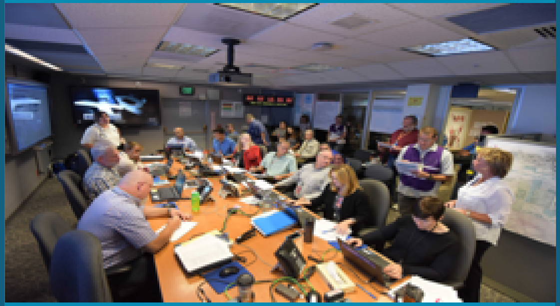
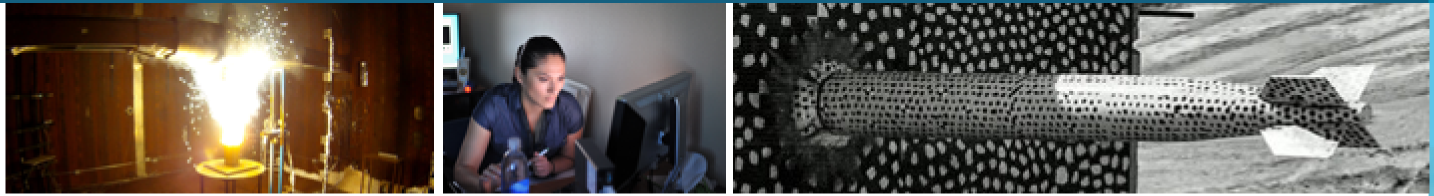
SAND2022-9786C

Modeling Ion Adsorption in Aqueous Solutions at Oxide Surfaces





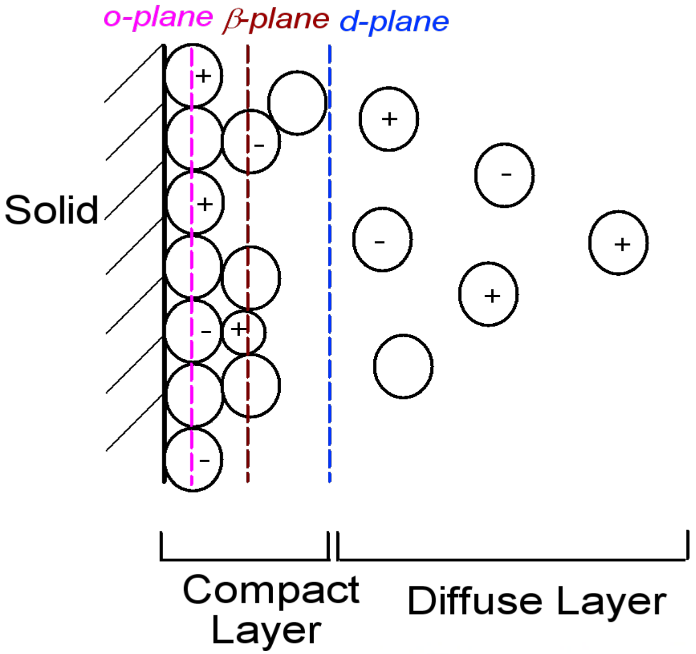
Louise J. Criscenti

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.

Cation Adsorption: Vignettes of Ion Pairing at Surfaces

- Bulk Thermodynamic Modeling of Adsorption
- Molecular Simulations of Ion Pairing and Adsorption
  - DFT Calculations (Ion Pairing)
  - Classical Force Field Modeling
- Nanoparticles
  - Cation Adsorption on Corners
- Nanoconfinement
  - Slit Pores
  - Subcritical Fracture

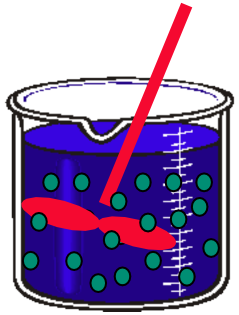
Electric Double Layer



Built on LDRD Laboratory Directed Research and Development

U.S. DEPARTMENT OF ENERGY | Office of Science

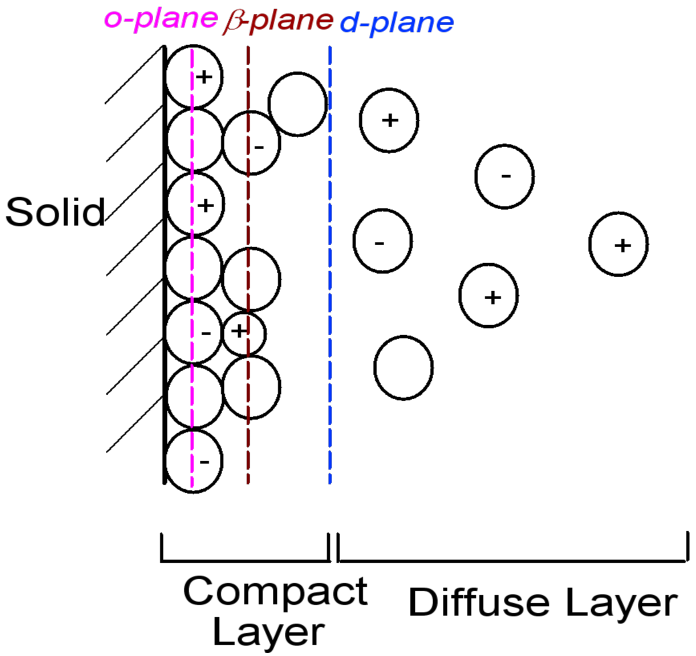
Surface Complexation Model: TLM



Ionic Strength
Electrolyte
Metal
Solid

Macroscopic Data

Surface Complexation Model
Electric Double Layer



$$> SOH + Mg^{2+} \leftrightarrow > SO^{-} - Mg^{2+} + H^{+}$$

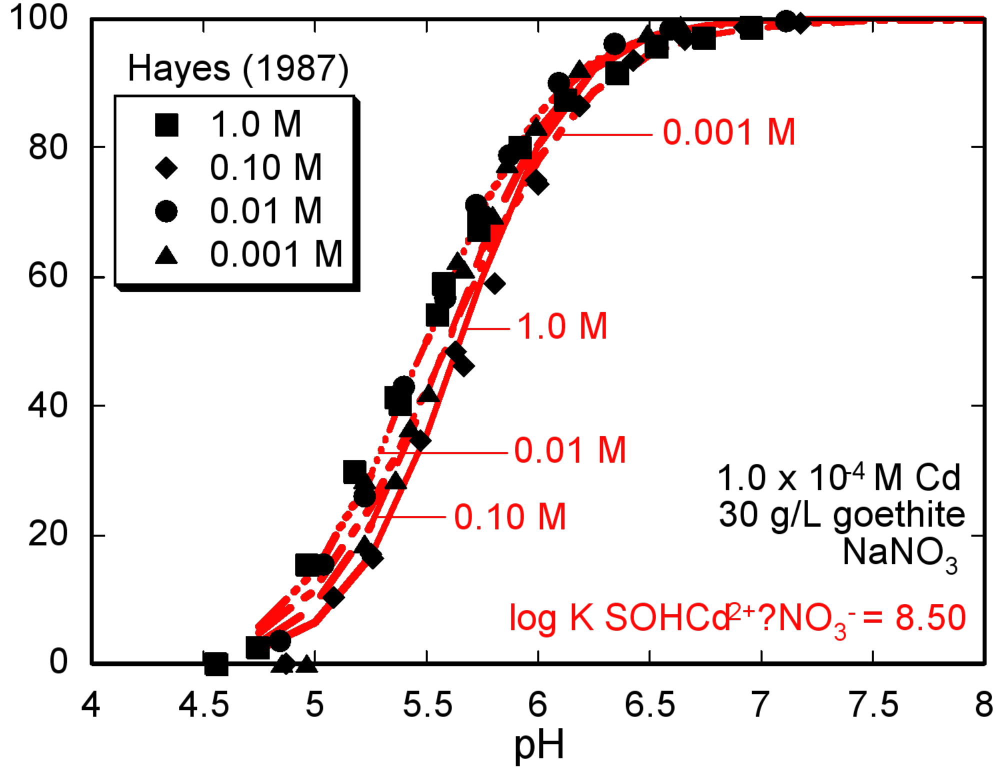
$$K = \frac{a_{>SO^{-}-Mg^{2+}}\, a_{H^{+}}}{> a_{>SOH}\, a_{Mg^{2+}}} 10^{F(2\Psi_{\beta}-\Psi_{o})/2.303RT}$$

$$C_1 = \sigma_o(\Psi_o - \Psi_\beta) \qquad C_1 = \frac{\varepsilon_d \varepsilon_o}{\beta}$$

