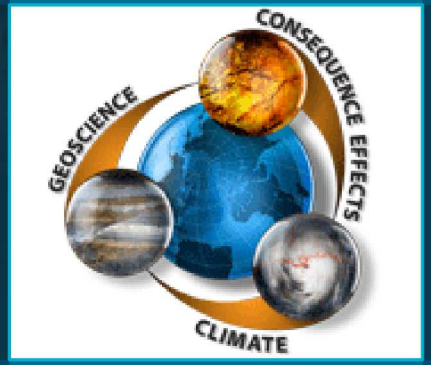
SAND2018-9247C

Sandia National Laboratories

Interfacial chemistry under nanoconfinement



U.S. DEPARTMENT OF ENERGY | Office of Science

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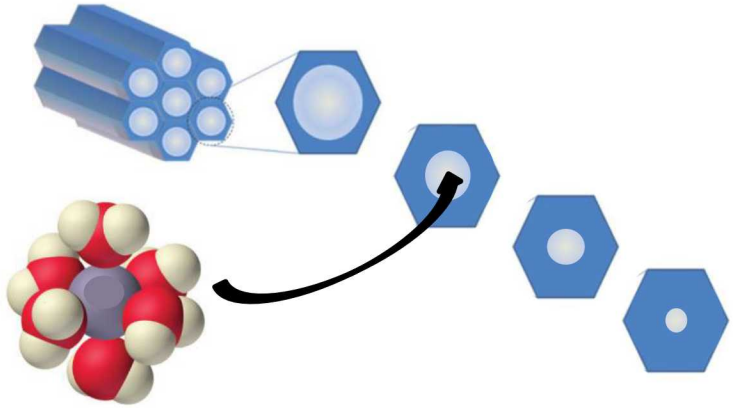
Studies on Nano-scale Confinement

- *Using both experimental and computational techniques investigate*:
  - Effect of pore size on adsorption and solute coordination in mesoporous materials.
  - Effect of confinement on water properties



Studies:

1. **Adsorption of $Na^{+}/Mg^{2+}/Cu^{2+}$ on Silica**
2. **Water diffusion in imogolite**
3. **Ion adsorption in multi-particle aggregates**

Mesoporous Silica

Table 1 Pore size and BET surface area of SBA-15-8, SBA-15-6, and SBA-15-4

Material	Pore size (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	% surface area from pores	–OH-density ($–OH/nm^2$)
SBA-15-8	7.0 ± 0.3	661 ± 5	1.21 ± 0.03	89 ± 6	1.8 ± 0.2
SBA-15-6	5.2 ± 0.2	603 ± 16	0.87 ± 0.03	80 ± 5	1.9 ± 0.2
SBA-15-4	4.4 ± 0.1	580 ± 13	0.67 ± 0.04	75 ± 6	2.3 ± 0.2

The BET surface areas were used to calculate the surface area normalized Cu adsorption

TEM of SBA-15

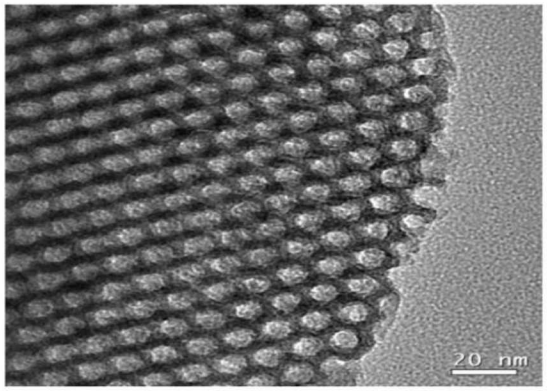


Image from Chen et al., 2009

- BET surface area, pore volume, % surface area from pores decrease with decreasing pore size
- -OH density increases with decreasing pore size

- Hexagonally-ordered cylindrical pores

Knight, Tigges, and Ilgen, 2018
Geochemical Transactions 19, 13-26

Adsorption of Cu^{2+} on Mesoporous Silica: The Effect of Nano-scale Confinement

Anastasia Ilgen, Andrew Knight (postdoc), Austen Tigges (student)

