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Ion Adsorption to Goethite-Water Interfaces

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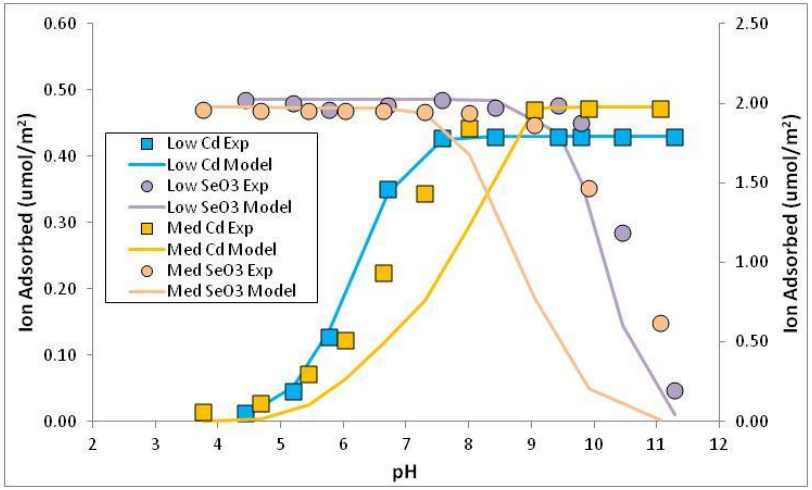
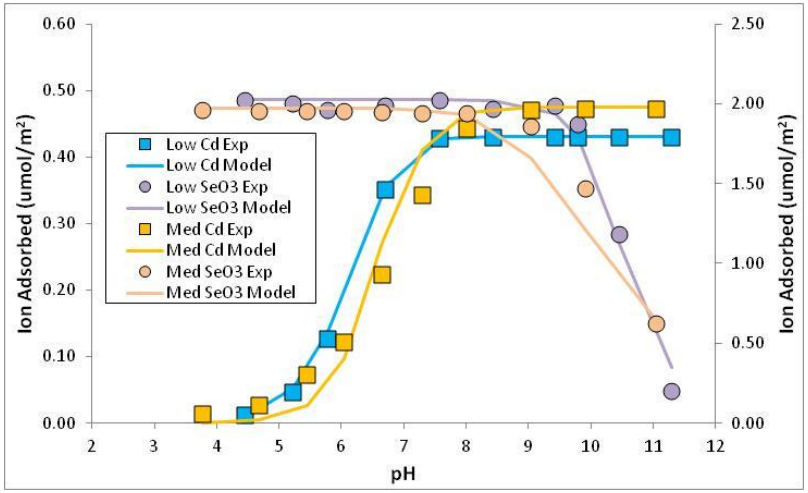
Multi-contaminant Adsorption on Goethite

Surface Complexation Modeling

Cd^{+2} and SeO_3^{-2} Bi-solute Competition ***without*** Ternary Complexes



Cd^{+2} and SeO_3^{-2} Bi-solute Competition ***with*** Ternary Complexes



Reactive Surface Sites (*fr. Villalobos*)

Site Type	Mineral Face Site Density (sites/nm^2)			
	(101) face	(001) face	(210) face	(010) face
XOH	2.29	0	0.00	2.22
X_2OH	0.00	0	0.00	1.11
X_3OH	2.29	0	0.00	0

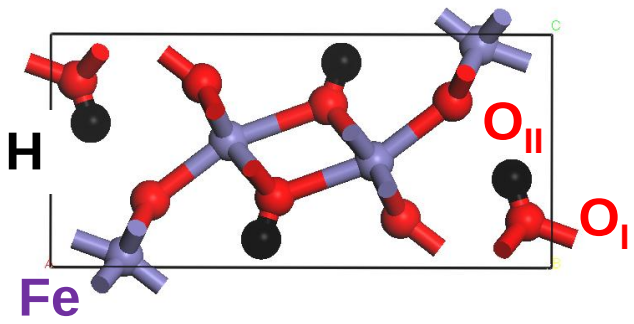
- Hiemstra-like CD-MUSIC model applied to ratio of different goethite surfaces according to experimental data.
- Experiments and modeling by *Manigold and Katz (UT-Austin)*

Long-Term Objective

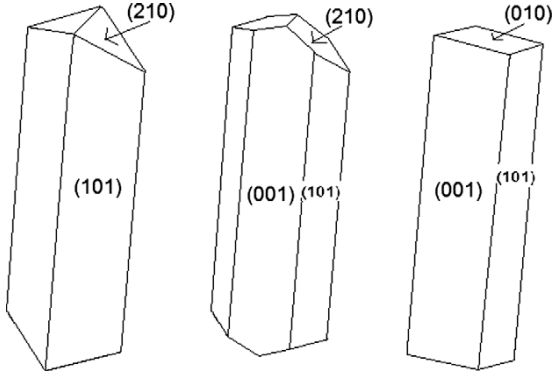
To use molecular modeling to investigate cation-anion adsorption as a function of surface concentration in complex systems

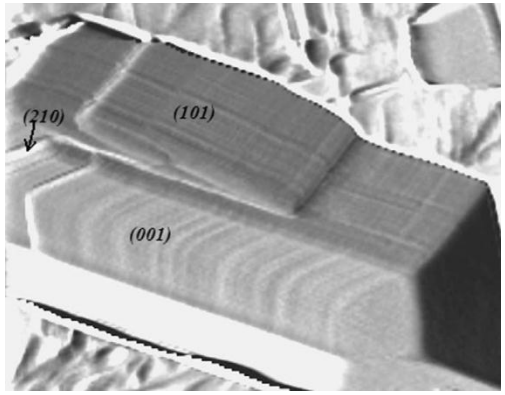
- Goethite-water and Goethite-NaCl
  (101) and (100) surfaces
- Alkaline Earth Metal – Chloride Complexation
- Heavy Metal Force Field Parameters
- Oxyanion (SO_4^{2-}) force field models

Goethite: Predominant Surfaces and Surface Sites



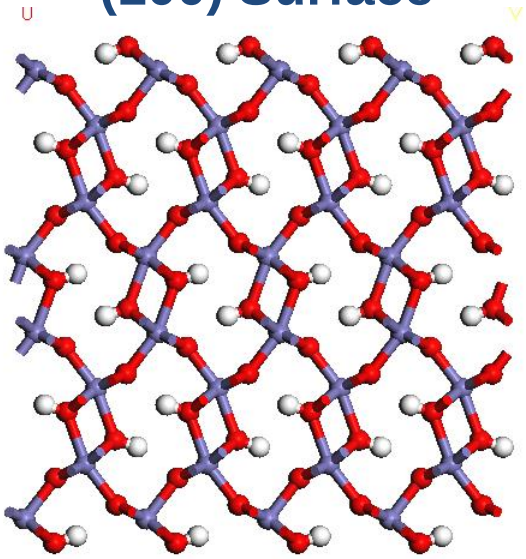
Goethite Unit Cell





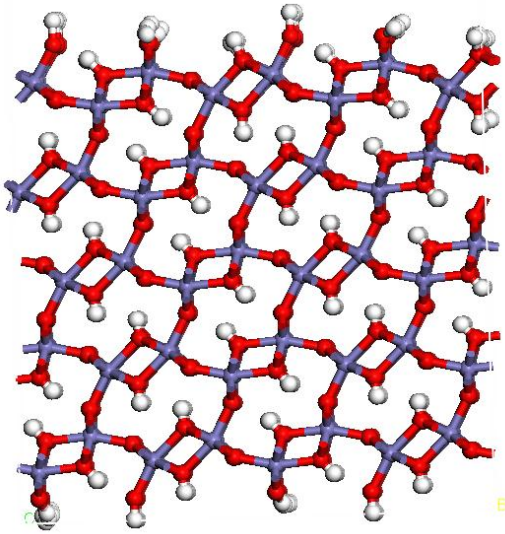
From Villalobos et al. (2009)

(100) Surface



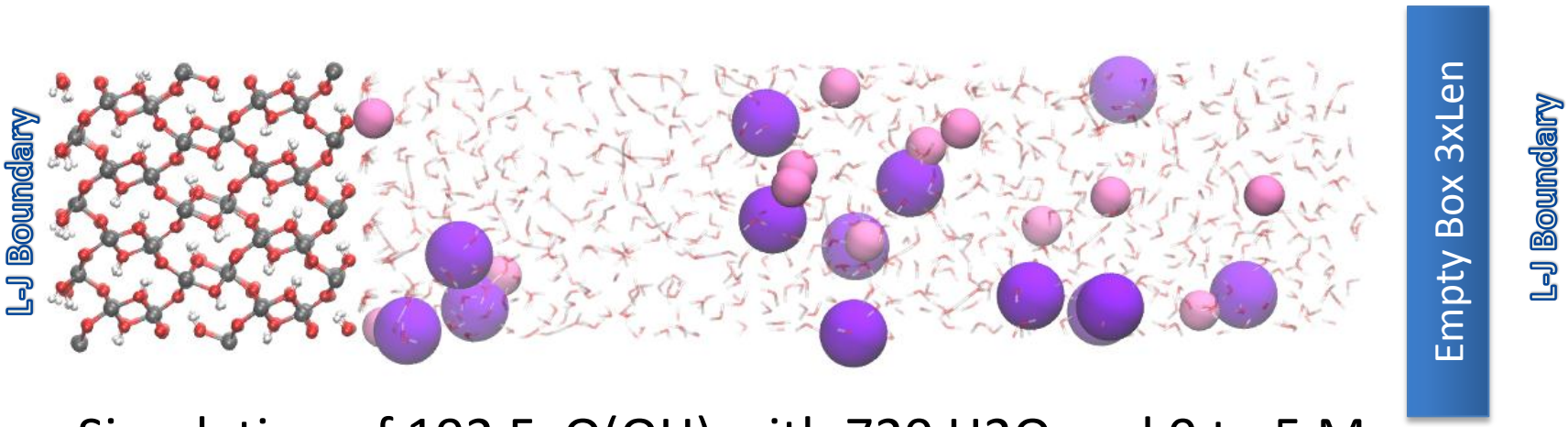
5-fold Fe
Fe_2O_IH
Fe_3O_{II}

(101) Surface



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

Computational Methods

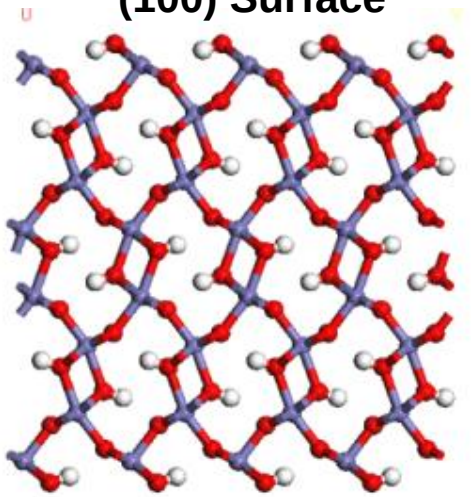


Simulation of 192 FeO(OH) with 720 H2O and 0 to 5 M NaCl

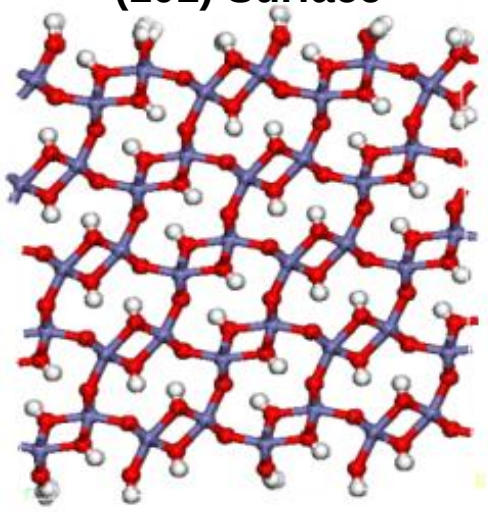
- Two faces: (100) and (101)
- Clayff used with LAMMPS MD code
  - NVE (50,000 fs)
  - NVT (200,000 fs)
  - NVT (10,000,000 fs)
- Snapshots every 2,000 fs
- Simulation Cell Size: 18.06 x 18.48 x 91.91 A