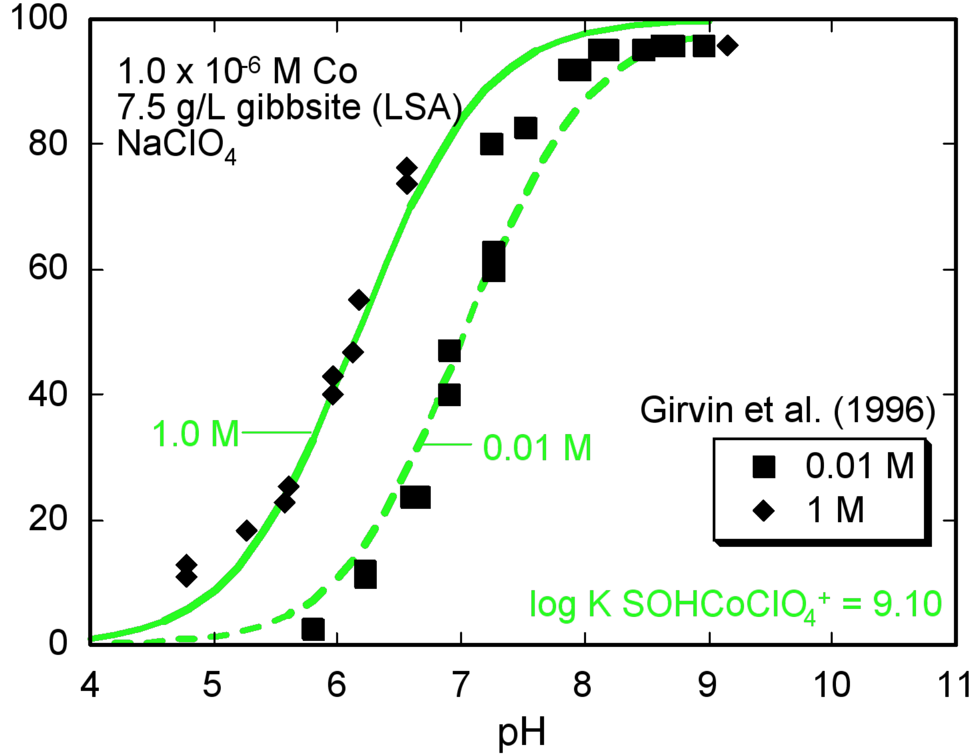
σ_o = charge on 0 plane
Ψ_o = electrostatic potential on 0-plane
Ψ_β = electrostatic potential on β-plane
C_1 = capacitance between 0 and β planes
ε_d = dielectric constant in the double layer region between 0 and β planes
ε_o = permittivity of free space
β = separation between planes

Ion Pairing to Fit Bulk Adsorption Data

$>SOH + Cd^{2+} + NO_3^- = >SOHCd^{2+}?NO_3^-$



$>SOH + Co^{2+} + ClO_4^- = >SOHCoClO_4^+$



(*Criscenti and Sverjensky, AJS, 1999*)

Are Ion Pairs preferred at Oxide Surfaces?

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{solv} + \Delta G^{o''}_{ii}$$

Adsorption

Short-Range Electrostatics

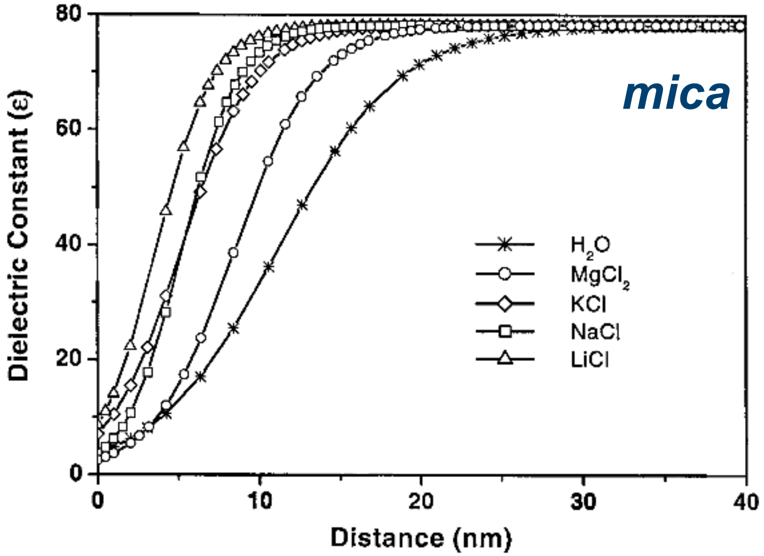
Born Solvation

Ion-Intrinsic

All three terms are a function of: $\left(\frac{1}{\varepsilon_{ifc}}\right)$

(Sverjensky and Sahai, 1996; Sahai and Sverjensky, 1997a, b)

Experimental Evidence



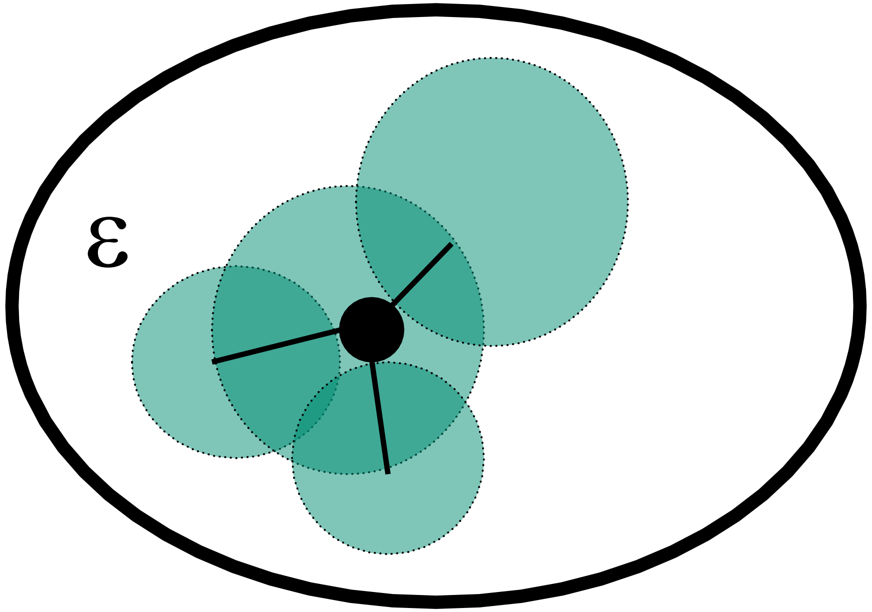
(Teschke et al. 2000)

AFM Study: Calculated dielectric constant as a function of distance from surface by fitting measured force vs. distance curves.

*Ion Pairing is expected at lower dielectric constants due to less electrical screening

Quantum Cluster Calculations

Polarizable Continuum Model (PCM) and Integral Equation Formulation (IEF)
(*Tomasi et al. 1994; Cances et al. 1997*)



Adapted fr. Foresman & Frisch (1993)

B3LYP/6-31G*

- **B3LYP**
  - Becke-style 3-Parameter Density Functional Theory using Lee-Yang-Parr correlation functional.
  - Allows for electron correlation
- **6-31G***
  - Basis set that can be used for 3rd row elements

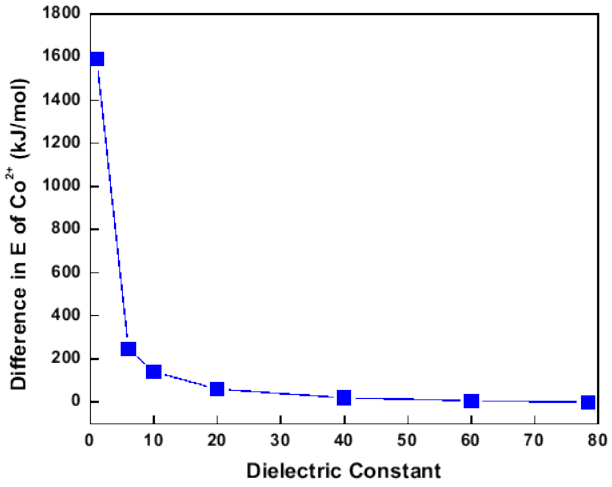
$$Co^{2+} + Cl^{-} \leftrightarrow CoCl^{+}$$

$$\Delta E_{CoCl^{+}} = E_{CoCl^{+}} - (E_{Co^{2+}} + E_{Cl^{-}})$$

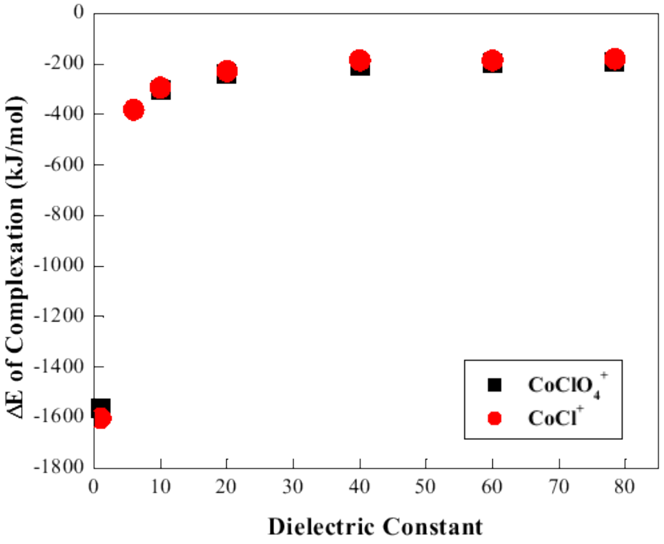
Criscenti & Kubicki (2001) 221st ACS National Meeting, San Diego, CA.