Cu^{2+} adsorption isotherms

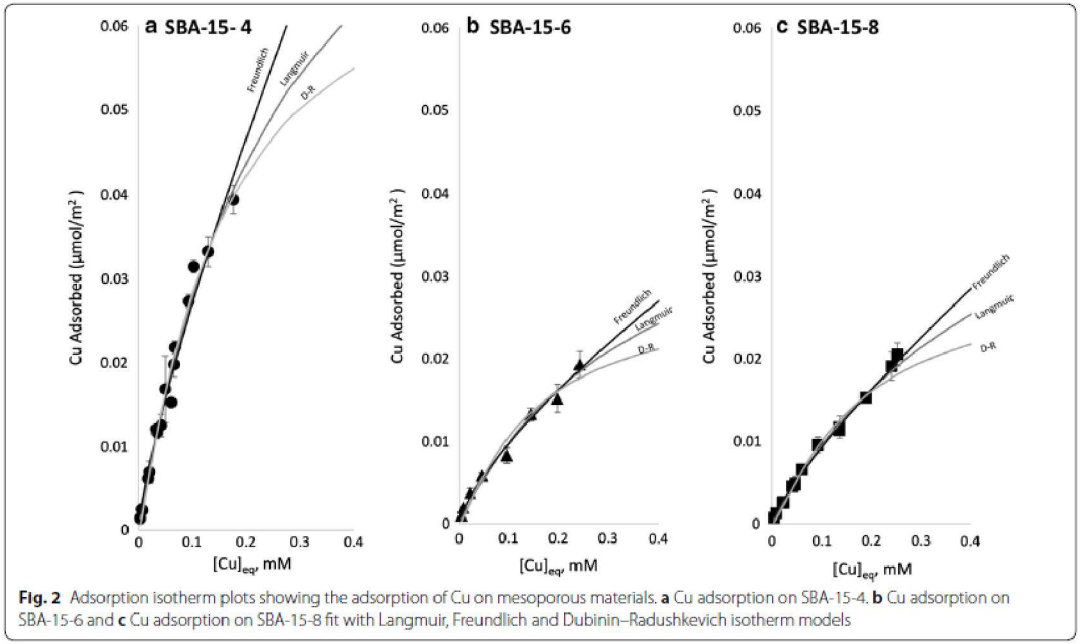


Fig. 2 Adsorption isotherm plots showing the adsorption of Cu on mesoporous materials. **a** Cu adsorption on SBA-15-4. **b** Cu adsorption on SBA-15-6 and **c** Cu adsorption on SBA-15-8 fit with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models

Cu^{2+} adsorption kinetics

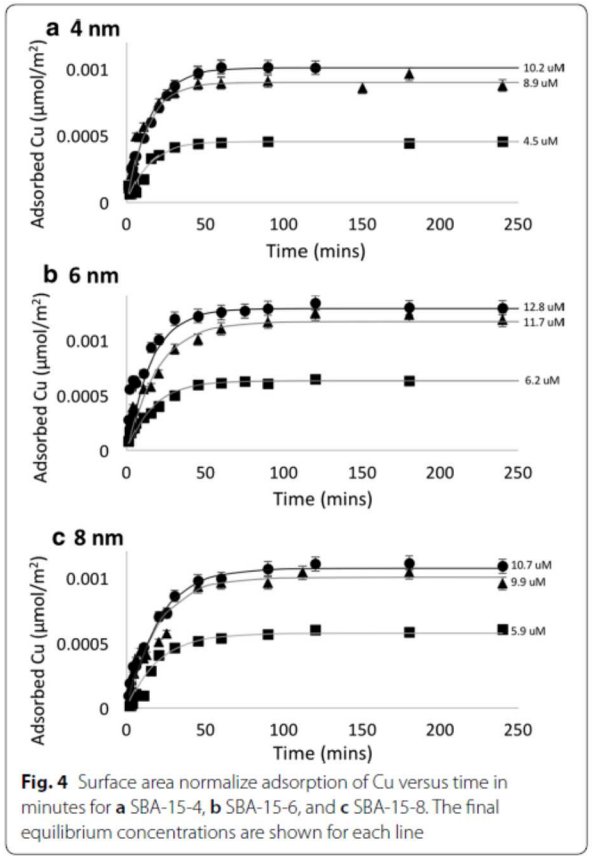


Fig. 4 Surface area normalize adsorption of Cu versus time in minutes for **a** SBA-15-4, **b** SBA-15-6, and **c** SBA-15-8. The final equilibrium concentrations are shown for each line

- Quantified the effect of nano-scale confinement on Cu^{2+} adsorption on mesoporous silica.
- Nano-scale confinement enhances the adsorption maximum
- Nano-scale confinement increases Cu^{2+} adsorption reaction rate as indicated by pseudo-1^{st}–order rate constant.
- External mass transfer diffusion constant increases with decreasing pore size: this rapid film diffusion in 4 nm pores may be responsible for the observed increase in adsorption rate.

Knight, Tigges, and Ilgen, 2018

Geochemical Transactions 19, 13-26

AIMD simulations of $Na^+/Cu^{2+}/Mg^{2+}$adsorption on silica

Kevin Leung, Louise Criscenti, Andrew Knight (postdoc), Jeff Greathouse, Anastasia Ilgen, Tuan Ho

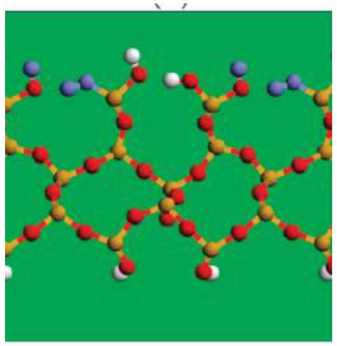
Objectives

- Understand adsorption mechanisms
- Predict binding constant between silica and $Na^+/Mg^{2+}/Cu^{2+}$.

Approach

- AIMD potential-of-mean-force (VASP).
  - Desorption from an SiO^- site
  - pKa of SiOH group is 7.0-8.1.
  - Charge-neutral cells ($Na^+/Mg^{2+}/Cu^{2+}$ compensated by one/two SiO^-).
  - Lateral harmonic constraints.
- Compare to competitive adsorption experiments.

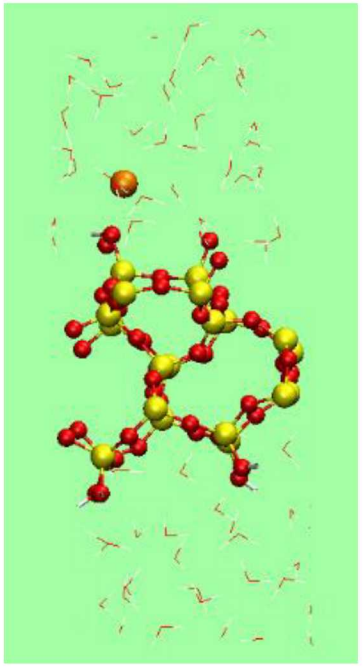
reconstructed (001)
ß-cristobalite surface