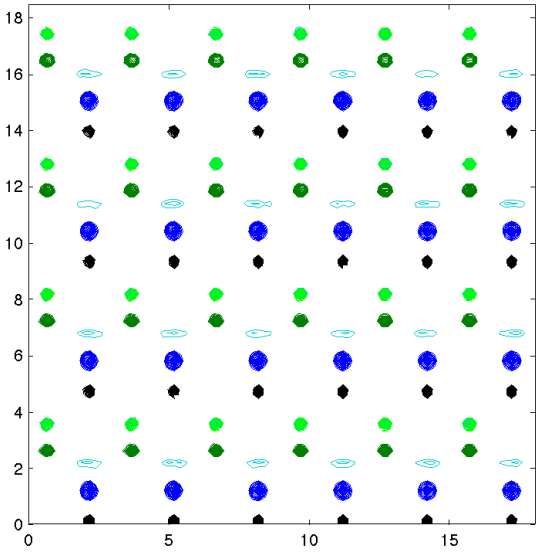
Classical Molecular Dynamics Simulations
Goethite (100) and (101) with H_2O

(100) Surface



(101) Surface



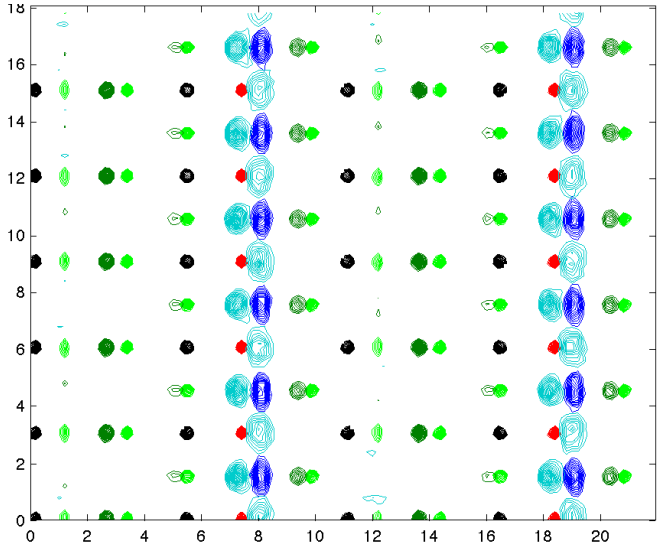


Fe

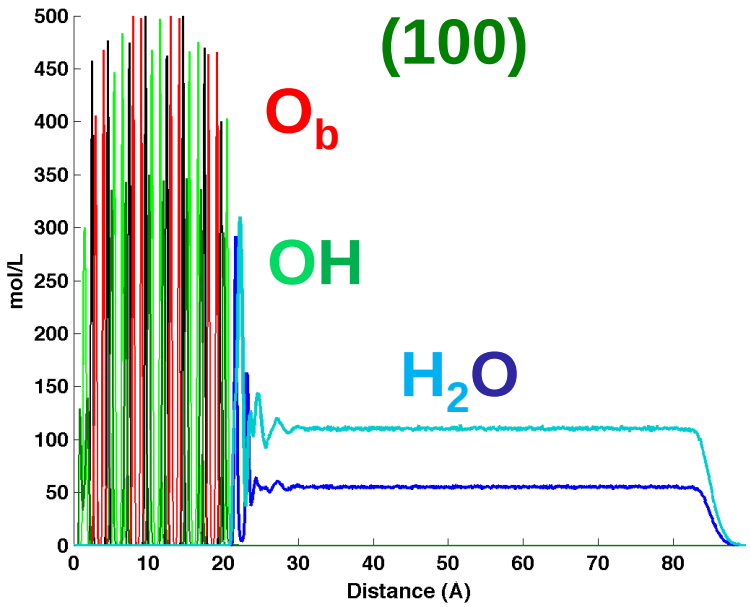
O_b

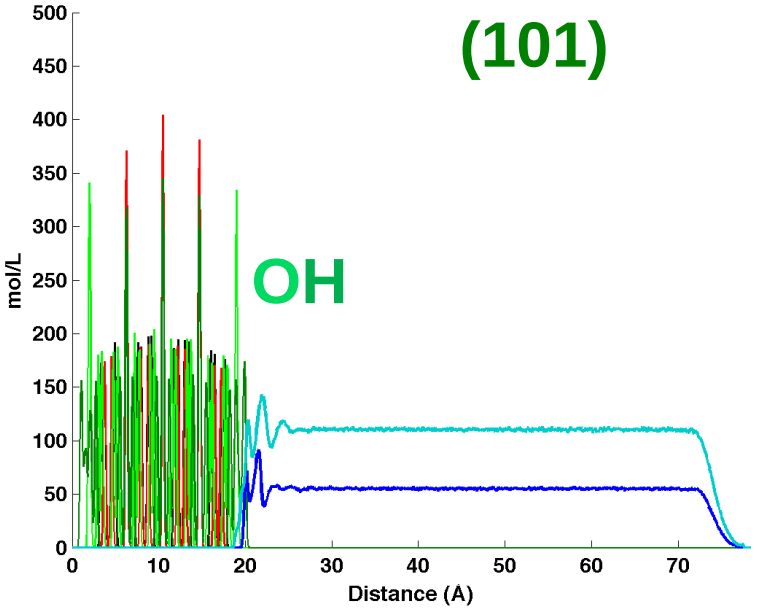
OH

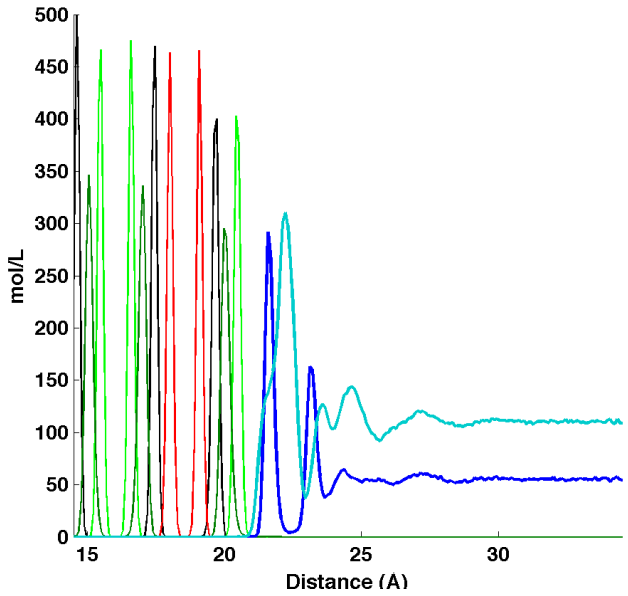
H_2O

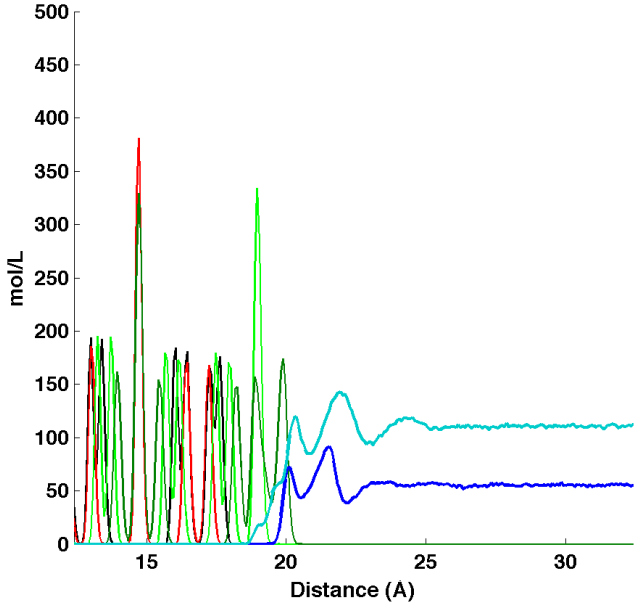


Goethite Surfaces with H_2O

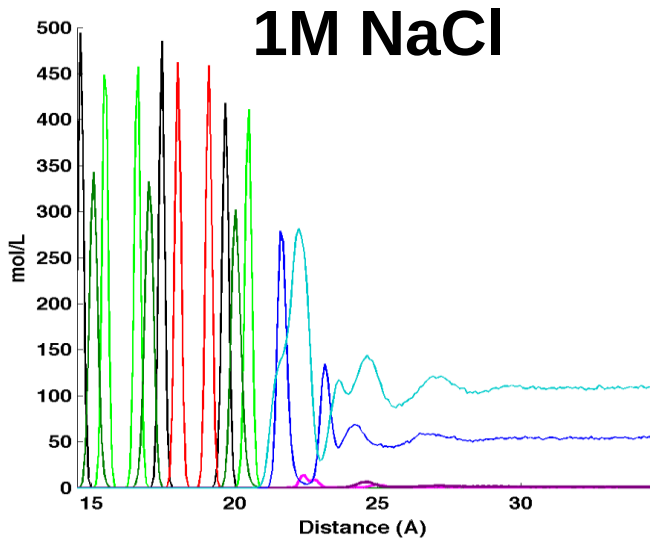


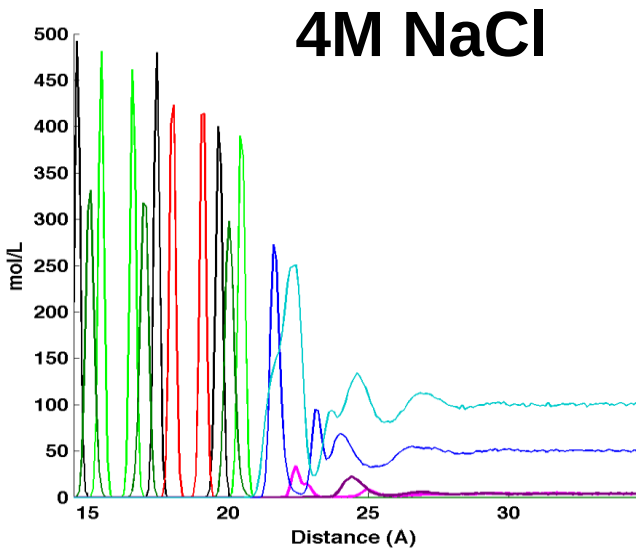


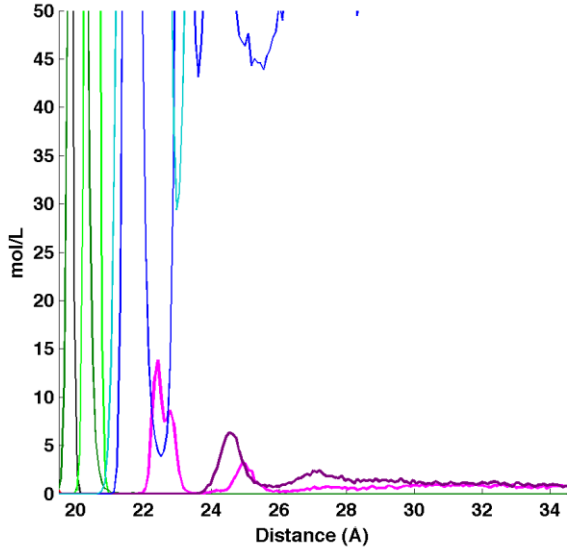


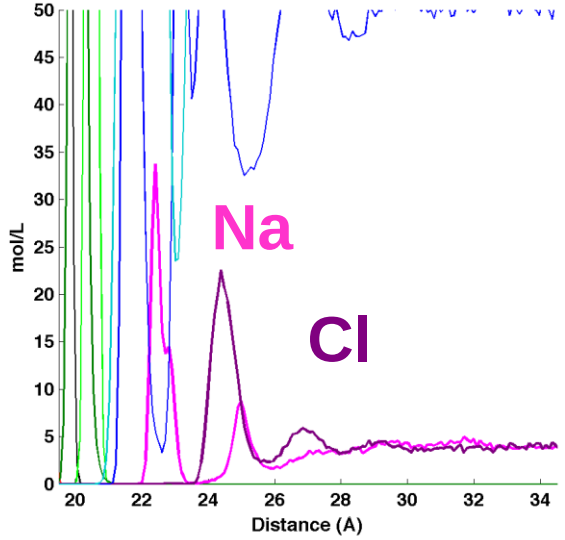


