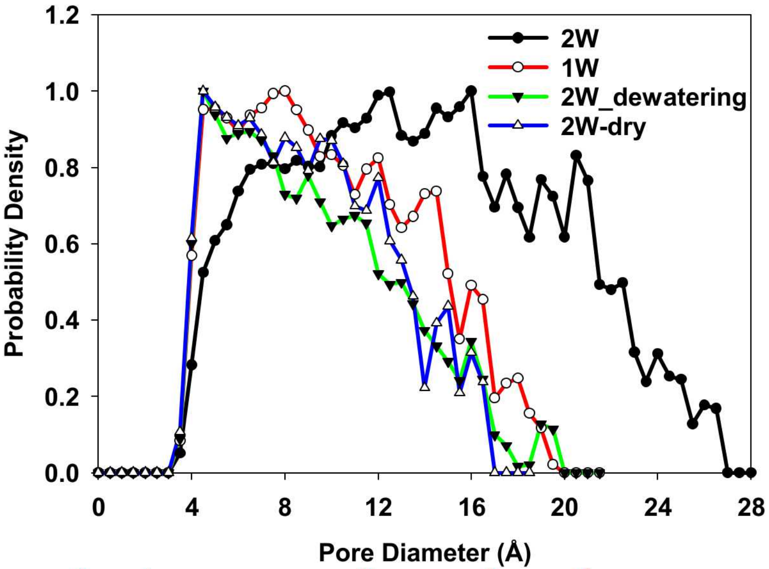
Ho et al.. Scientific Reports 7:15286

Pore properties

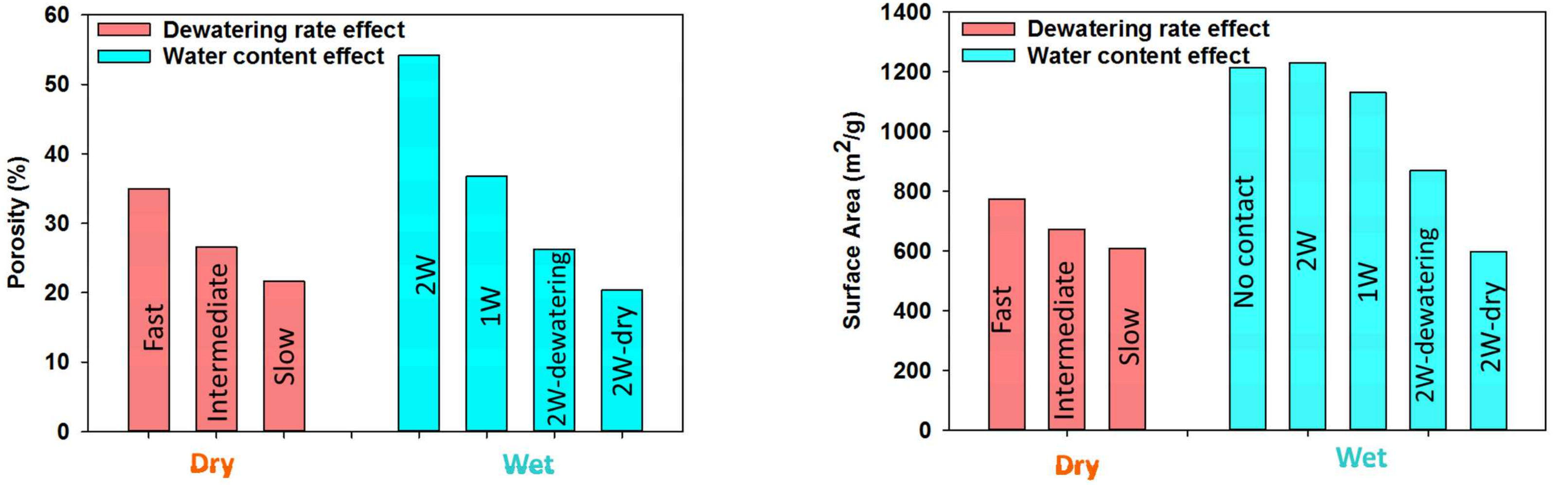
Effect of dewatering on PSD



Effect of water content on PSD



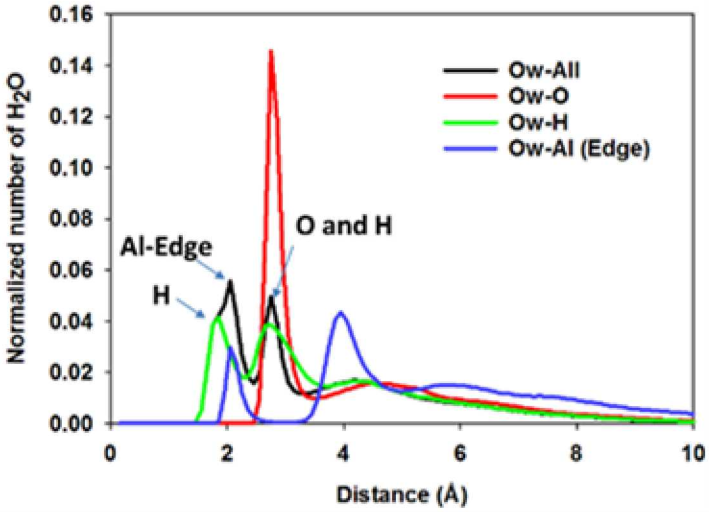
Effect of dewatering rate and water content on porosity and surface area