pKa ~ 7-8.1

4/nm² SiOH

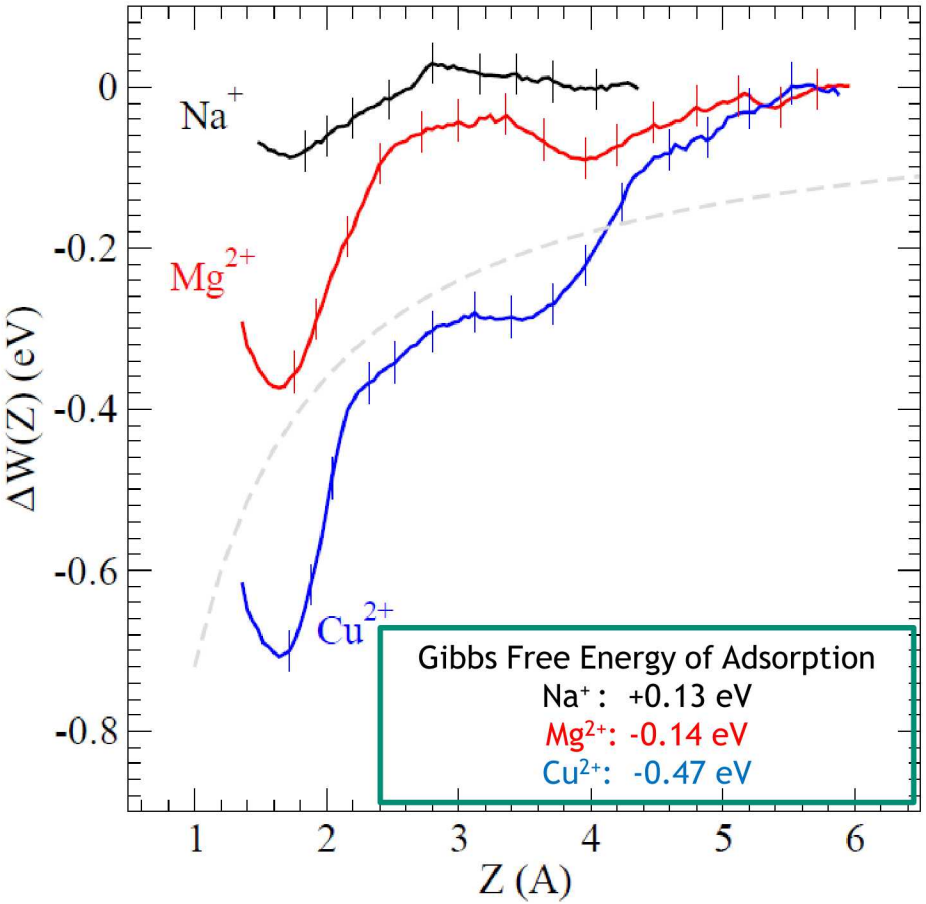
add water, cation



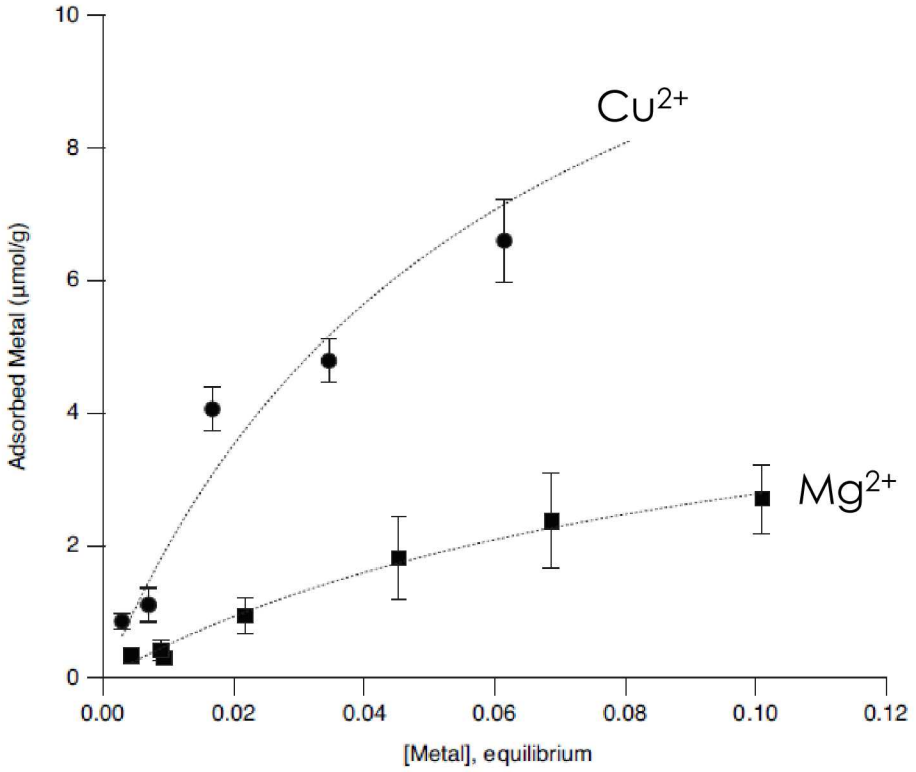
AIMD simulations of Cu^{2+} and Mg^{2+} adsorption on silica

Kevin Leung, Louise Criscenti, Andrew Knight (postdoc), Jeff Greathouse, Anastasia Ilgen, Tuan Ho