Goethite (100) with NaCl Solution





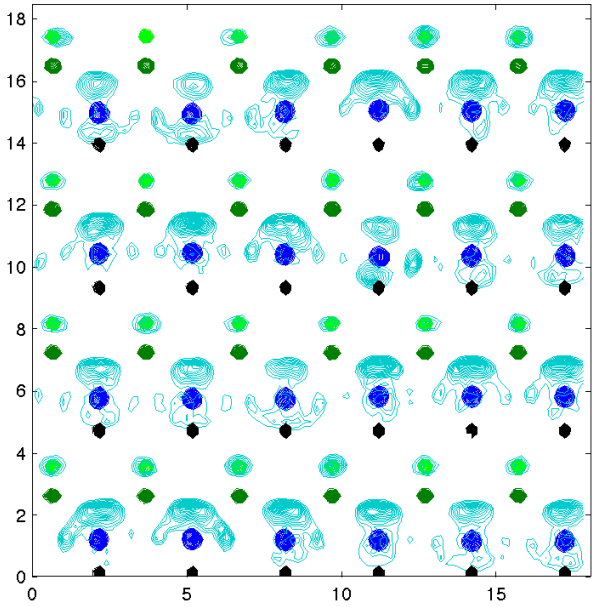


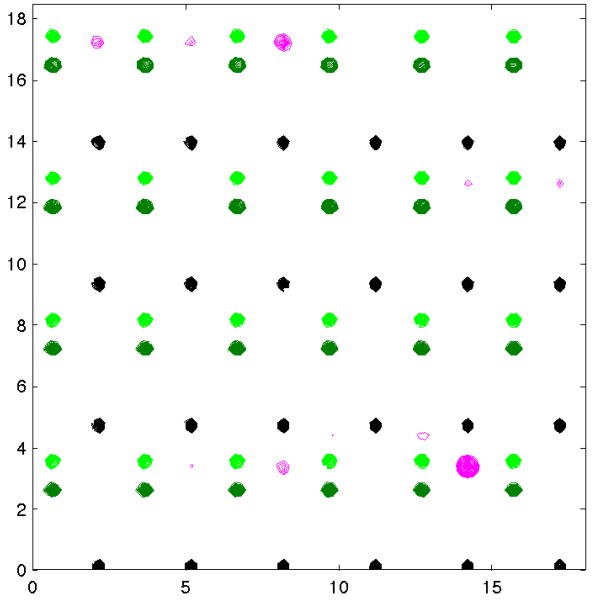


Goethite (100) with 1 M NaCl Solution

Layer 1

H_2O

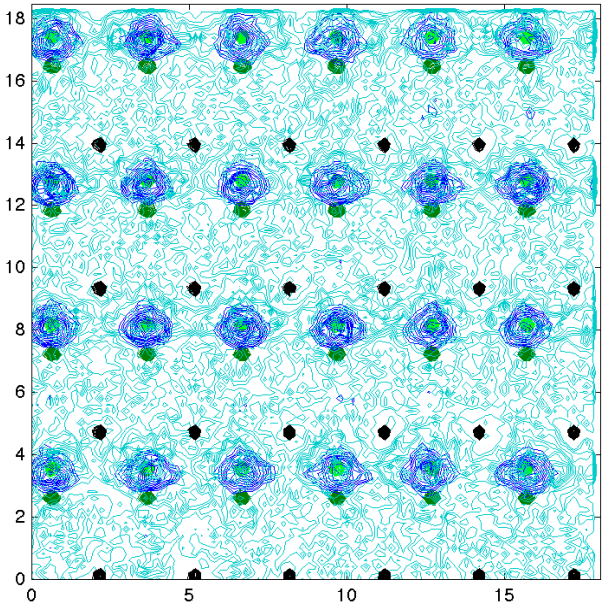


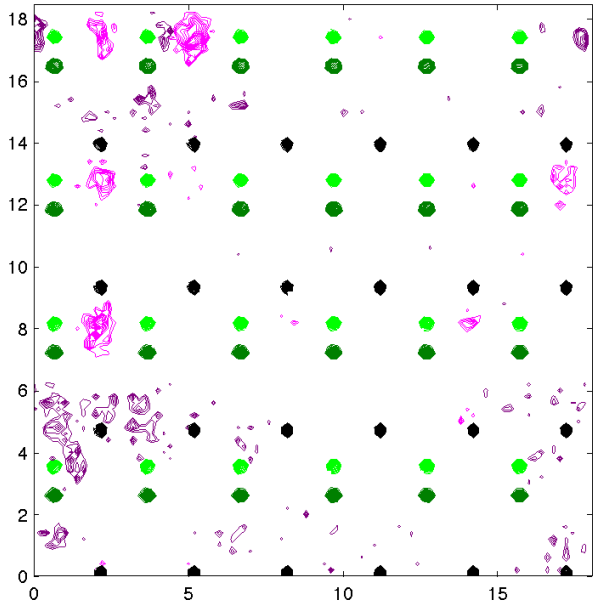


Fe

Na

Layer 2





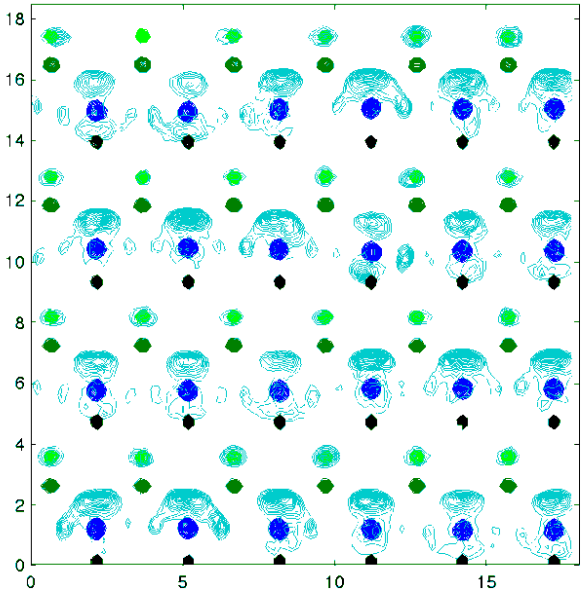
OH

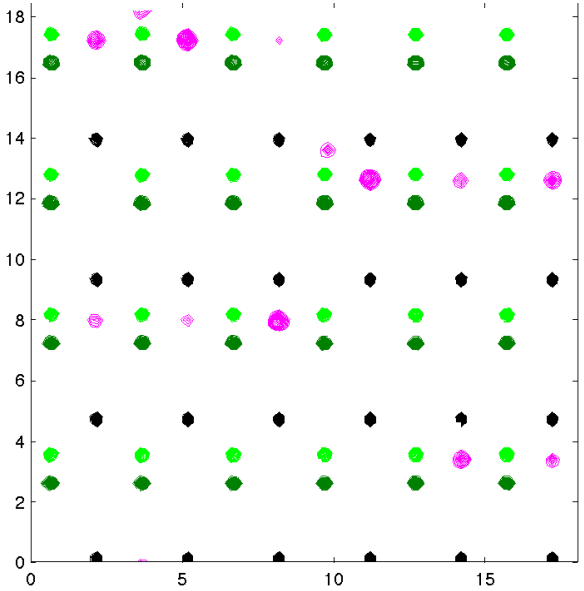
Cl

Goethite (100) with 4 M NaCl Solution

Layer 1

H_2O

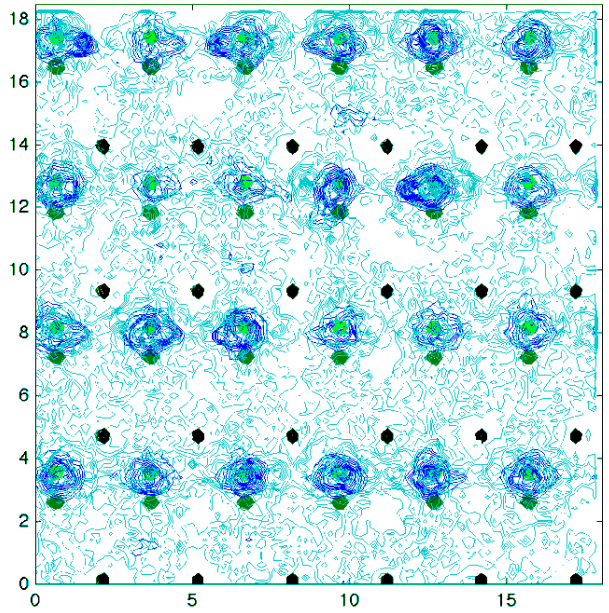


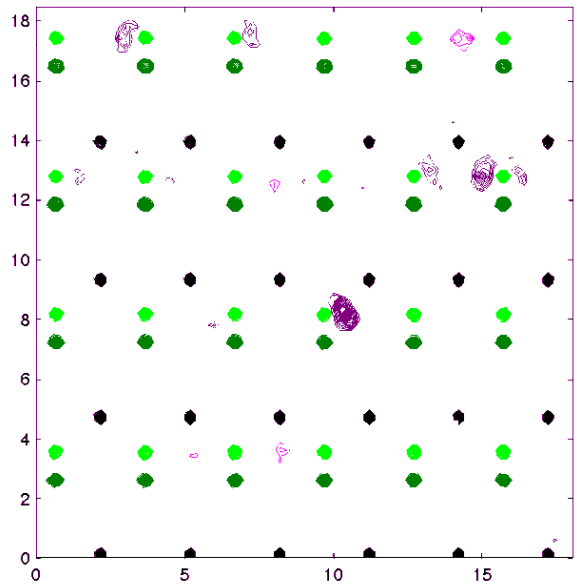


Fe

Na

Layer 2

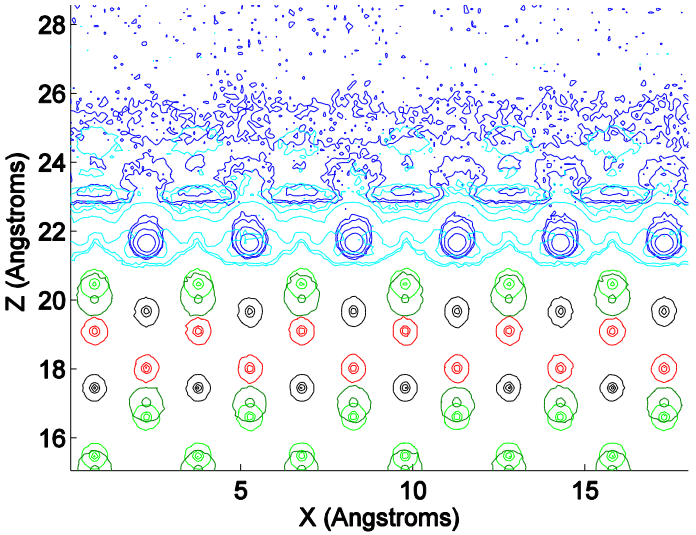