Gaussian Results

Change in Co^{2+} Energy with Dielectric Constant

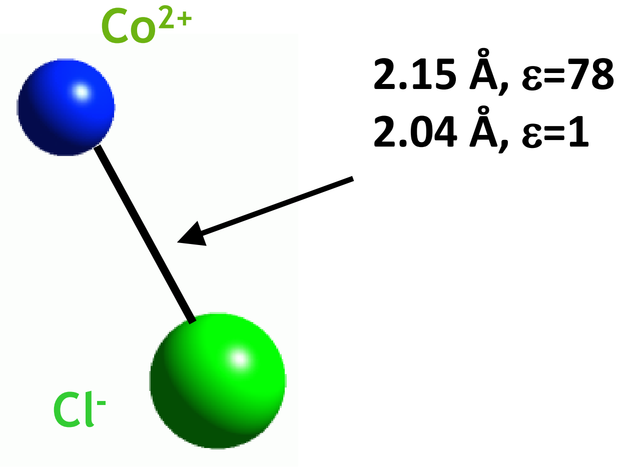


ΔE of Co^{2+} Complexation with Dielectric Constant

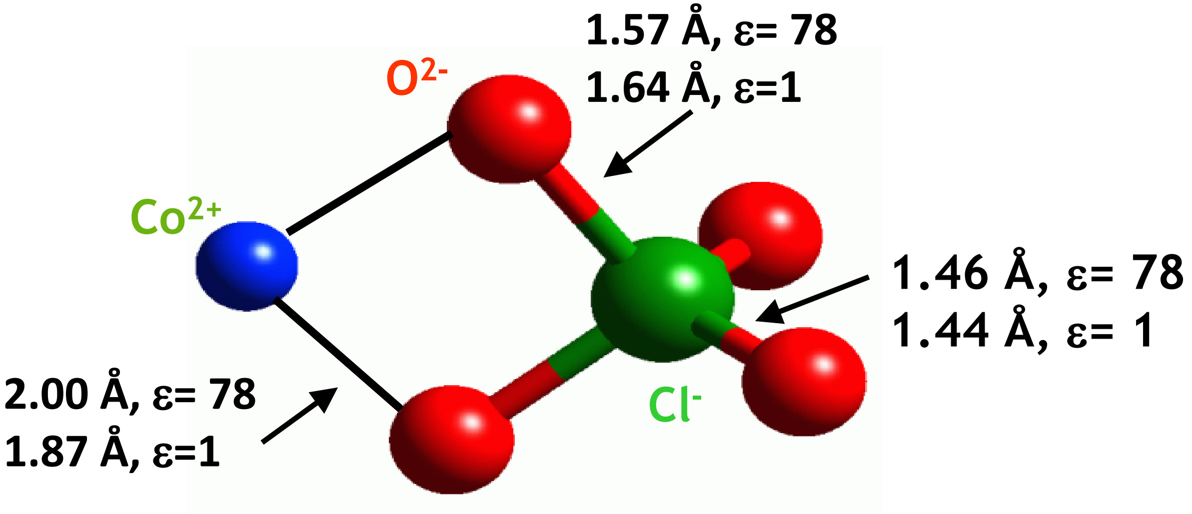


Criscenti & Kubicki (2001) 221st ACS National Meeting, San Diego, CA.

Changes in Metal-Anion Structure with Dielectric Constant



2.15 Å, ε=78
2.04 Å, ε=1

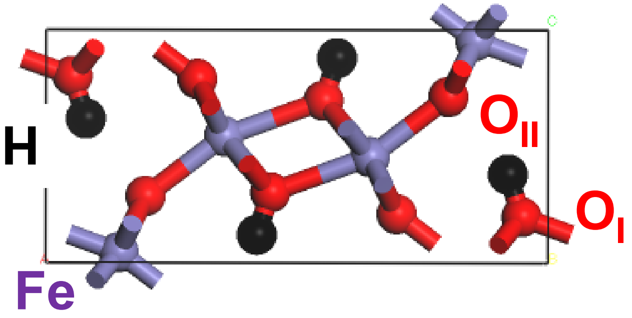


1.57 Å, ε= 78
1.64 Å, ε=1

1.46 Å, ε= 78
1.44 Å, ε= 1

2.00 Å, ε= 78
1.87 Å, ε=1

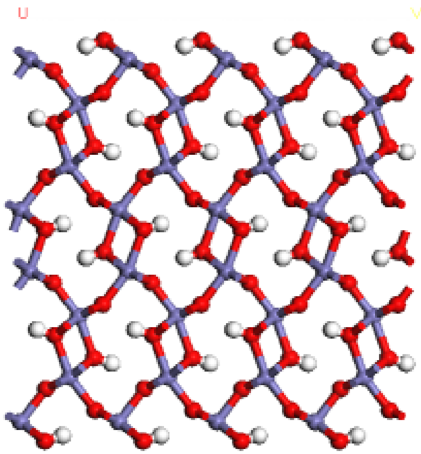
Goethite: Predominant Surfaces and Surface Sites



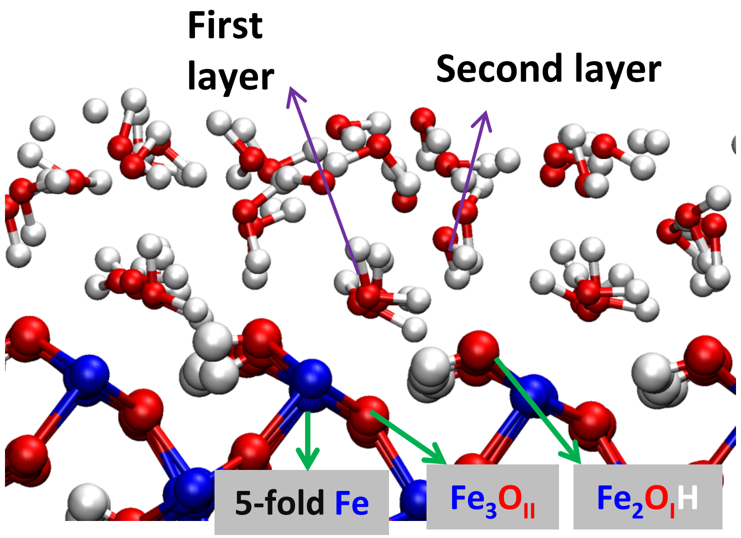
Goethite Unit Cell

- H-bonds between surface sites
- (100) surface, the 1st H_2O layer binds to Fe; the 2nd to Fe_2O_IH
- (101) surface, 1st layer H_2Os form H-bonds with 2 neighboring sites, 2nd layer interacts with 3 types of sites.
- ***Roughness leads to less structured H_2O.***

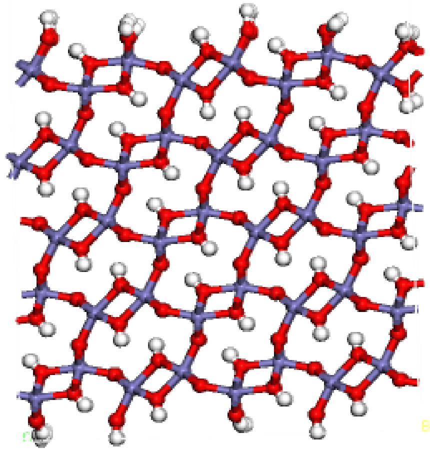
(100) Surface



5-fold Fe
Fe_2O_IH
Fe_3O_{II}

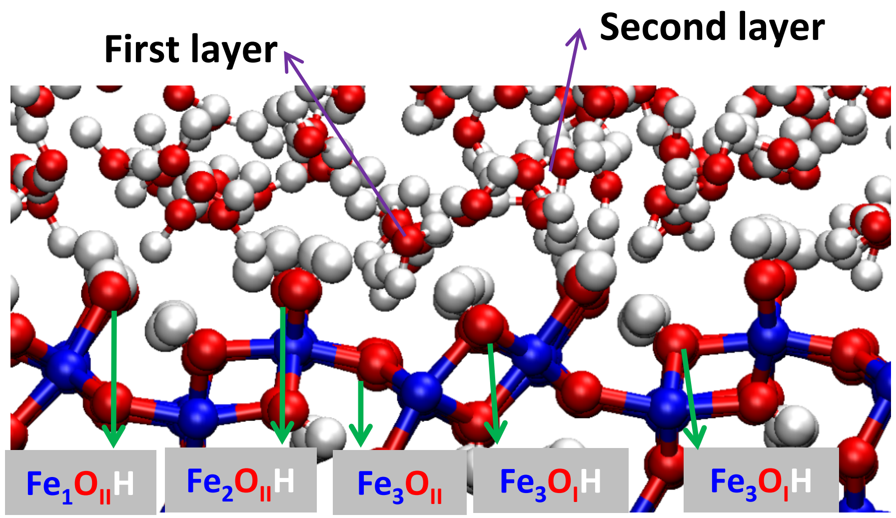


(101) Surface



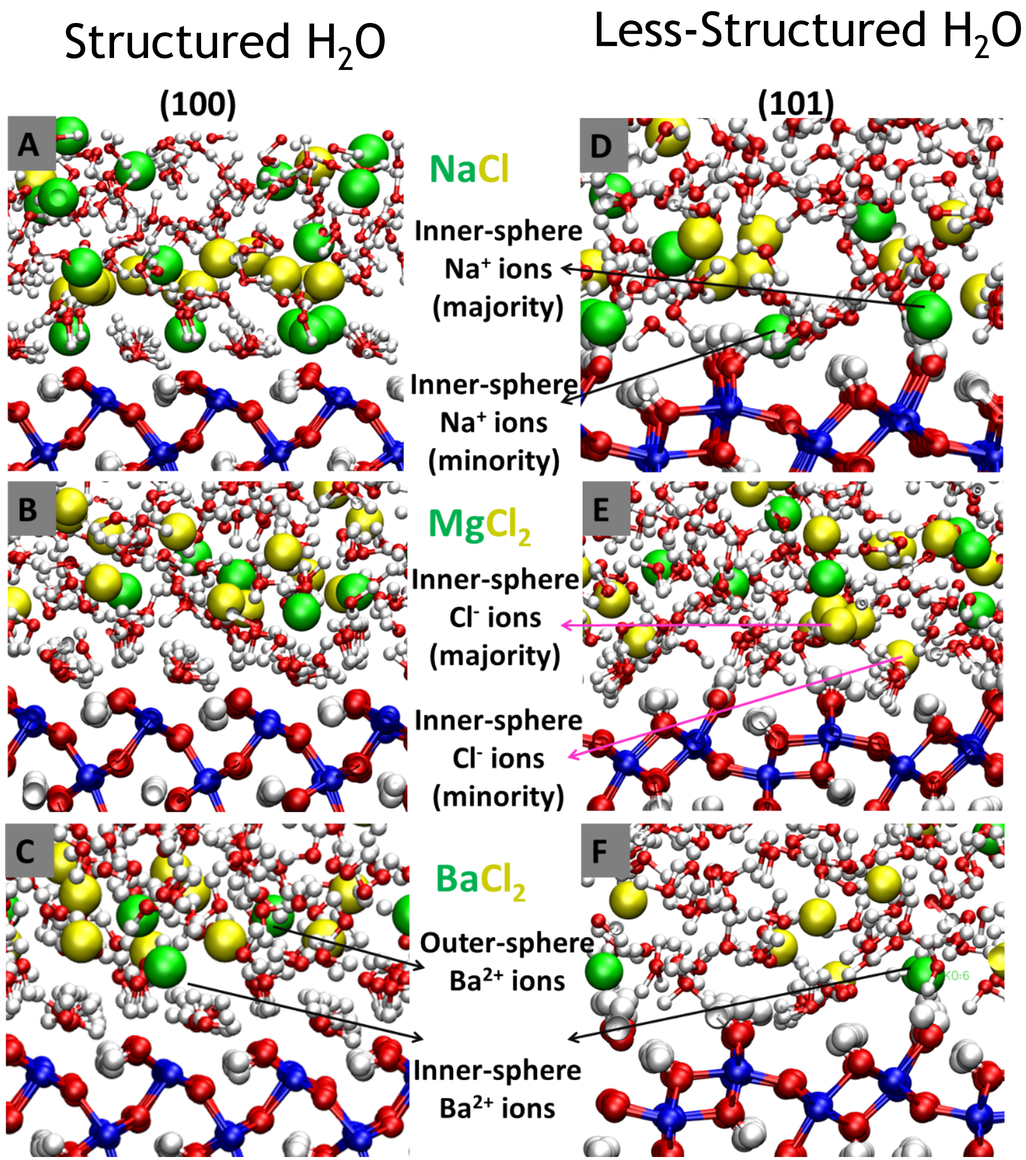
$Fe_1O_{II}H$
$Fe_2O_{II}H$
Fe_3O_{II}
Fe_3O_IH