AIMD potentials-of-mean-force



Competitive adsorption



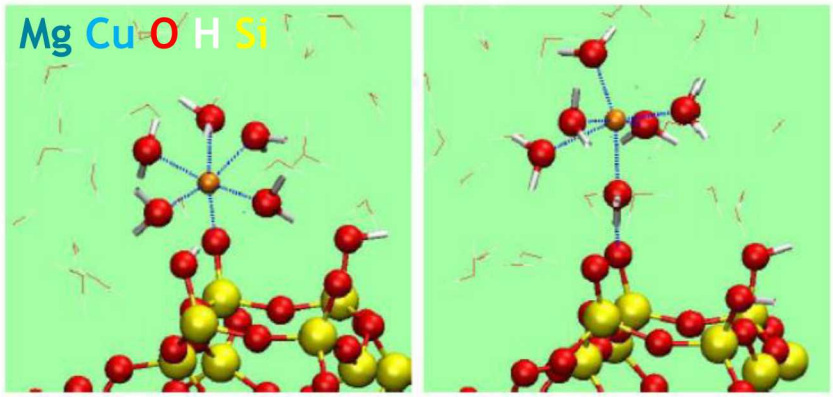
$$\Delta G_{\mathrm{ads}}/k_{\mathrm{B}}T = -\log\{\int_{\Omega} d\Omega \exp[-\Delta W(Z)/k_{\mathrm{B}}T]/(V_o)\}$$

Leung, et al.

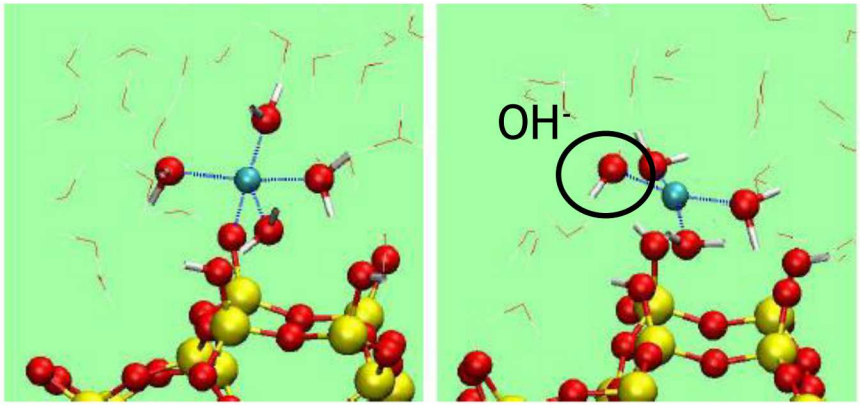
Submitted to The Journal of Physical Chemistry Letters

AIMD simulations of Cu^{2+} and Mg^{2+} adsorption on silica

Snapshots of cation desorption

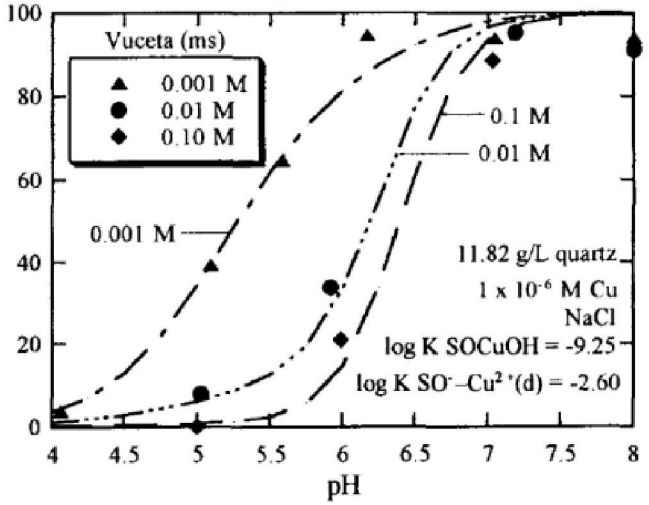


Mg^{2+}, 6 H_2O or 5 H_2O/SiO^- , octahedral



Cu^{2+} desorbs as $Cu^{2+}(H_2O)_3$ (OH^-) complex!

- Cu desorbs as $Cu^{2+}(OH^-)$ (this depends on pKa of surface OH group).
- SCMs have suggested Cu adsorbs as a $CuOH^+$ IS species.
- Cu^{2+} forms dimer and/or precipitate; our results indicate precursor to such behavior.