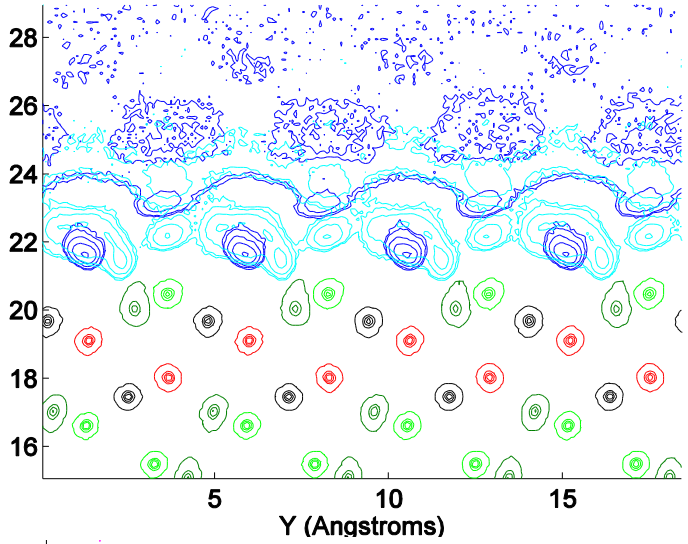


Cl

OH

Goethite (100) with 5 M NaCl

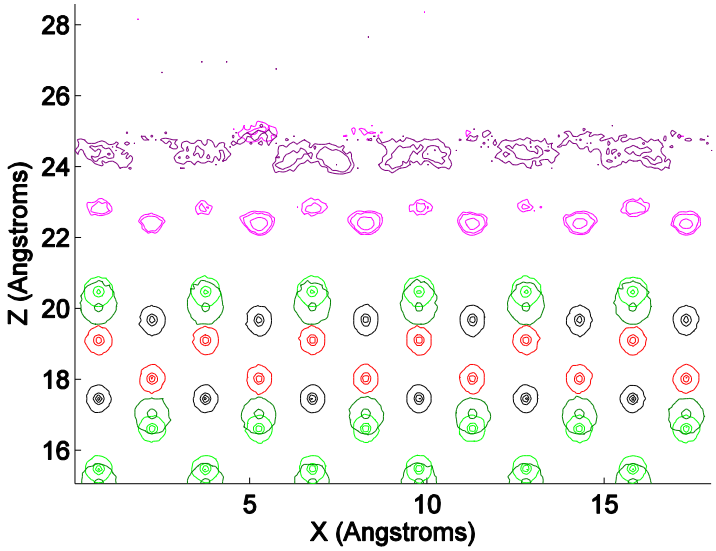


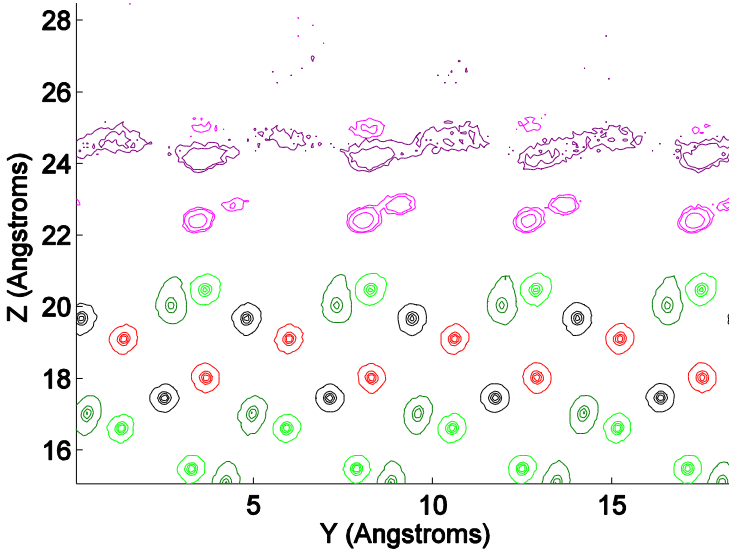


H_2O

OH

O_b



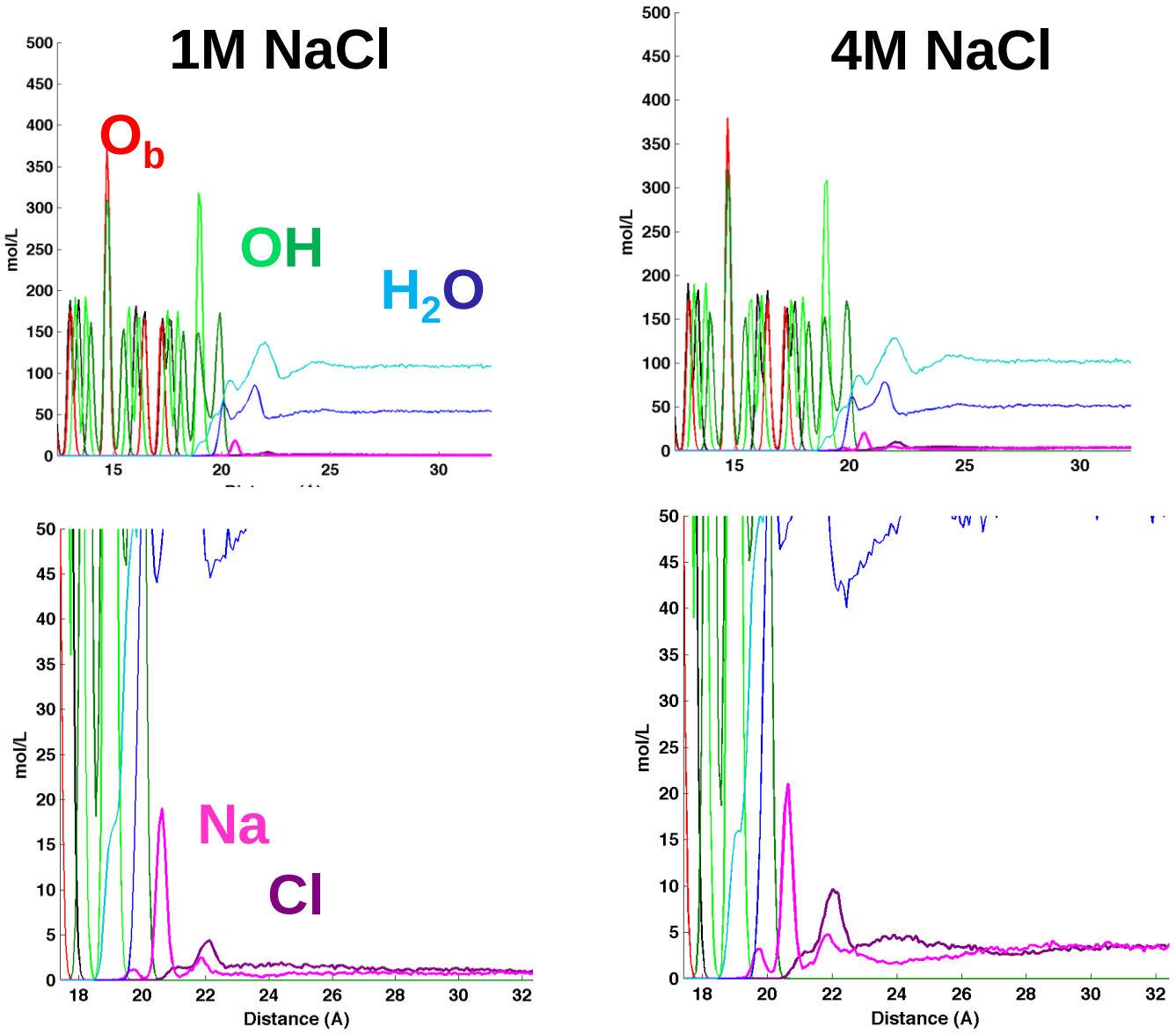


Cl

Na

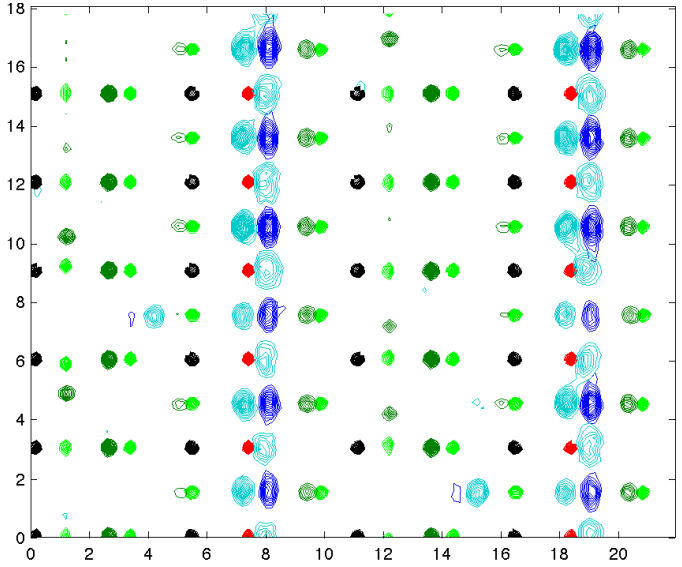
Fe

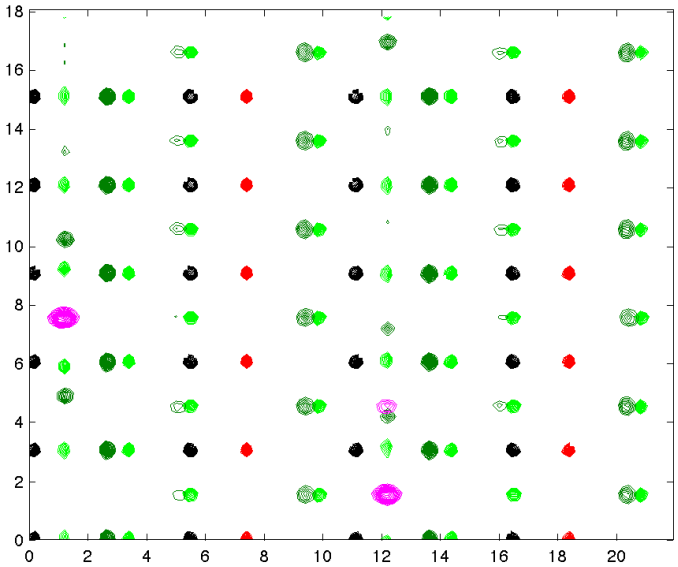
Goethite (101) with NaCl Solution



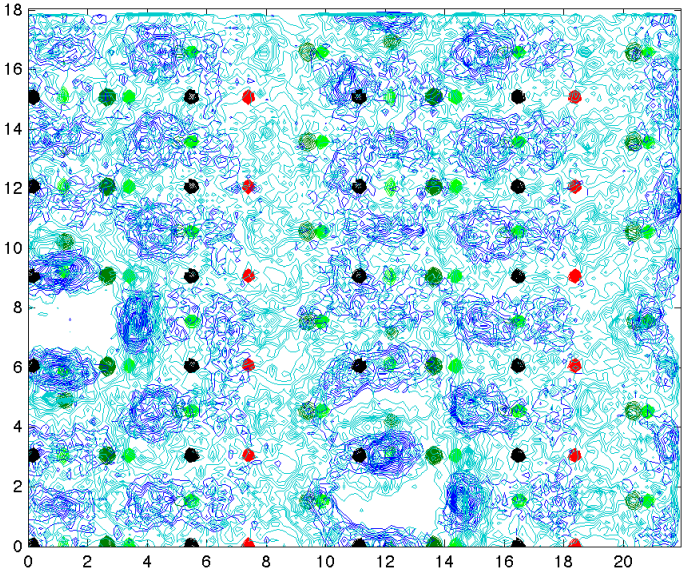
Goethite (101) with 4 M NaCl Solution

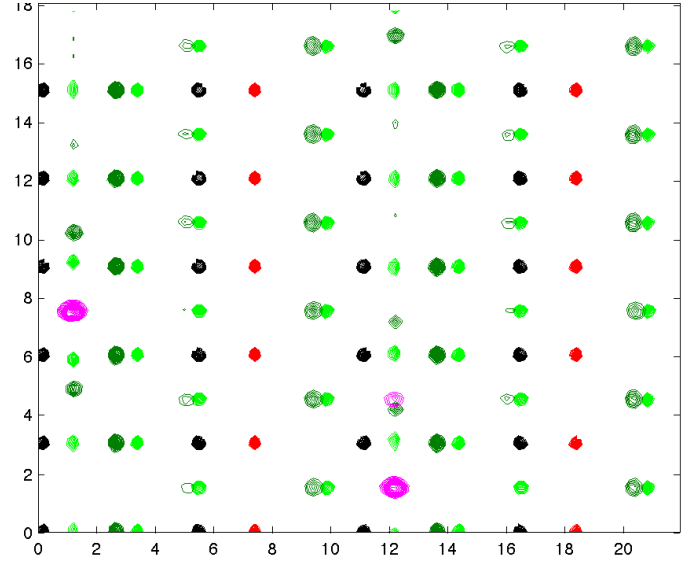
Layer 1A



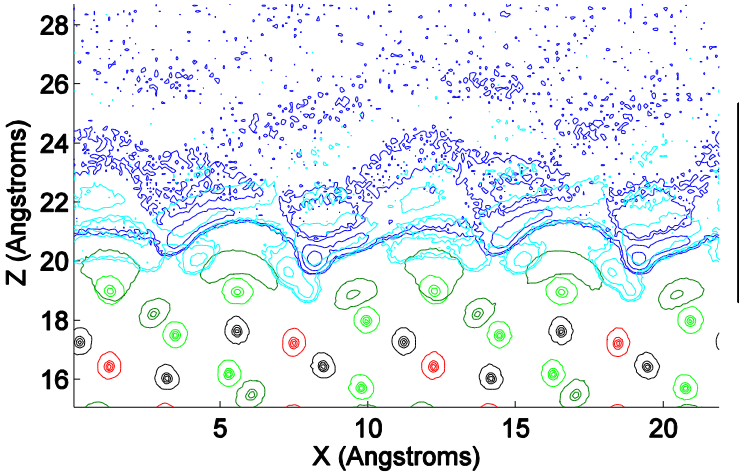


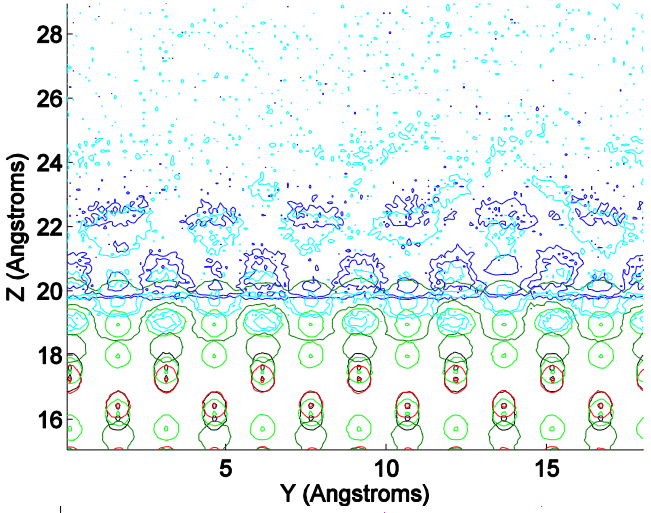