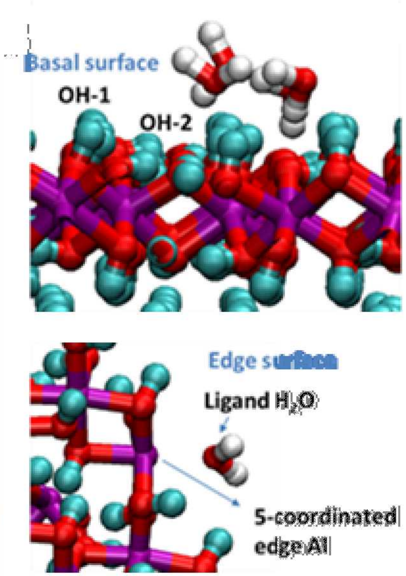


Ho et al.(2017) Scientific Reports 7:15286

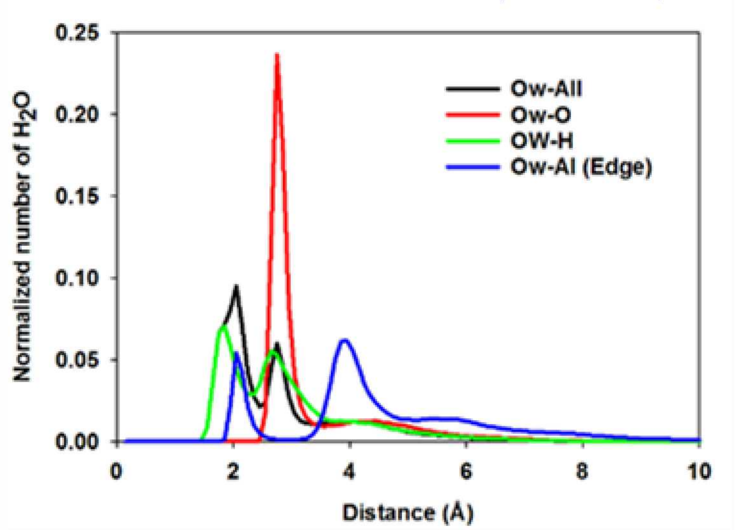
Water structure: 1D atomic density profiles

2W water content (37 wt%)





1W water content (22 wt%)



Distinct peaks due to water at basal vs edge surfaces.