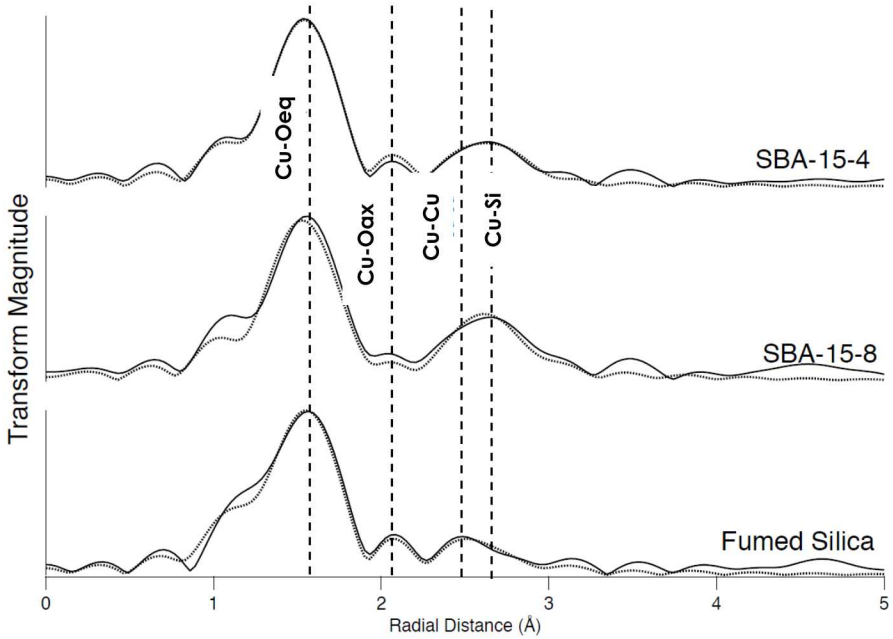


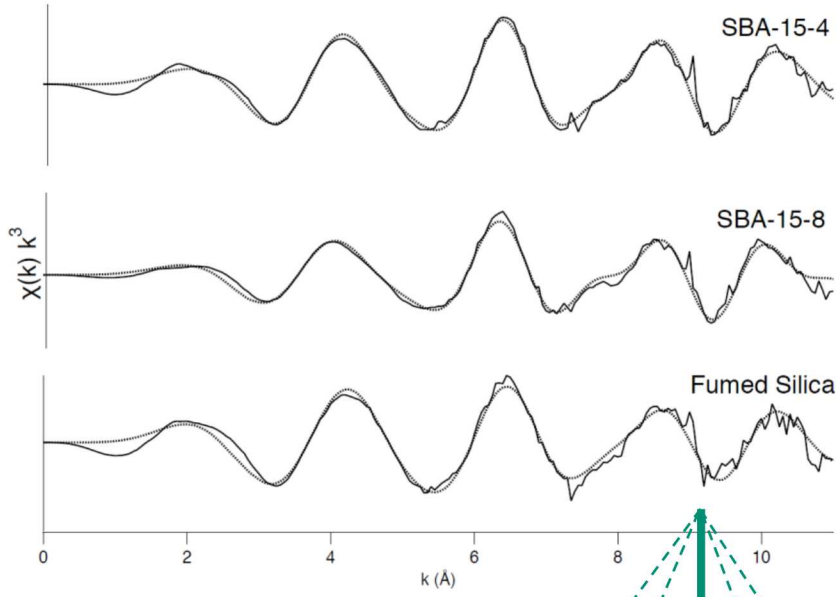
Criscenti and Sverjensky, 1999

X-ray Absorption Spectroscopy

Anastasia Ilgen, Andrew Knight (postdoc)

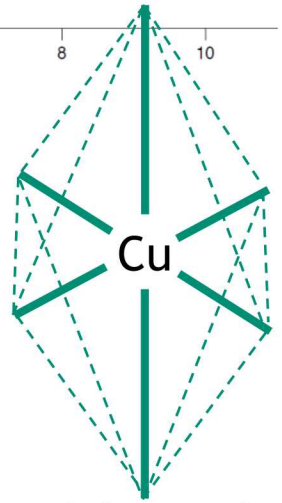
Advanced Photon Source
Argonne National Laboratory





Preliminary results

- XAS data collected at APS.
- Coordination chemistry of adsorbed Cu^{2+} is pore-size dependent.
- With decreasing pore size, the Cu-O(eq) becomes slightly shorter, potentially due to increasing distortion.
- The Cu-Cu CN is higher for porous, compared to non-porous silicas, potentially due to enhanced dimer formation inside the pores.

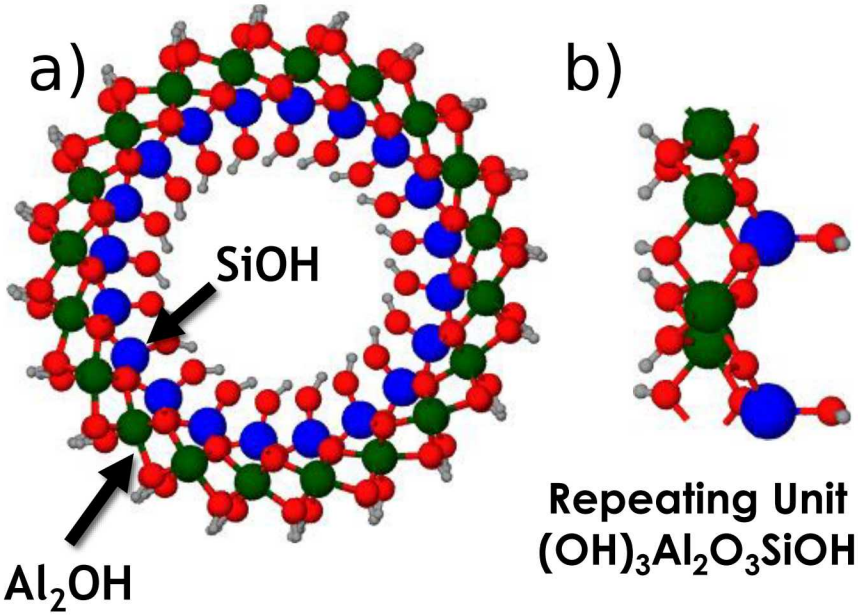


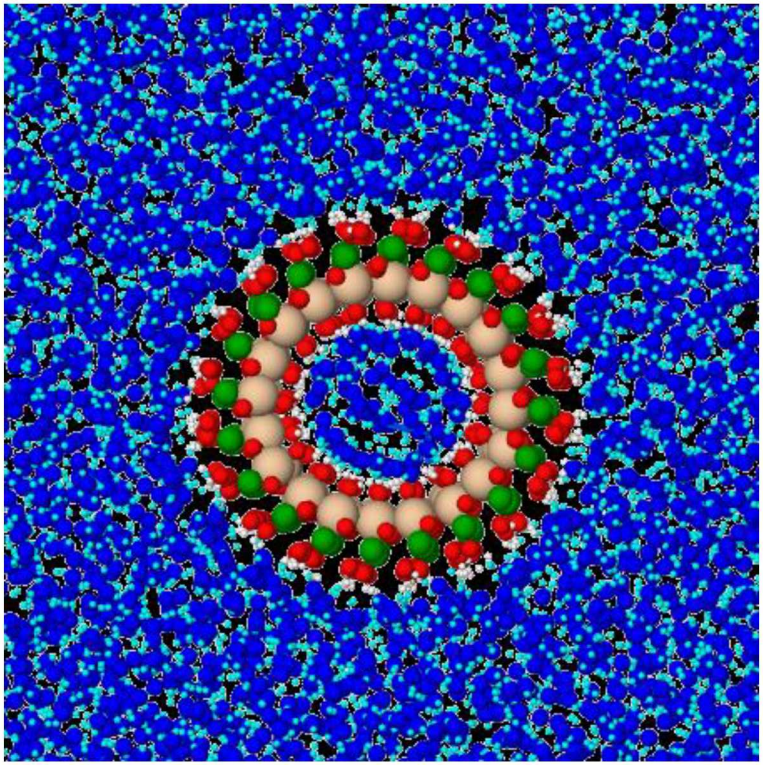
Knight, et al.
In prep.