Layer 1B





Goethite (101) with 5M NaCl Solution

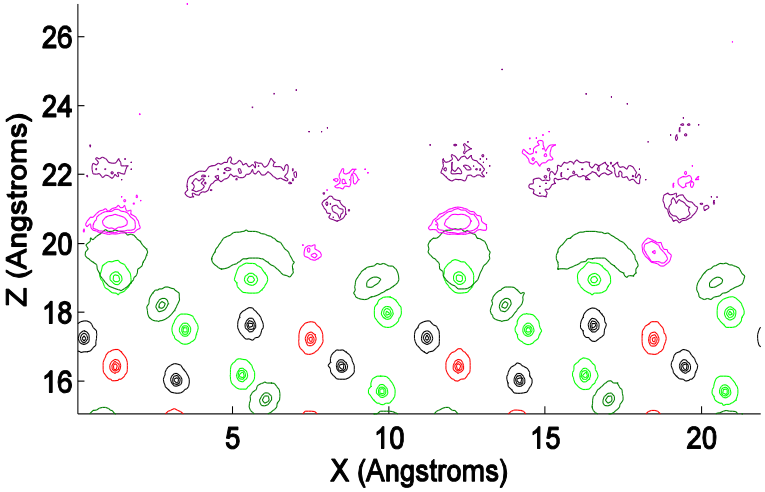


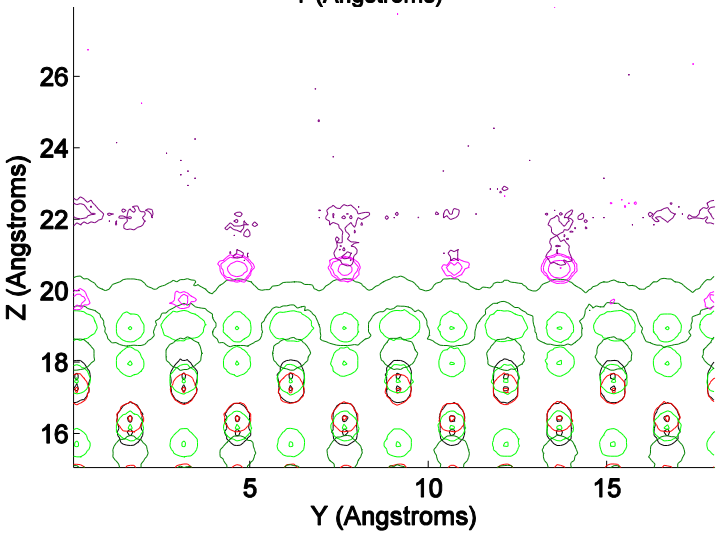


H_2O

OH

O_b





Cl

Na

Fe

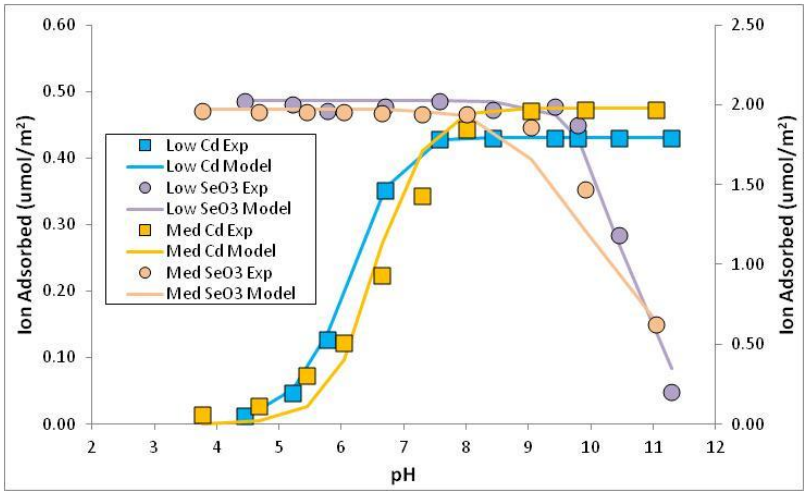
Summary

- H_2O is more structured on (100) surface than on (101) surface of goethite.
- Na^+ adsorbs both Inner-Sphere and Outer-Sphere.
- Cl^- adsorbs as an OS complex.
- NaCl pairing w/ Na^+ as IS evident on (100) at high NaCl concentrations
- Na^+ and Cl^- adsorption does not impact water structure on (100), but Na^+ does impact H_2O structure on (101)