2 populations of Fe_3O_1H



Criscenti, L.J. et al., 2018, Langmuir, 34, 14498-14510.

Differences in Ion Adsorption on Goethite Surfaces



Na^+ inner-sphere (IS) complexes on both surfaces
Mg^{2+} outer-sphere (OS) complexes on both surfaces

Ba^{2+} mostly OS complexes on (100) surface; IS on (101) surface
Cl^- OS on (100) surface; IS on (101) surface.

Mg^{2+} has a large hydration enthalpy; it is always surrounded by its solvation shell.

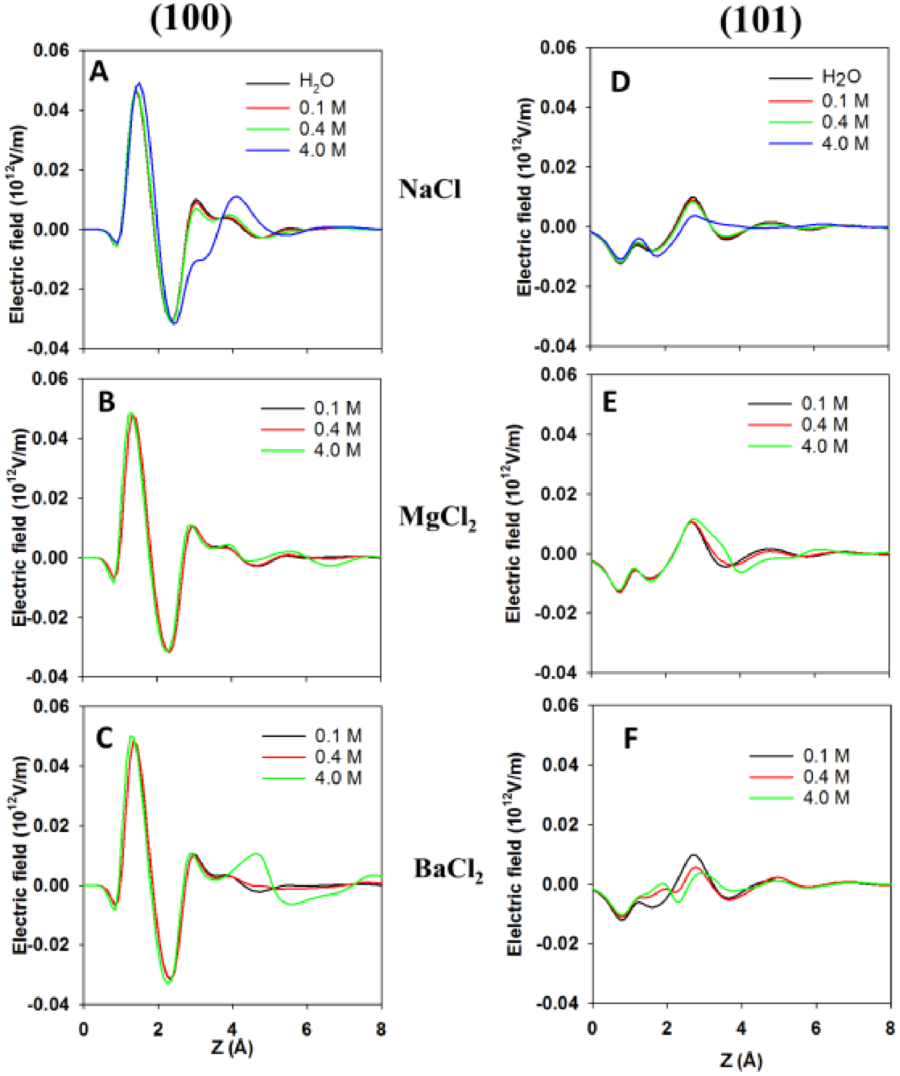
H_2O binding is weaker on (101) than (100) surface; this favors IS adsorption.

Ba^{2+} HE < Mg^{2+} HE. Easier to remove hydration shell. Both weaker H_2O binding to (101) and lower HE support IS Ba^{2+} adsorption.

Criscenti, L.J. et al., 2018, Langmuir, 34, 14498-14510.

Structural Properties of Aqueous Solutions at Goethite Surfaces

Electric Field Profiles



Observations

- ➢ The (101) goethite-solution interface exhibits less water structure and therefore weaker electric double layer oscillations.
- ➢ At low ionic strengths, ions on surface do not impact “averaged” electric field as a function of distance from the surface

Implications

- ➢ Differences in interfacial properties for these surfaces suggest that the adsorption properties of one goethite surface cannot be used to represent goethite interfaces present in soils and sediments.

Criscenti, L.J. et al., 2018, Langmuir, 34, 14498-14510.

Ion Pairs on Goethite Surfaces

% Ion Pairs within 0-6 Å Slab from Surface

Ion Pairs	(100) Face			(101) Face		
	0.1 M	0.4 M	4.0 M	0.1 M	0.4 M	4.0 M
Na-Cl	1.2	12.4	61.4	0.9	5.8	36.6
Na-H_2O-Cl	7.2	27.2	33.1	6.7	33.4	57.9
Na-2H_2O-Cl	3.0	19.5	0.8	5.1	18.0	2.4
Total NaCl	11.4	59.1	95.3	12.7	57.2	96.9
Mg-Cl	0	0	37.6	0	33.3	38.5
Mg-H_2O-Cl	0.6	15	30.3	1.8	20.0	36.3
Mg-2H_2O-Cl	0	8.9	1.7	1.4	8.1	2.4
Total $MgCl^+$	0.6	23.9	69.6	3.2	61.4	77.20
Ba-Cl	6.4	30.5	64.1	0.5	19.3	43.6
Ba-H_2O-Cl	12.2	16.4	13.1	18.0	33.3	31.4
Ba-2H_2O-Cl	10.5	9.1	3.2	10.1	13.6	2.02
Total $BaCl^+$	29.1	56.0	80.4	28.6	66.2	77.02

	(100)	(101)
NaCl	CIP Na^+(IS)Cl^-(OS)	SSHIP Na^+(IS)Cl^-(IS)
$MgCl_2$	CIP Mg^{2+}(OS)Cl^-(OS)	CIP Mg^{2+}(OS)Cl^-(IS)

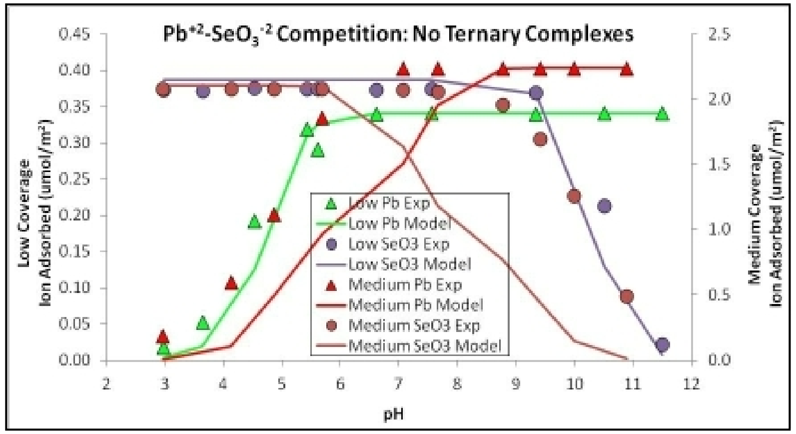
- Hypothesis: More structured water = lower dielectric constant = more ion pairing?

Observations

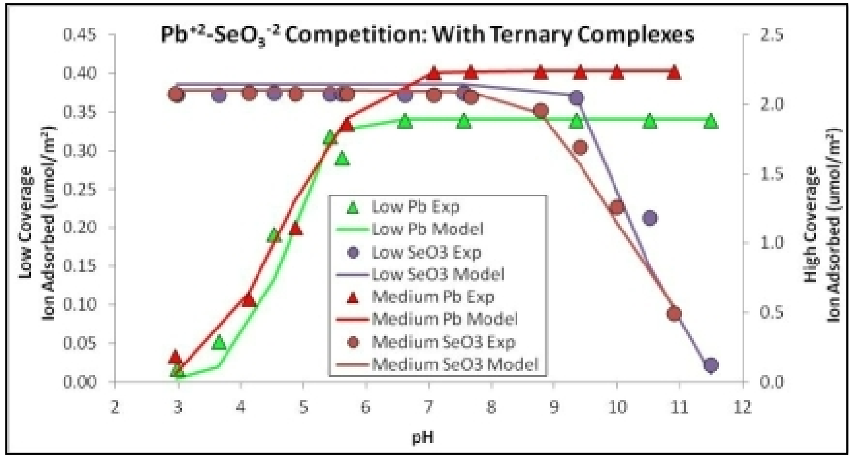
- NaCl: CIP preferred on (100) surface; SSHIP on the (101) surface
- $MgCl_2$: Mg is always OS; Cl^- is OS on (100) and IS on (101)
- $BaCl_2$: SSHIP doubles with ionic strength on (101), not true on (100).
- More CIP on (100) face for NaCl and BaCl.