MD Simulation of Water Structure in Imogolite

Rafael Gonzalez (U. Mayor, CHILE), Jeffery Greathouse

- Single-walled nanotubes with silica interior and alumina exterior surfaces.
- Nanotube diameter depends on number of repeating units (*N*).
- Newly developed ClayFF parameters for surface SiOH and AlOH groups are used to model water adsorption properties at interior and external surfaces.

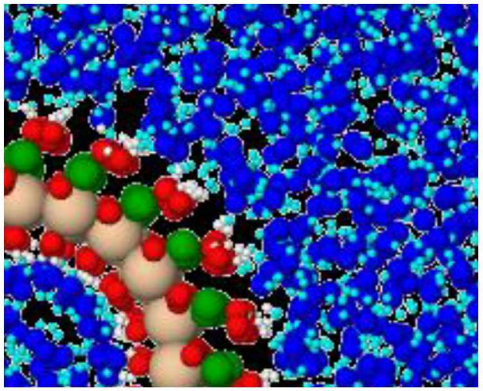




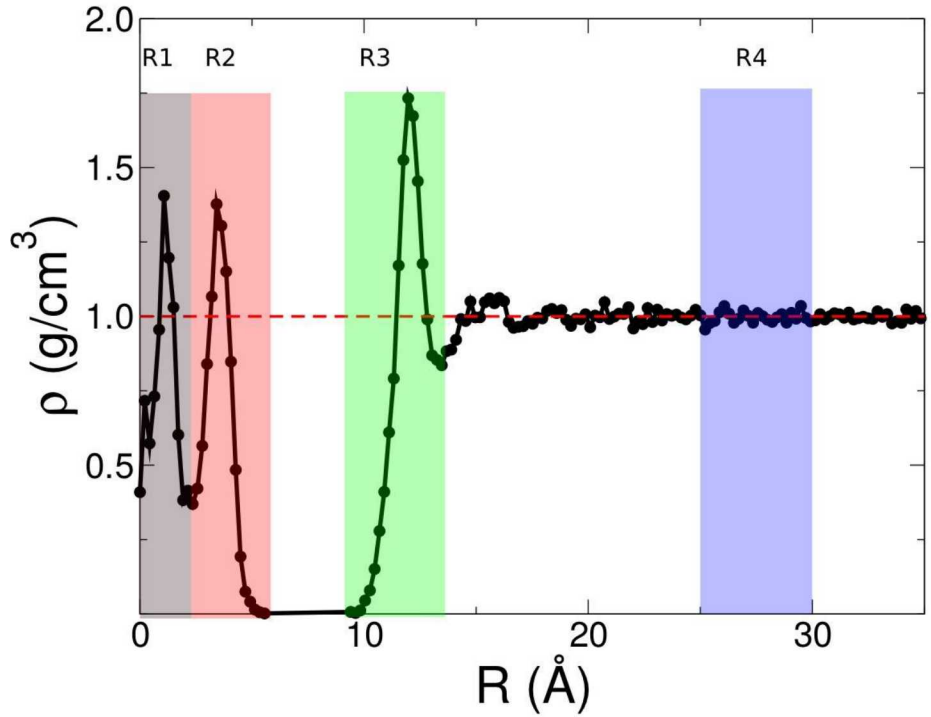
MD snapshot at 300 K showing a *N* = 10 nanotube with water (blue) in interior and outer regions.

MD Simulation of Water Structure in Imogolite

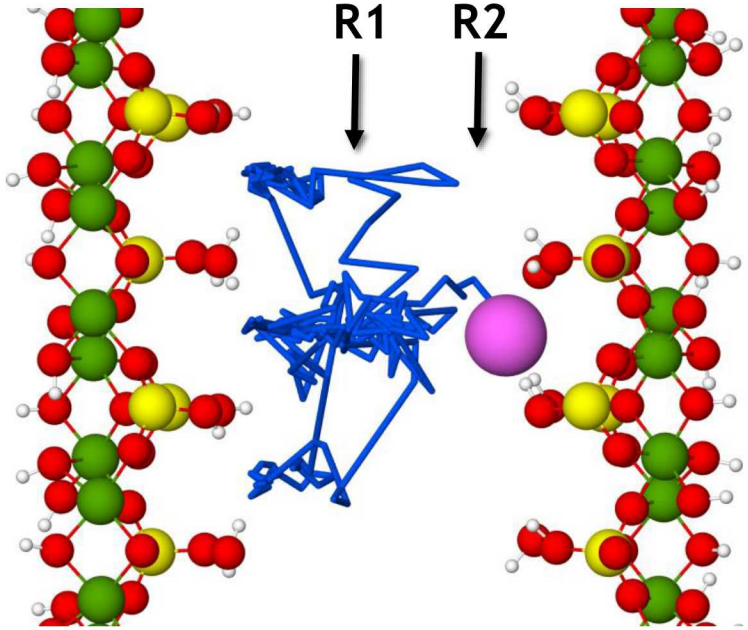
Rafael Gonzalez (U. Mayor, CHILE), Jeffery Greathouse



Radial water density profile for N = 10 imogolite showing two interior water layers (R1 and R2).