Multi-contaminant Adsorption on Goethite

From Na^+ and Cl^- Adsorption to →

Cd^{+2} and SeO_3^{-2} Bi-solute Competition ***with*** Ternary Complexes

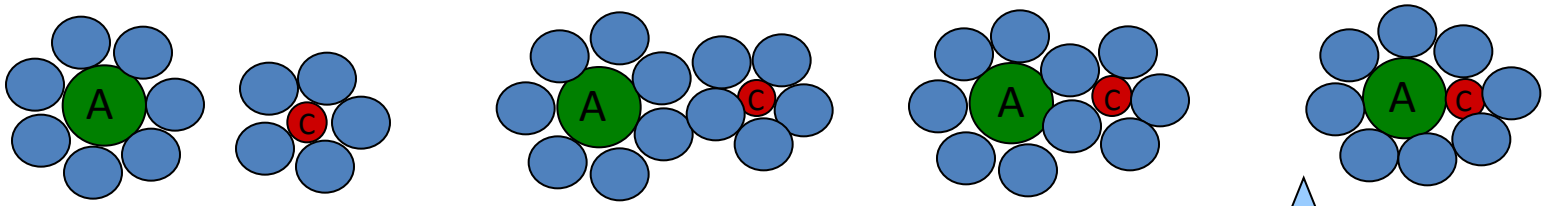


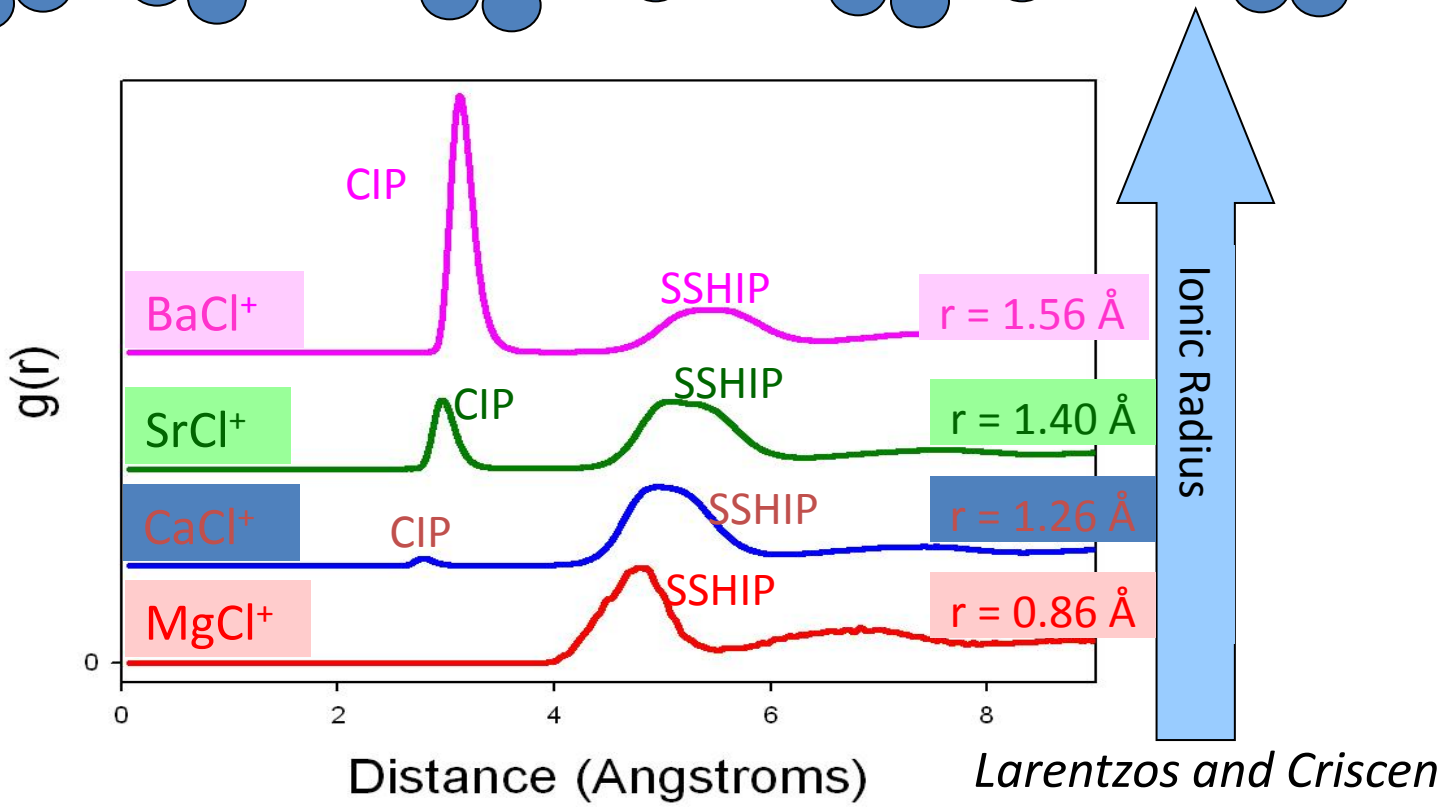
1. Divalent Metal Cations
    1. Alkaline Earth Metals
    2. Heavy Metals
2. Oxyanions
3. Divalent Metal Cations + Anions

Alkaline Earth M^{2+}-Cl^- Radial Distribution Functions:

$$A + C \Leftrightarrow A \| C \Leftrightarrow A | C \Leftrightarrow AC$$

free ions SSIP SSHIP CIP





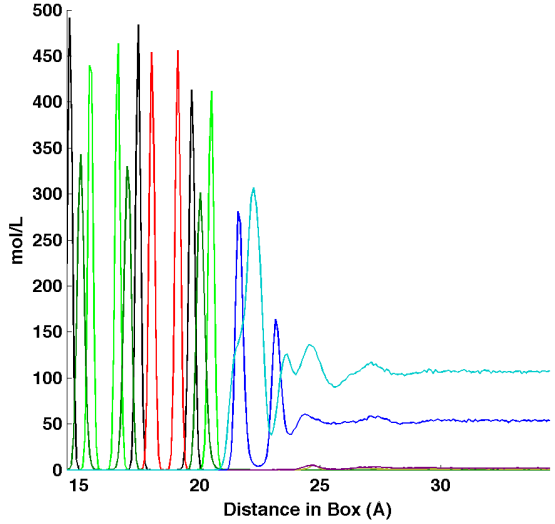
Larentzos and Criscenti, 2008

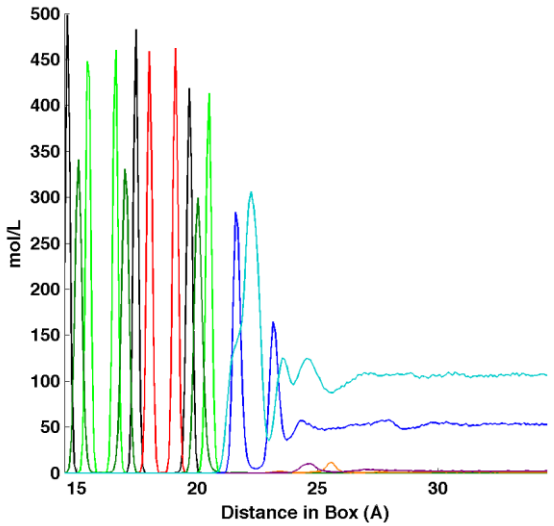
Heavy Metal Force Field Development

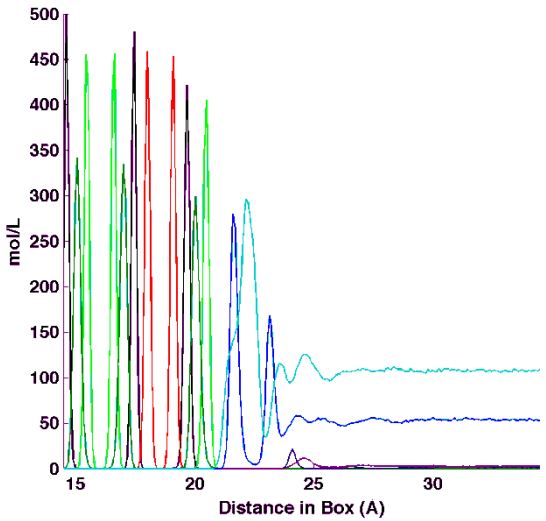
Matthews and Naidoo (JPC, 114, 2010)

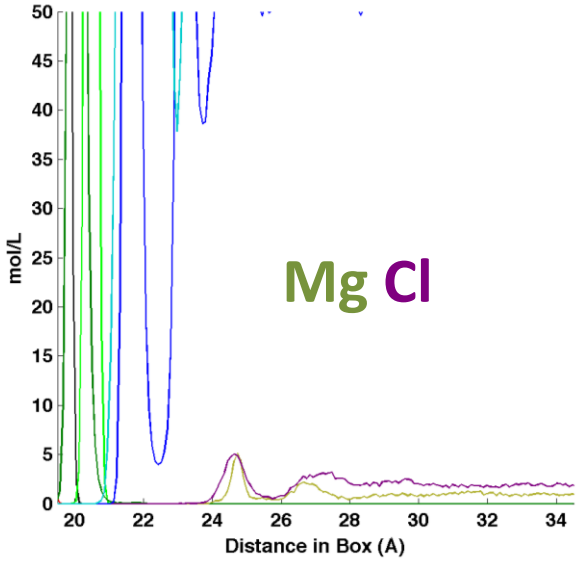
- **Developed method to produce force field for divalent metal ions in $M^{2+}SO_4^{2-}$ solutions**
  - Cannon et al. (1994) for SO_4^{2-} , TIP3P for H_2O
  - Metal-water interaction energies fitted with MP2/6-311++G(3d,3p)
  - Lennard Jones parameters for Mg^{2+} were tuned so that calculated absolute free energy of hydration of Mg^{2+} matches experimental data.
  - L-J parameters for other divalent ions including Co^{2+}, derived from a series of FEP calculations in which ions were perturbed from Mg^{2+}
- **Calculated log Ks for CIP, SSHIP and SHIP for M^{2+}-SO_4^{2-} are in agreement with available ultrasonic and dielectric spectroscopic data.**