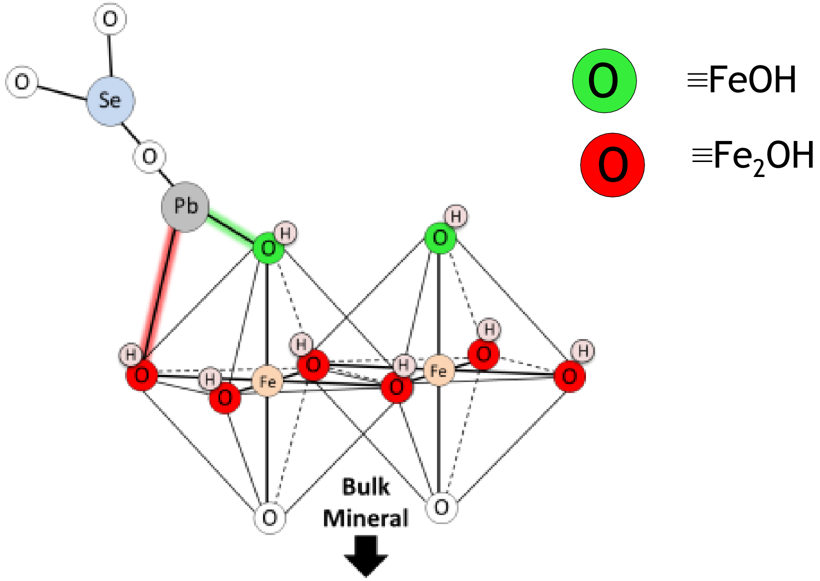
CD-MUSIC Fit for Pb^{2+}/SeO_3^{2-} Bi-solute Adsorption Edges

Without Ion Pairing



With Ion Pairng

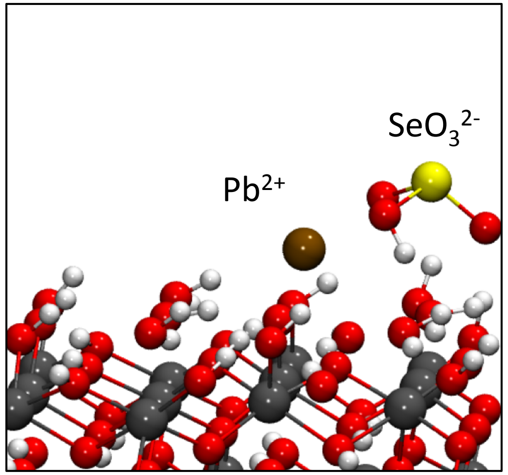




- SCMs can now be used to fit both metal and oxyanion adsorption data using the same surface site density!!
- This requires the adsorption of metal-oxyanion pairs. SCMs require a ternary complex on the (210) surface to fit the data for Pb^{2+} and SeO_3^{2-} data.
- The complex used is (>FeOH)-PbOSeO$_2$-(Fe$_2$OH) involving two sites along the edge of an Fe octahedron.

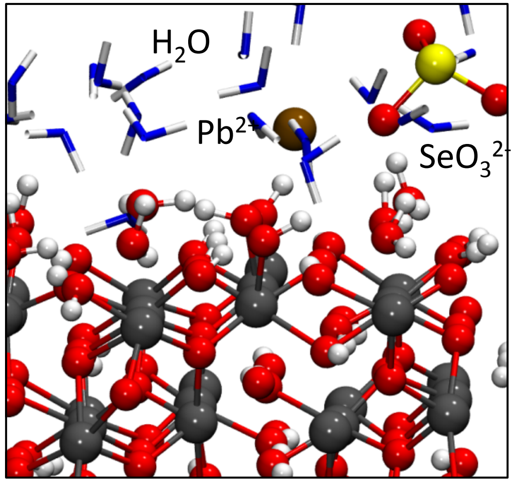
Can we test the viability of this complex using *ab initio* MD?

Ab Initio MD: Pb(II)/SeO_3^{2-} pair on goethite (210) surface



static, T=0K; SeO_3H^- most stable without added H_2O

add water, simmer at T=400* K for 4 ps

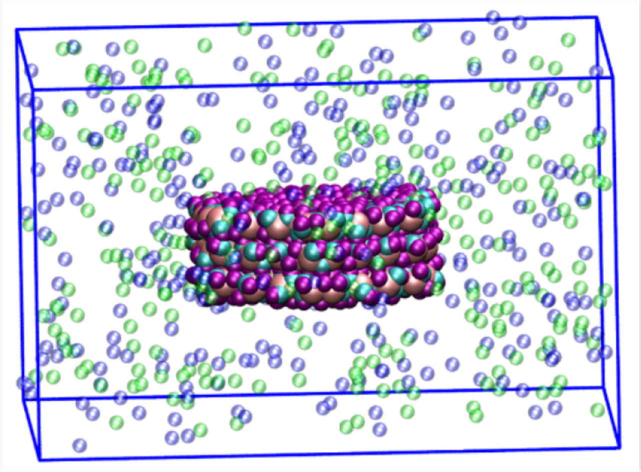


AIMD in liquid water; SeO_3H^- loses H^+ to FeOOH (210) surface

- Pb(II)/SeO_3^{2-} contact ion pair appears to be stable on surface
- in agreement with CD-MUSIC analysis
- (EXAFS in the future)

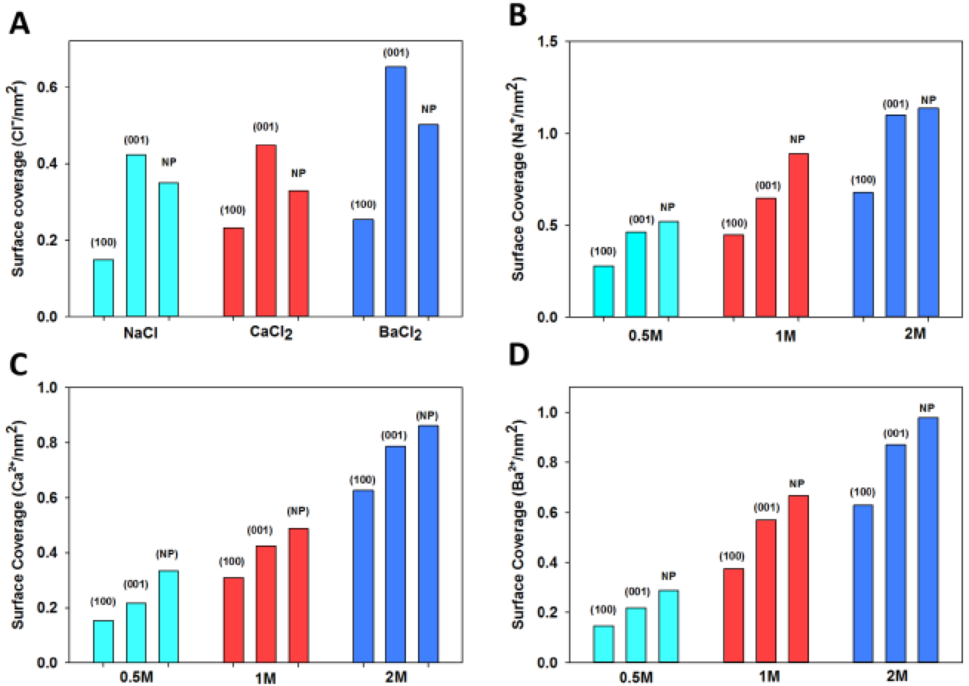
Leung and Criscenti, *J. Phys. Condens. Matter*
2017 **FRONT COVER**

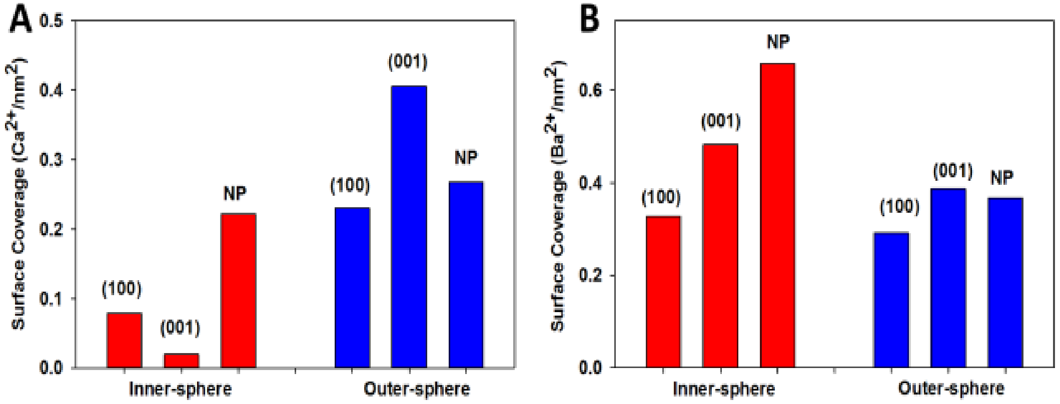
Nanoparticles: Cation Adsorption to Gibbsite Nanoparticles