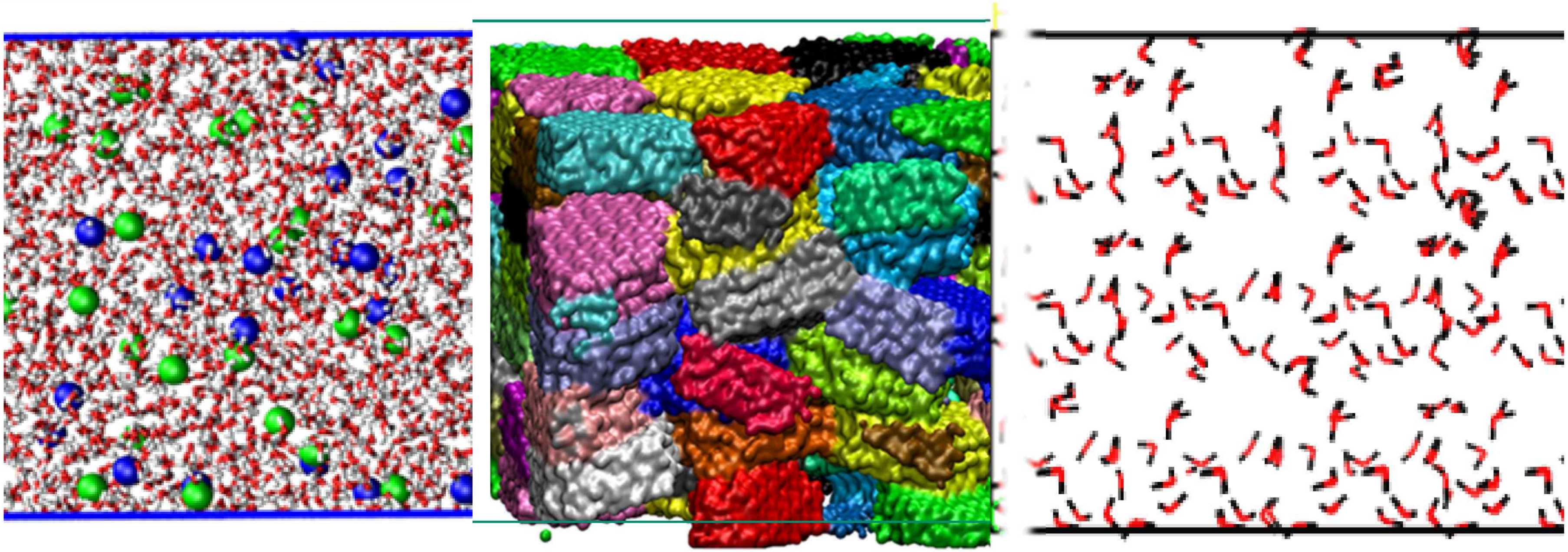
Water structure at nanoparticle surfaces qualitatively the same regardless of water content.

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

Ho, T.A., Greathouse, J.A., Wang, Y. and Criscenti, L.J. (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. Scientific Reports 7:15286

What’s next?

Flow through Columns?



Breakthrough Curves?

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.
- For the nanoparticle aggregates, slow dewatering creates more compact aggregates that fast dewatering.
- For the aggregates, the amount of water present strongly affects the particle-particle interactions and the aggregate structure.