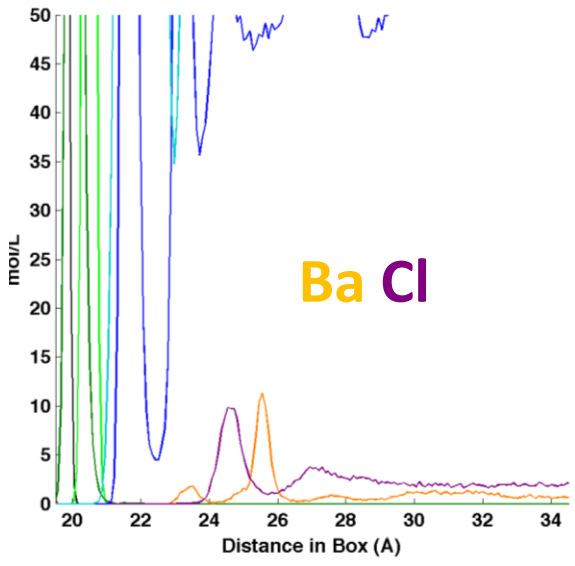
Goethite (100) 1 M $MgCl_2$, $BaCl_2$, $CoCl_2$

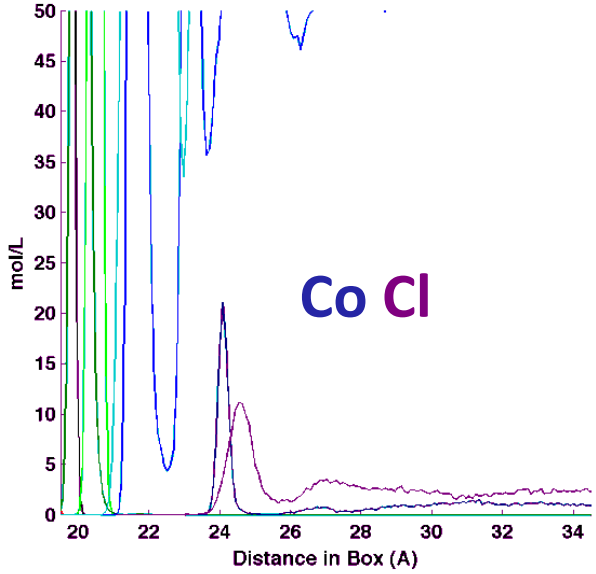








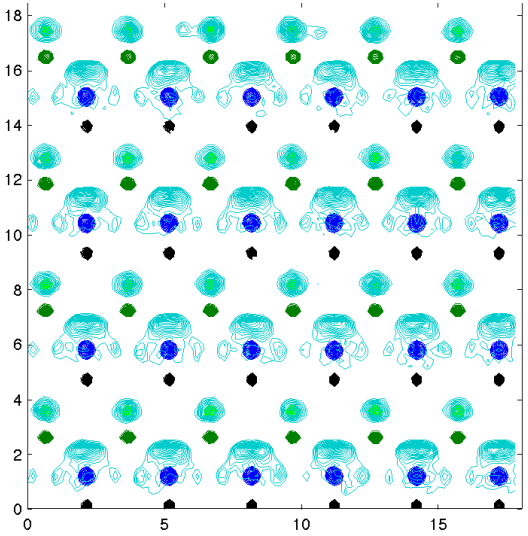


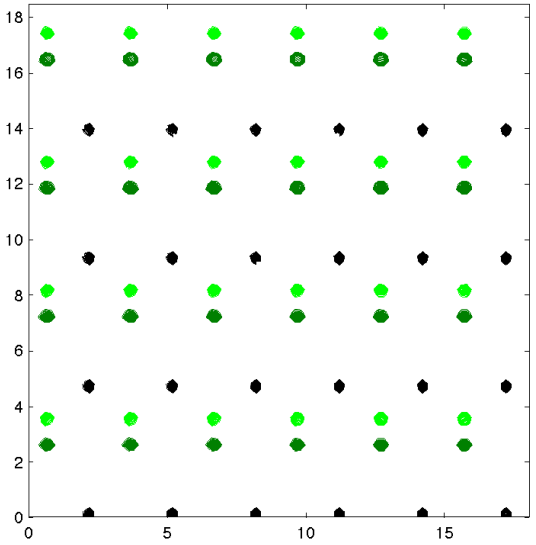


Consistent with Katz et al. (in press) for Gibbsite

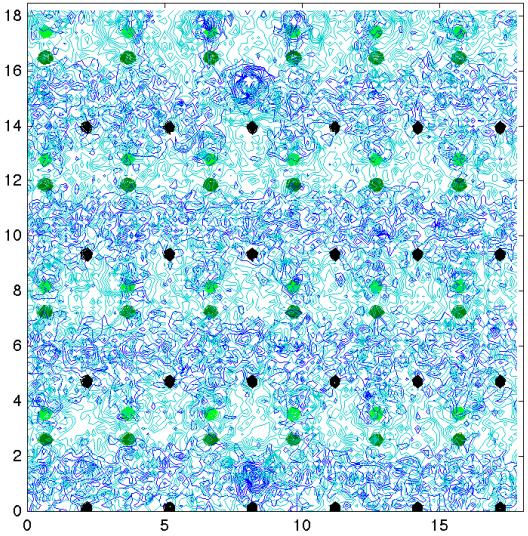
Goethite (100) 1 M $MgCl_2$

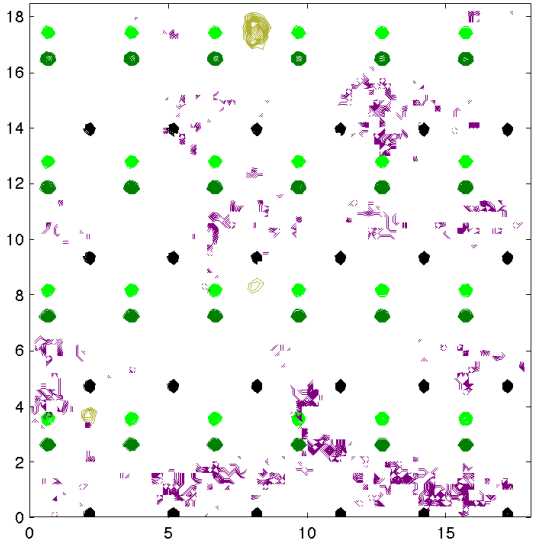
Layer 1





Layer 2



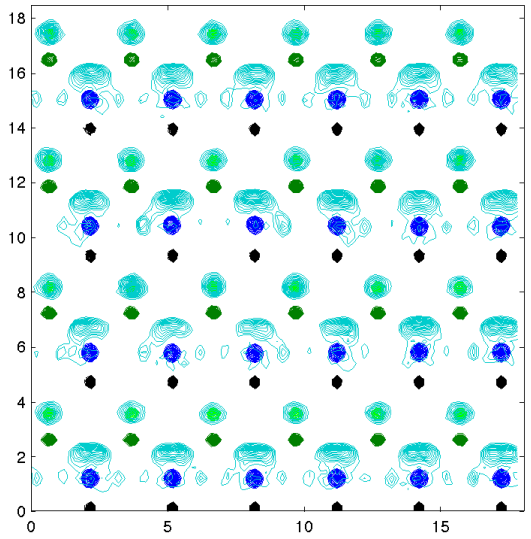


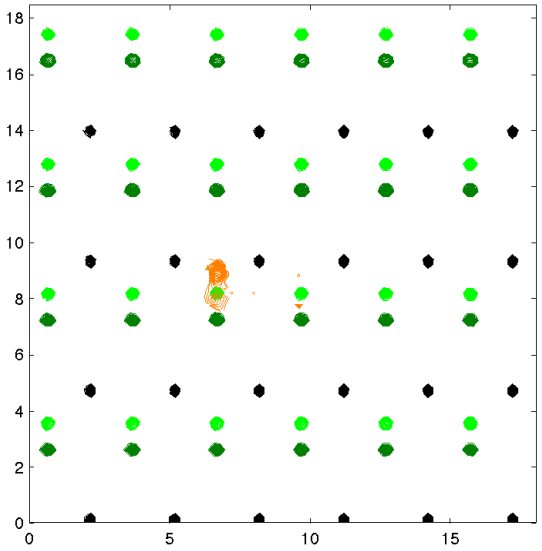
Mg Cl

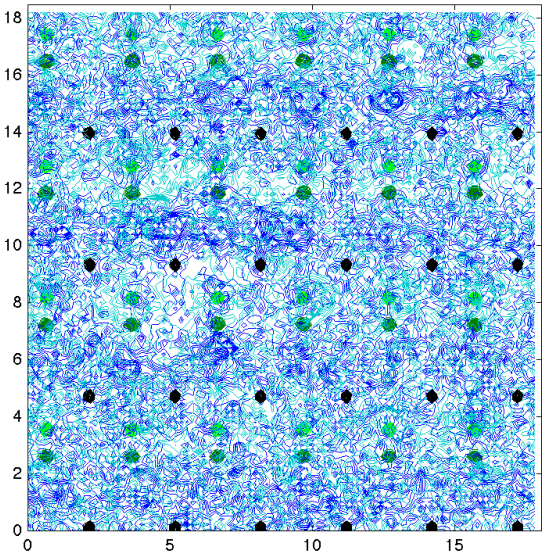
Goethite (100) 1 M $BaCl_2$

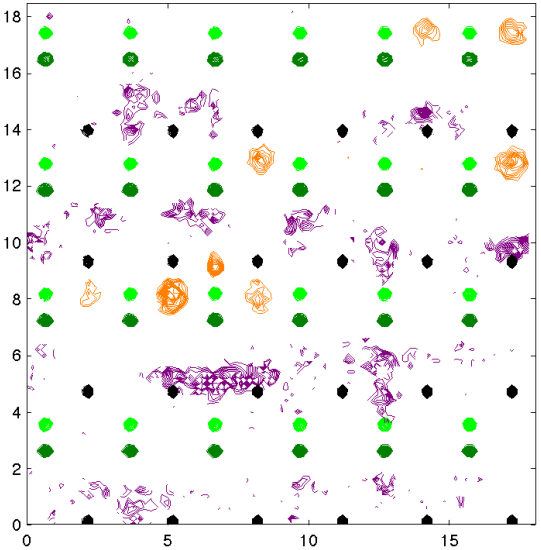
Layer 1

Layer 2





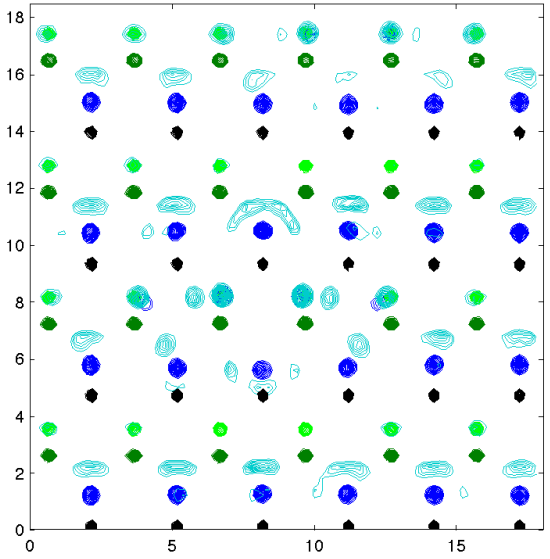


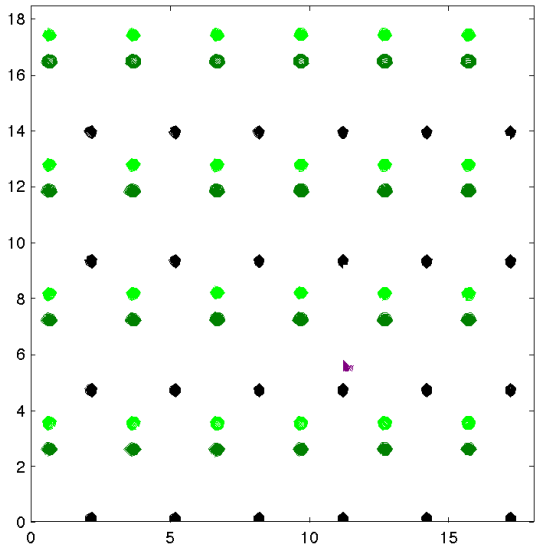


Ba Cl

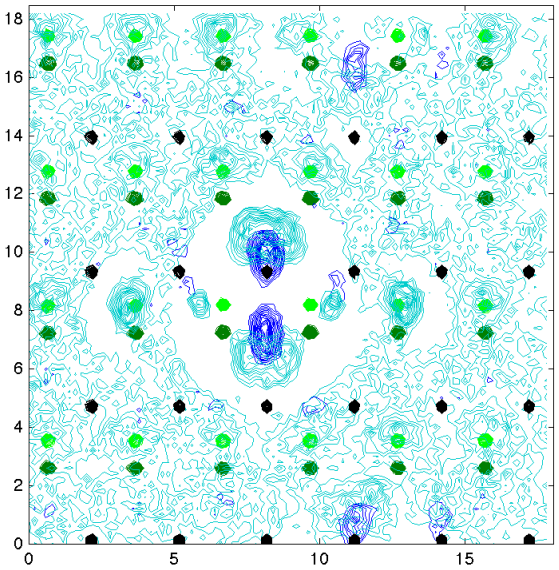
Goethite (100) 1 M $CoCl_2$

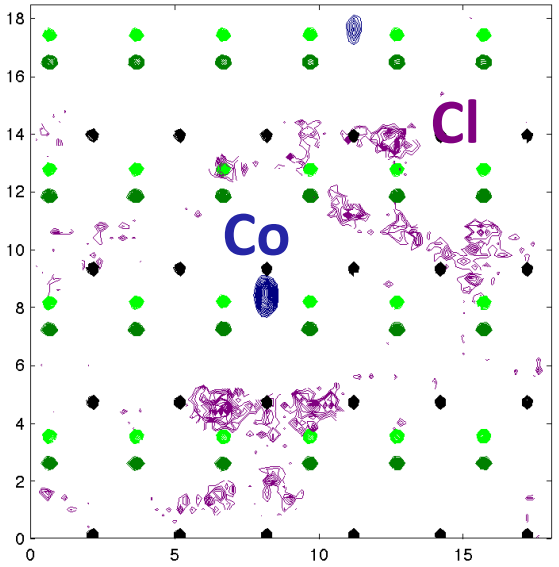
Layer 1