- 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

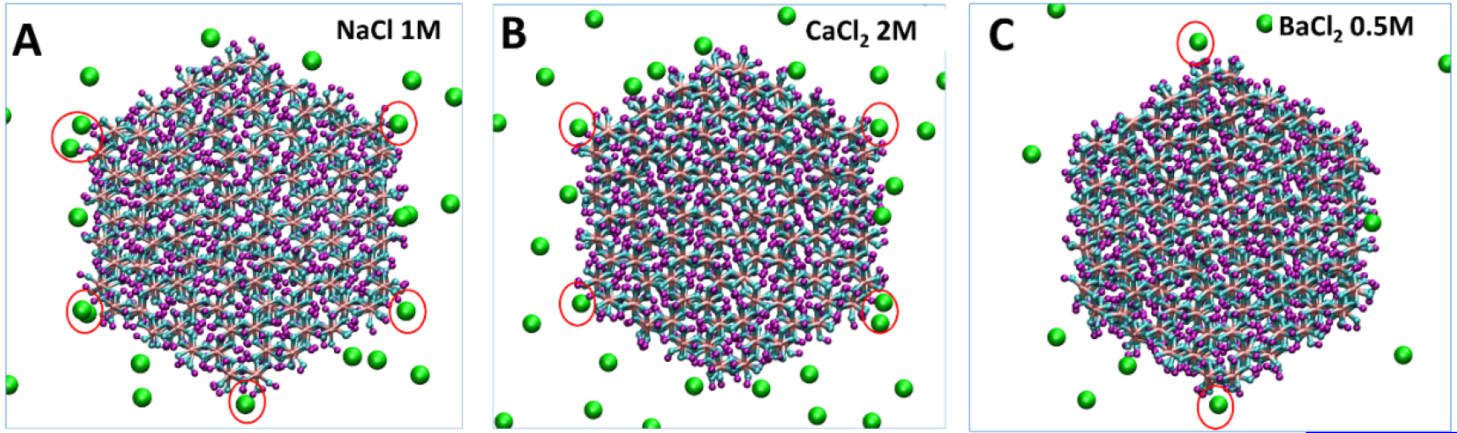
Ho, T.A. et al. (2018) Langmuir 34, 5926-5934.

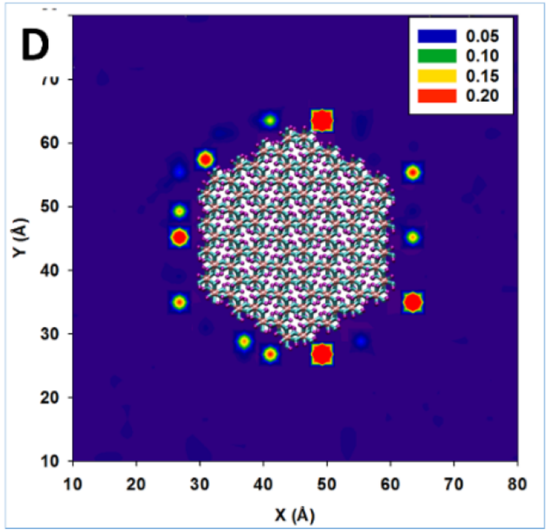




Cation Adsorption on Nanoparticle Corners

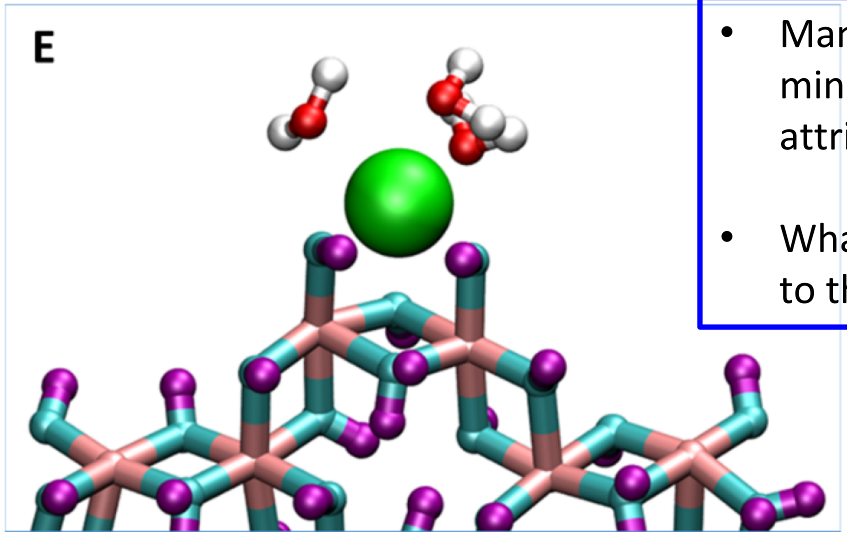
Snap-shots





Planar density distribution

Na$^+$ over 10 ns

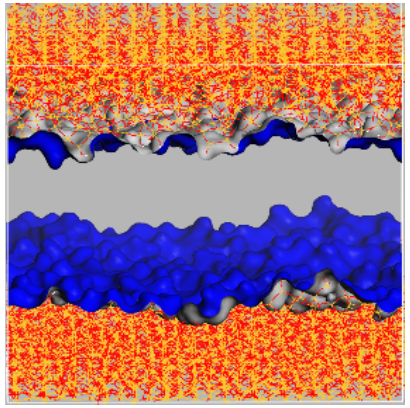


- Many SCMS rely on a 2-site model with a minor number of strong sites that are attributed to defects.
- What is the difference in adsorption energy to these sites?

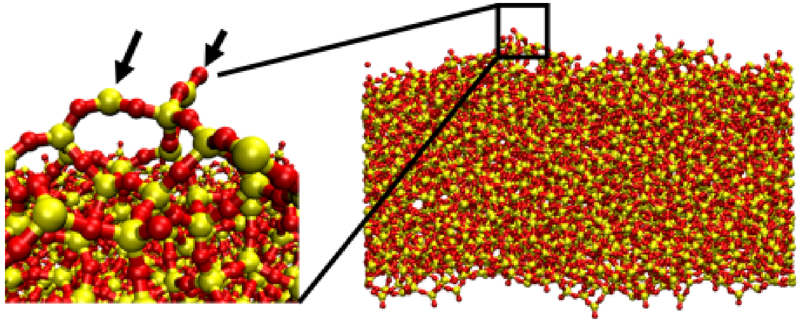
Ho, T.A. et al. (2018) Langmuir 34, 5926-5934.

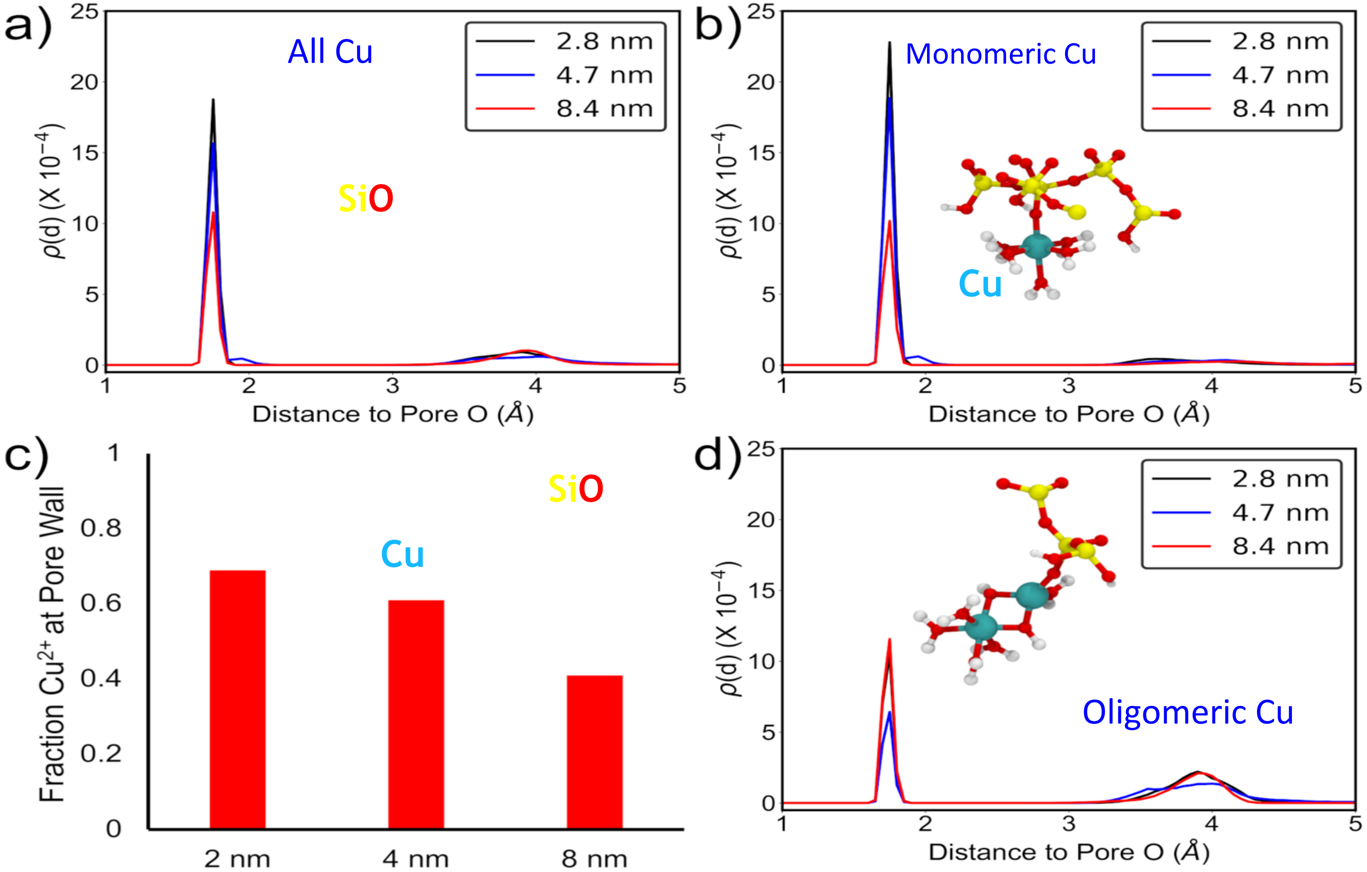
Classical Molecular Dynamics Simulations of Cu(II) on Mesoporous Silica