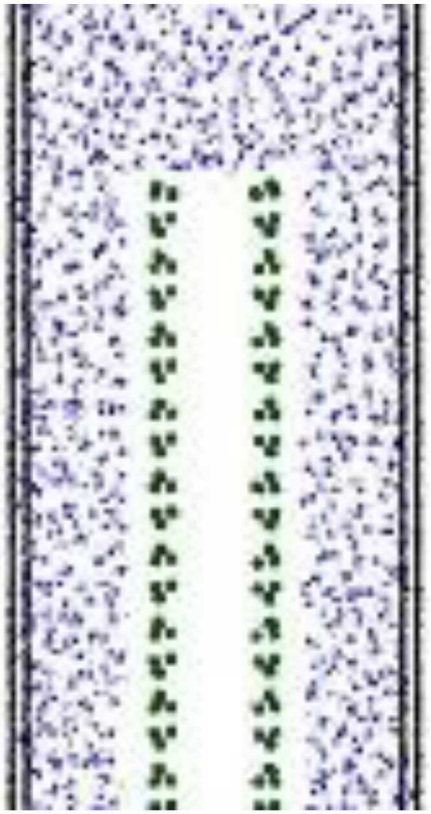
MD trajectory of interior water showing that transport through the nanotube only occurs in the inner water layer (R1).



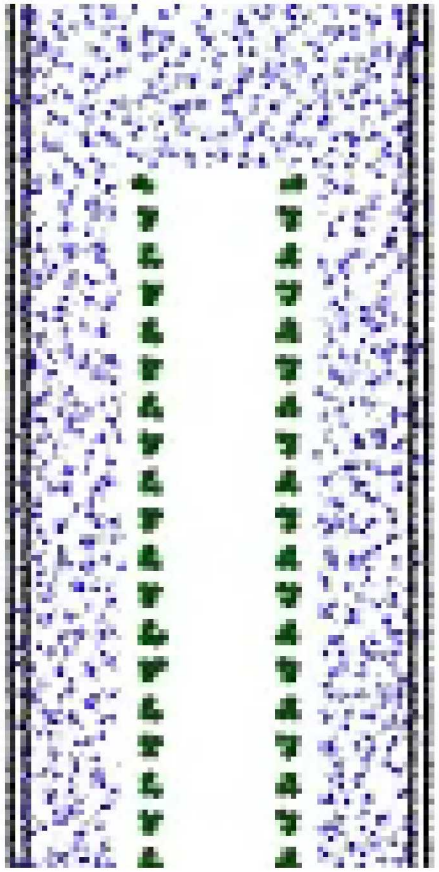
MD Simulation of Water Structure in Imogolite

Rafael Gonzalez (U. Mayor, CHILE), Jeffery Greathouse

N = 8 (4.0 Å)
300 K, 3.0 ns



N = 10 (7.2Å)
300 K, 2.5 ns

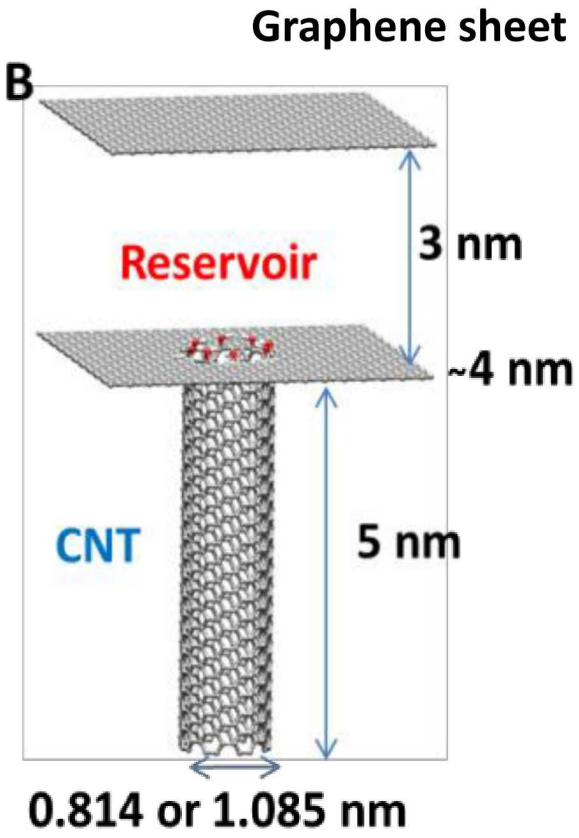


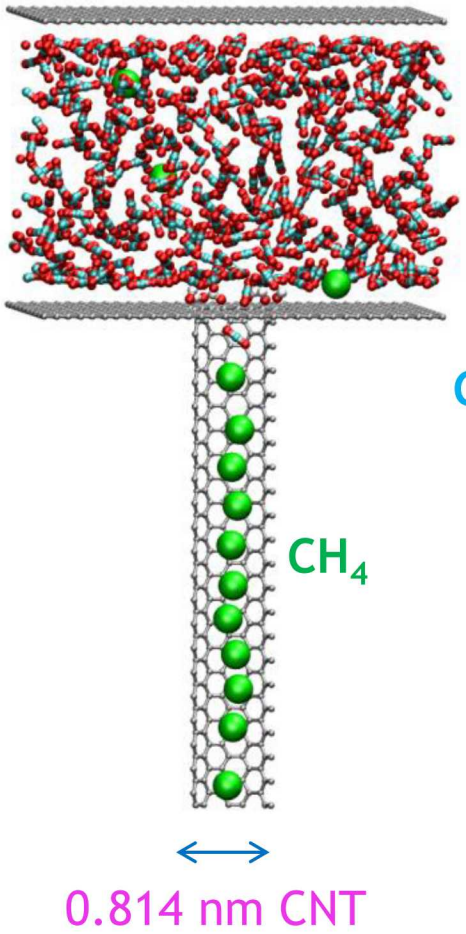
Non-equilibrium MD of pore size effects on water filling