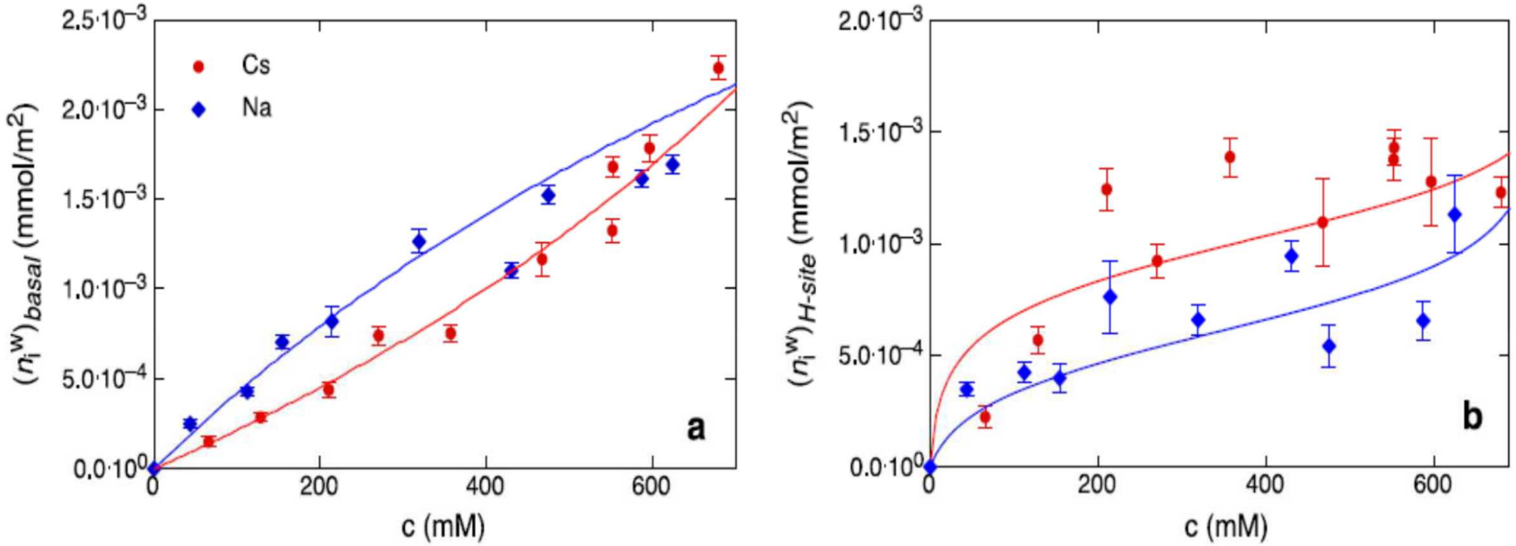


Fig. 6. Adsorption isotherms for Na (blue diamonds) and Cs (red circles) determined from the ten 50 ns MD simulation runs on (a) basal surfaces and (b) edge H-sites. Isotherms were fitted using the thermodynamic model Eqs. (8) and (9). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Lammers et al. (2017) Molecular dynamics simulations of Cs+ adsorption on illite

Cation exchange is thermodynamically ideal on basal surfaces

Exchange on edge surfaces and within interlayers show complex, thermodynamically non-ideal behavior. Basal surfaces are weakly Cs-selective, while edges and interlayers have much higher affinity for Cs.

Development of fully-flexible clay mineral nanoparticles with stable edge surfaces.

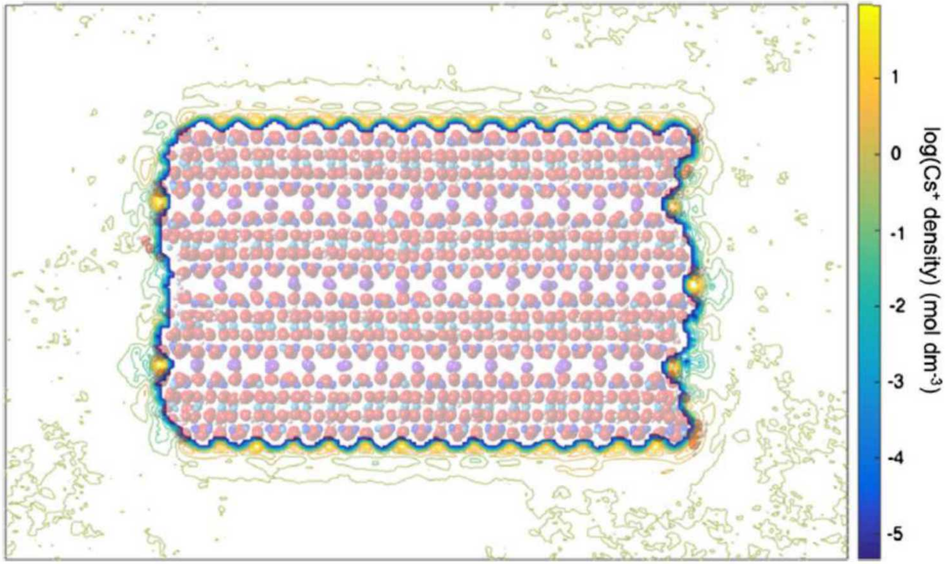


Fig. 3. Map of Cs density averaged over the entire 50 ns simulation with x_{Cs} = 0.5. Cesium primarily binds to ditrigonal cavities on the basal surfaces and to "cleaved cavities" at edge surface H-sites.

Surface Complexation Models

Some SCMs can fit bulk data with an average surface site and then invoke the use of a second, low density, high energy site to better fit bulk adsorption data – hypothesizing that this second generic surface site represented defect, corner, and edge sites (Davis and Kent, 1990).