- Rough interface Total SA = 138.38 nm^2 compared to flat surface = 42.13 nm^2
- Functionalized the surface with hydroxyl groups
- Both silanol and geminol sites created
- OH site density ~2.0 OH nm^2 to match with SBA glass.
- Created a net charge of -1.0e per SiO$^-$
- Negative surface charge (-0.25 C/m^2)



Under-coordinated Si's & O's





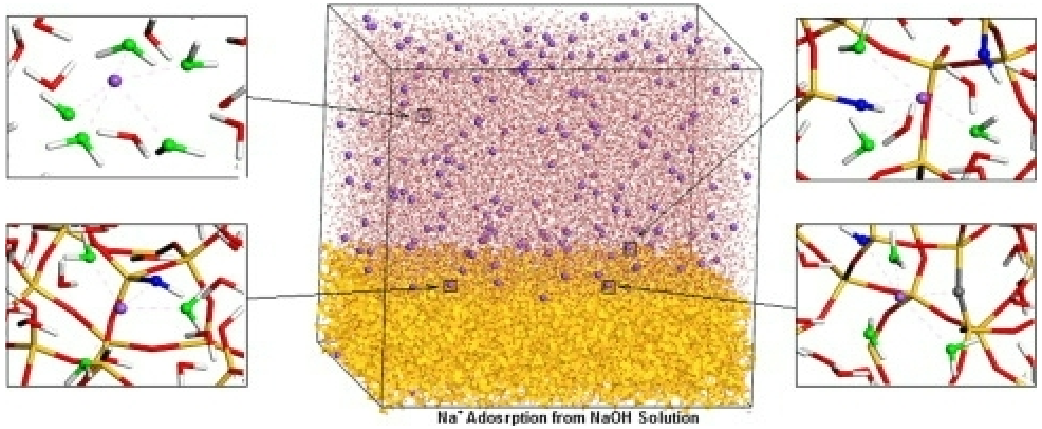
Determined from Cu densities in <2Å region

0.1 M Cu(II) charge-balanced with negative silica surface and OH$^-$

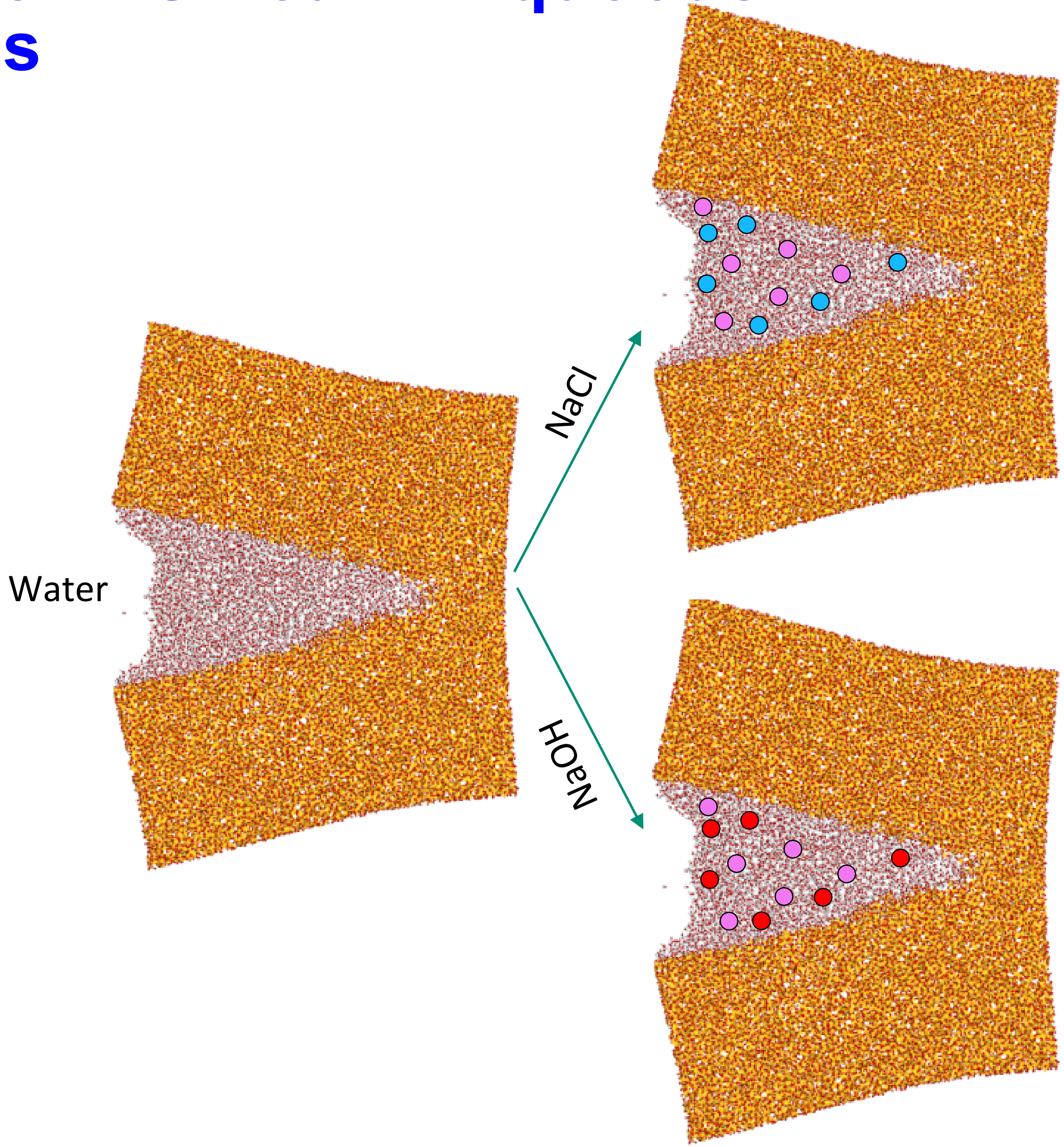
Knight et al. Environmental Science-Nano ***2020**, **7 (1)**, **68-80**.*

Complex Nanopores: Fracture in Silica in Aqueous Solutions

- Investigated three different aqueous solutions (Water, 1M NaCl, 1M NaOH)
- During each loading step one NaCl or NaOH molecule was added to the widest point of the fracture and then the system was relaxed for 5ps
- Requires GCMC (Grand canonical Monte Carlo) method of inserting water into the fracture to maintain surface wetting
- Changes H^+ and OH^- concentration in the reacting fluid
- Compare with previous results on NaOH interaction with a flat silica surface

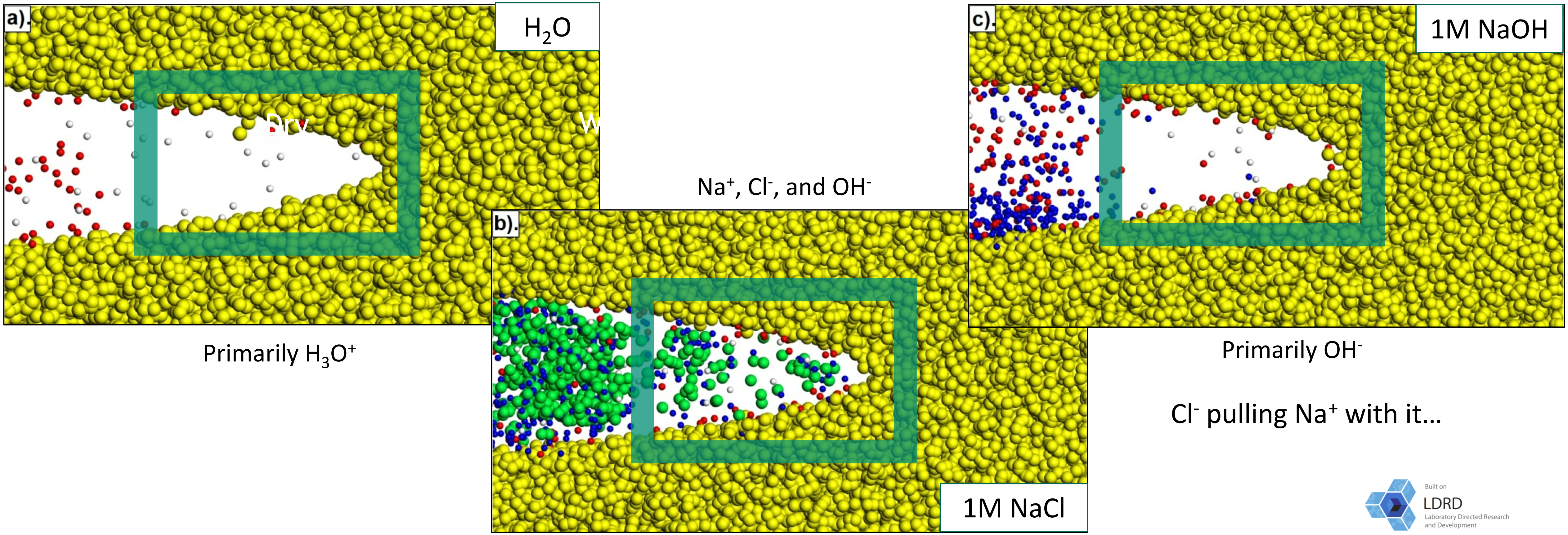


Rimsza et al. (2018) JCIS, 516, 123-137.