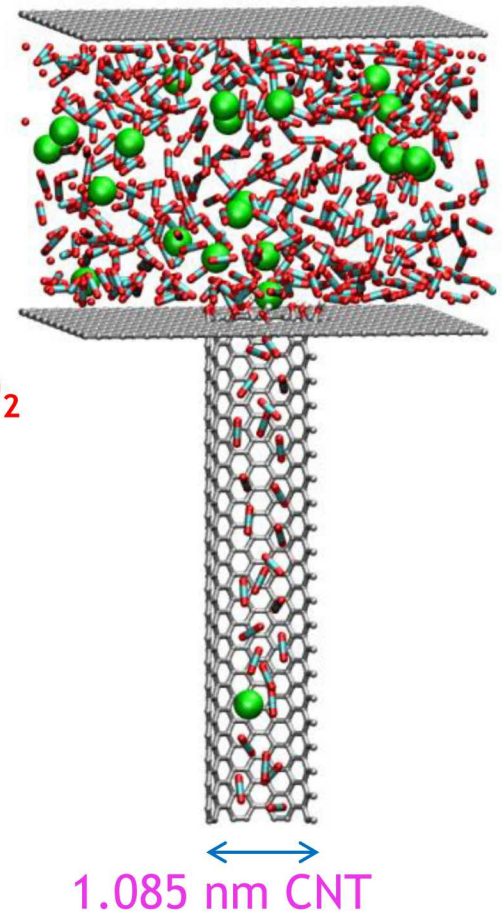
N = 8
- 4.0 Å pore diameter
- Single-file water transport (slow)

N = 10
- 7.2 Å pore diameter
- Multiple water layers
- Faster transport

Impact of pore size on enhanced gas recovery







Pore is too small for the invasion of CO_2

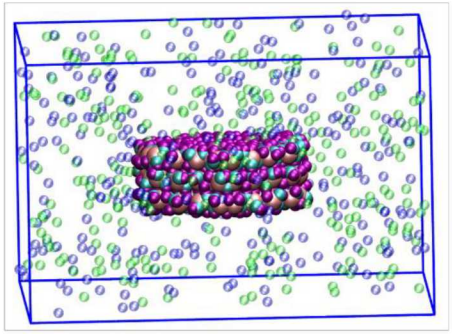
Pore is big enough for the invasion of CO_2

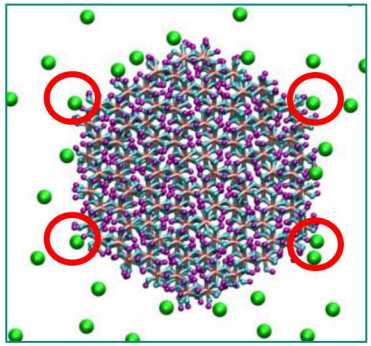
Ho, Wang, Criscenti 2016
Scientific Reports
Research funded by SNL LDRD

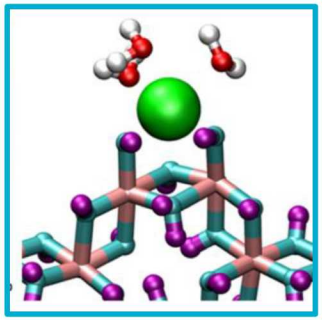
Molecular Modeling of Nanoparticle-Water Interactions: Adsorption and Aggregation

Louise J. Criscenti, Tuan A. Ho, Andrew S. Lee, Jeffery A. Greathouse, Kevin Leung, and Yifeng Wang

Ion Adsorption to Gibbsite Nanoparticle



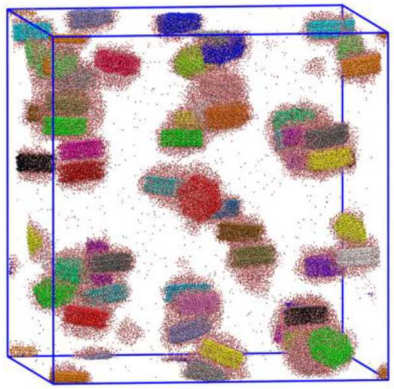


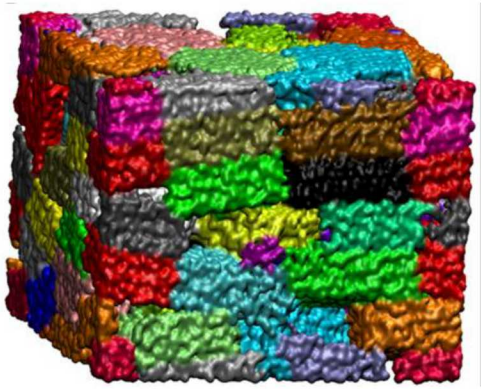


Cation adsorption is enhanced on nanoparticles due to significant inner-sphere complexation to the corners.

Ho et al. (2018) Enhanced Ion Adsorption on Mineral Nanoparticles. Langmuir, 34, 5926-5934

Particle Aggregation Model





Slower dewatering rate results in smaller pores, lower porosity, and better stacking of nanoparticles

Ho et al. (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. Scientific Reports, 7:15286.