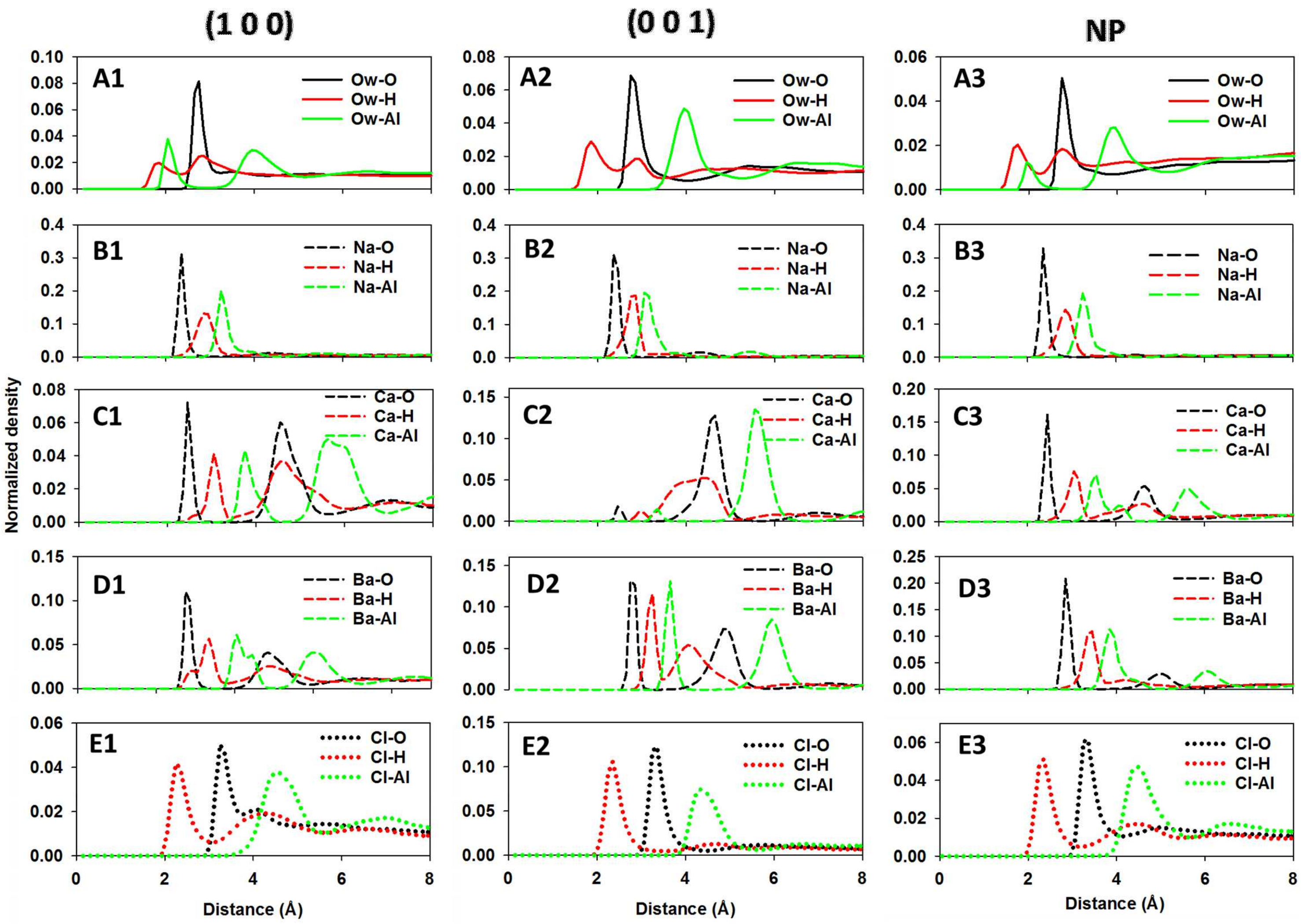
- Adsorption Isotherms: Typically, the isotherms have a slope of 1 at extremely low metal concentrations and a slope of <1 at higher concentrations that give rise to maximum surface coverages well below the surface coverage of one monolayer.

Many investigators, propose that a slope of <1 = adsorption to more than one type of surface site.
Venema et al. (Venema,1996) modeled Cd2+ adsorption onto goethite using only 2 site types; Each found on a different crystal face.
Recent molecular static studies on the surface site types of an ideal goethite Suggest that the difference in surface site types of an idea goethite crystal did not Lead to large differences in surface protonation constants (50; Rustad et al., GCA, 1996)).

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 the nanoparticles, cation surface coverages are enhanced, due to the significant number of inner-sphere cations found at nanoparticle corners.
- For the nanoparticle aggregates, slow dewatering creates more compact aggregates that fast dewatering.
- For the aggregates, the amount of water present strongly affects the particle-particle interactions and the aggregate structure

Extra Slide


(1 0 0)
(0 0 1)
NP
A1
A2
A3
Ow-O
Ow-H
Ow-Al
B1
B2
B3
Na-O
Na-H
Na-Al
C1
C2
C3
Ca-O
Ca-H
Ca-Al
D1
D2
D3
Ba-O
Ba-H
Ba-Al
E1
E2
E3
Cl-O
Cl-H
Cl-Al
Normalized density
Distance (Å)
0
2
4
6
8