Crack Tip Accessibility

- Not all molecular species can access the fracture tip in order to cause reactions to take place



Primarily H_3O^+

Na^+, Cl^-, and OH^-

Primarily OH^-

Cl^- pulling Na^+ with it…

Built on
LDRD
Laboratory Directed Research and Development

Atomic positions of Na^+, Cl^-, OH^-, and H_3O^+ molecules inside the crack tip for three different solutions (a) water, (b), 1M NaCl, and (c) 1M NaOH. Water is not shown for clarity. All twelve replicates are overlaid to sample the variety of atomic positions and are at a constant loading of 0.2 MPa√m. Atom types: Si (yellow), Na^+ (blue), Cl^- (green), OH^- (red), H_3O^+ (white).

Rimsza et al. Frontiers in Materials 2019, 6.

Conclusions

- Low dielectric constants at the mineral/water interface will favor ion pairing.
- This tendency may be extended to polymerization under nanoconfinement & crystal growth.
- Ion pairing may also have an impact on cation diffusion into nanopores and crack tips.
- Ion pairing in complex waste streams between contaminants may play a key role in metal adsorption.
- Surface complexation models are required to incorporate atomistic information into meso-scale or field-scale models.
- For Discussion: what are the most important properties observed at the atomistic level that are required in a continuum model?

Co-Authors:
Dimitri Sverjensky (JHU)
James Kubicki (PSU)

SNL:
Anastasia Ilgen, Jeffery Greathouse, Jacob Harvey, Tuan Ho, Reese Jones, Kevin Leung, Jessica Rimsza

Tyler Duncan (KU undergraduate intern)

Built on LDRD Laboratory Directed Research and Development

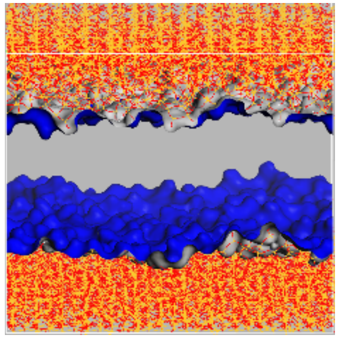
U.S. DEPARTMENT OF ENERGY | Office of Science

Extra Slides

Nanopores

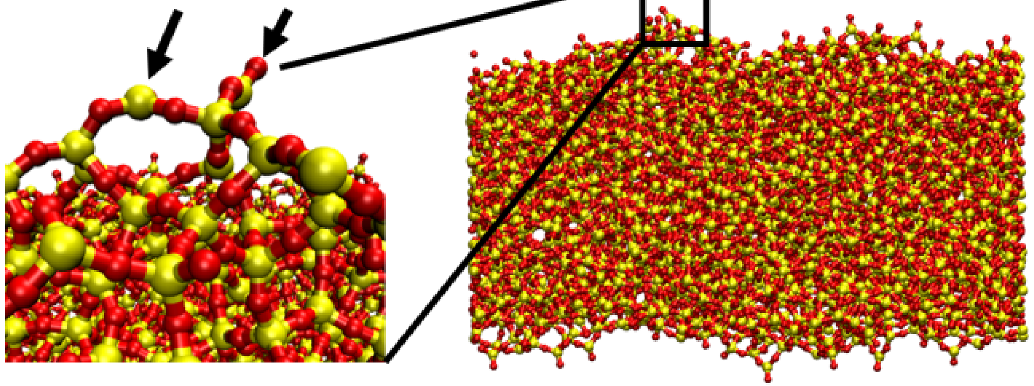
Surface Preparation

4000 K, NPT



- 5 nm vacuum added to both sides of slab before cooling from 4000 to 300 K
- Cooling in NVT ensemble with a vacuum layer results in rough interface
- Total SA = 138.38 nm^2 compared to flat surface = 42.13 nm^2

- Functionalized the surface with hydroxyl groups
- Both silanol and geminol sites created
- OH site density ~2.0 OH nm^2 to match with SBA glass.
- Created a net charge of -1.0e per SiO^-
- Negative surface charge (-0.25 C/m^2)



Under-coordinated Si's & O's

Knight et al. Environmental Science-Nano ***2020, 7 (1), 68-80.***

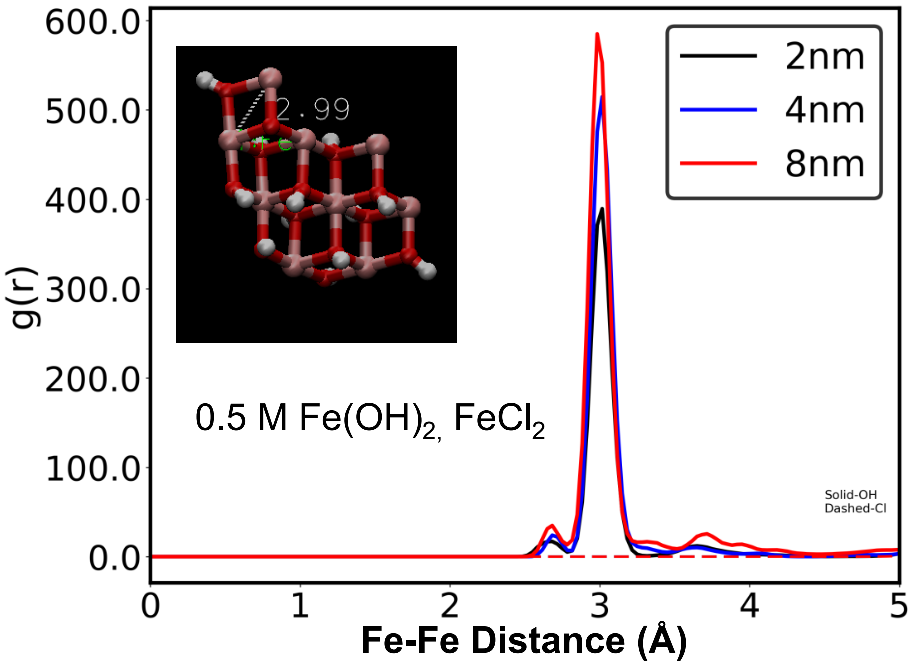
Fe(II)/Fe(III) Adsorption on Mesoporous Silica

Tyler Duncan (student), J. Harvey (postdoc), A. Knight (postdoc), J. Greathouse, A. Ilgen, L. Criscenti

Comparison of Fe Coordination, MD and XAFS

Pore Size (nm)	Fe(II)	MD (Å)	XAFS (Å)
4nm	Fe-O	2.00-2.55	2.08-2.89
	Fe-Fe	3.00-3.75	3.18
	Fe-Si	3.25	2.72-3.28

Pore Size (nm)	Fe(III)	MD (Å)	XAFS (Å)
4nm	Fe-O	2.00-2.10	1.89-2.09
	Fe-Fe	2.80-3.00	2.51
	Fe-Si	3.60-4.40	2.75
8nm	Fe-O	1.95-2.00	1.90-2.08
	Fe-Fe	2.80-3.50	2.51
	Fe-Si	3.50	2.76-3.28



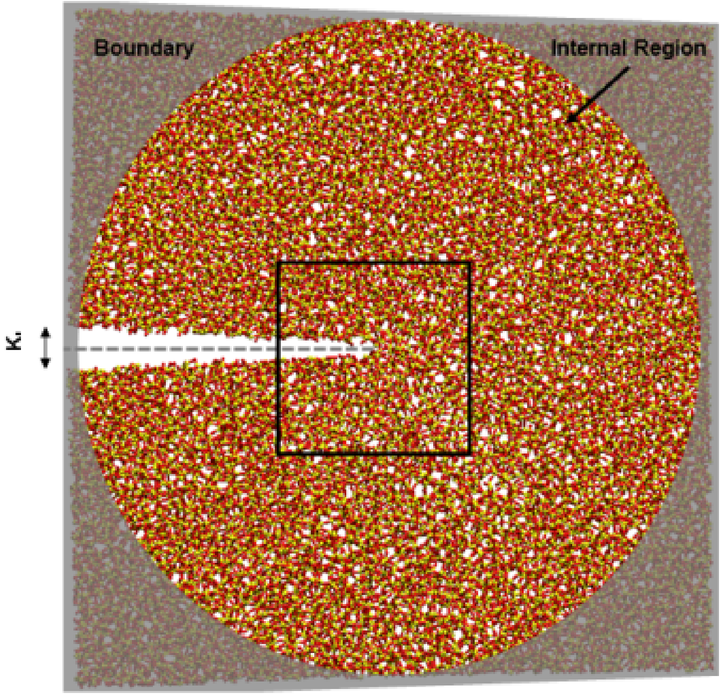
Conclusions:

- Surface adsorption has a pore size dependence. Inner sphere adsorption is favored for higher concentrations and Fe(II)/charged systems.
- Fe speciation and surface complexation has a concentration dependence.
- Cl^- does not form Fe-Fe complexes with Fe(II) or Fe(III).
- OH^- forms complexes and crystalline precursors.
- Calculations are consistent with XAFS data – validation of force fields.

Greathouse et al., Environmental Science-Nano, submitted.

Complex Nanopores: Fracture in Silica

- Amorphous silica, system size: 38400 atoms (143Å x 143Å x 28Å)
  - Melt and quenched from ß-cristobalite system
  - 12 different cracks (three different silica structures with four different crack locations)
- Slit crack is formed by removing neighboring, creating a singular high stress condition
- Boundary atoms are fixed and atomic positions are adjusted to introduce far-field loading as a mode I fracture
- Interior atoms are allowed to freely move by integration with a microcanonical (NVE) ensemble
- Stress is introduced iteratively by increasing the crack width
- Reactive Force Field: (ReaxFF) allows for bond making and breaking. Yeon and van Duin (2015) JPC C 120: 305-317.



Schematic of silica slit crack, crack width, as well as boundary and internal regions. Atoms: oxygen (red), silicon (yellow)

Rimsza et al. (2018) JACer, 101, 1488-1499.