Layer 2

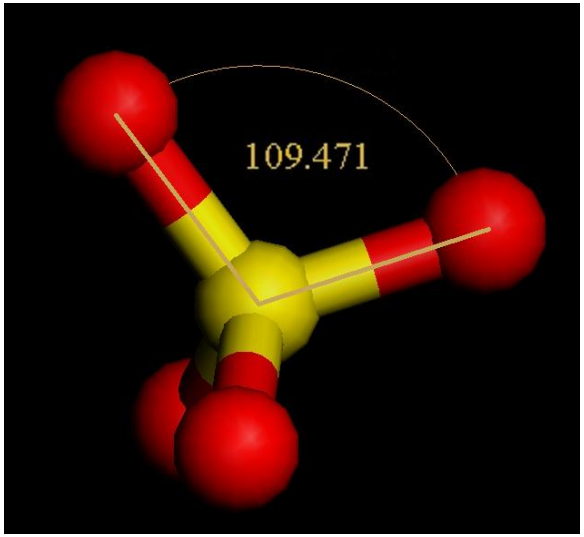


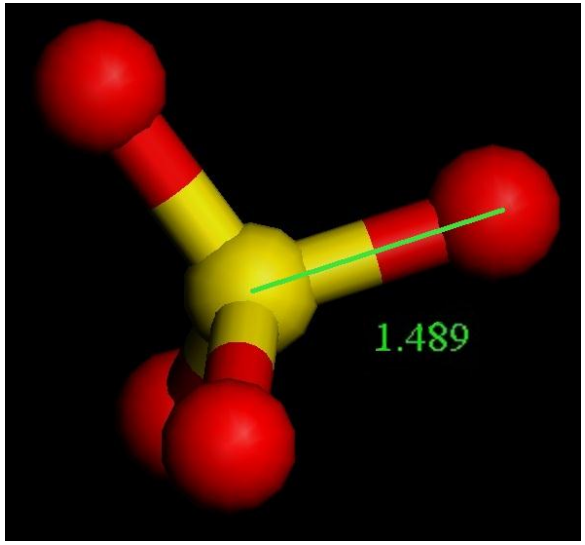


OS Co^{2+} does not agree with experimental data

Oxyanion Adsorption to Goethite

- Started with Sulfate
  - Force field models
    - Cannon et al. (1994), J. Phys. Chem., 98, 6225-6230 .





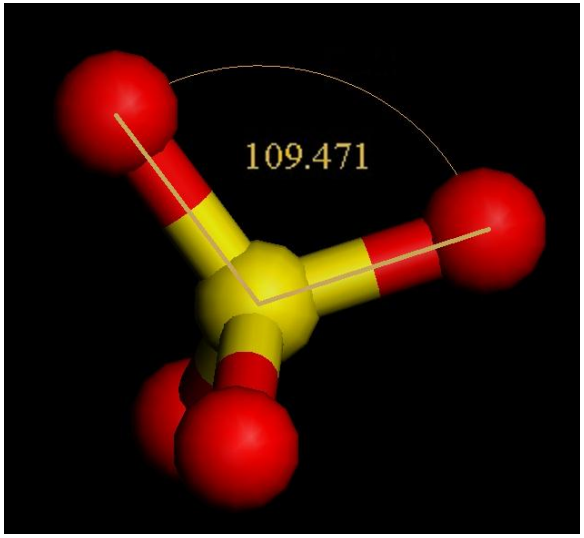
Rigid Anion
Rigid TIP3P H_2O

Kalinichev Force Field Model for Sulfate

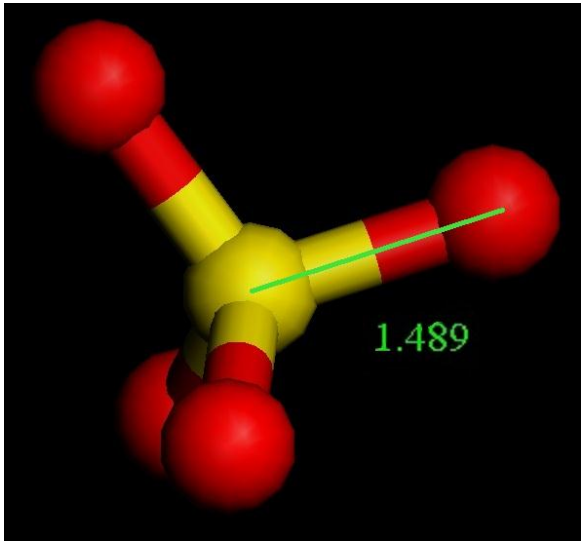
- **Added flexibility to Cannon et al.'s Rigid Model**

IR in aqueous solution	Kalinichev in gas phase
Bend = 451 cm^{-1}	Bend = 482 cm^{-1}
Stretch = 1104 cm^{-1}	Stretch = 1273 cm^{-1}

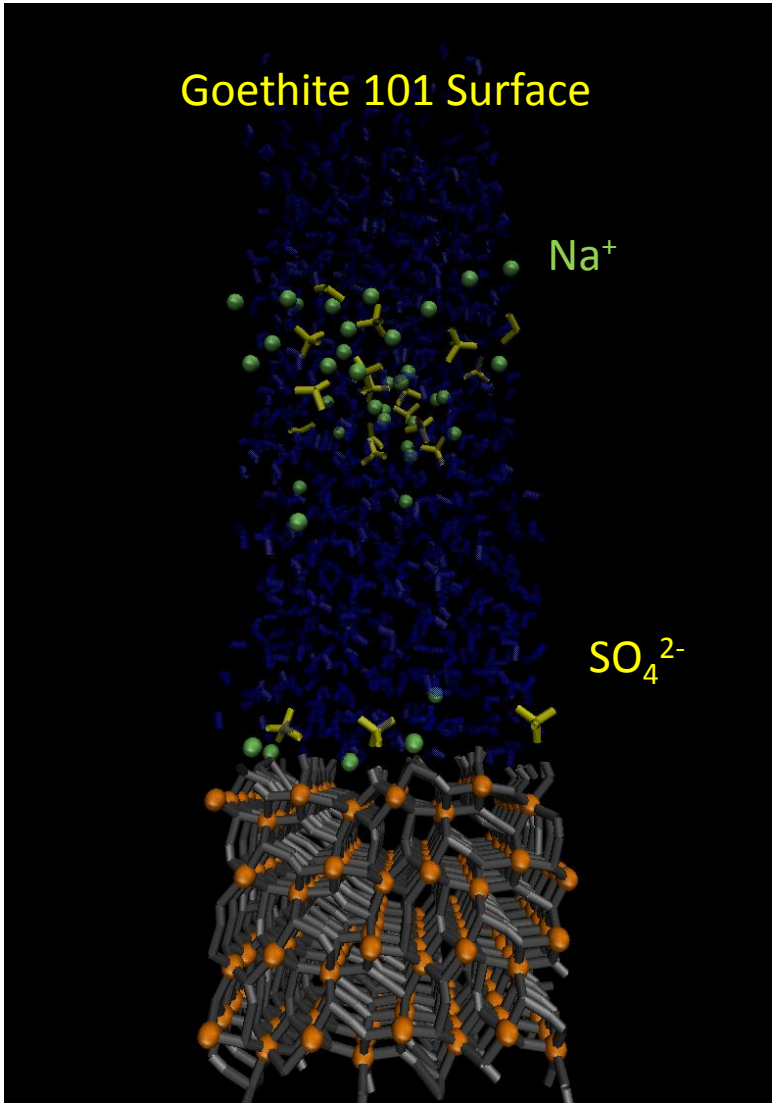
IR data: Kloprogge et al. (2002) American Mineralogist, 87, 623.



Cannon Rigid TIP3P Interaction Energy	Kalinichev Flexible SPC Interaction Energy
-225.26 kcal/mol	-248.55 kcal/mol

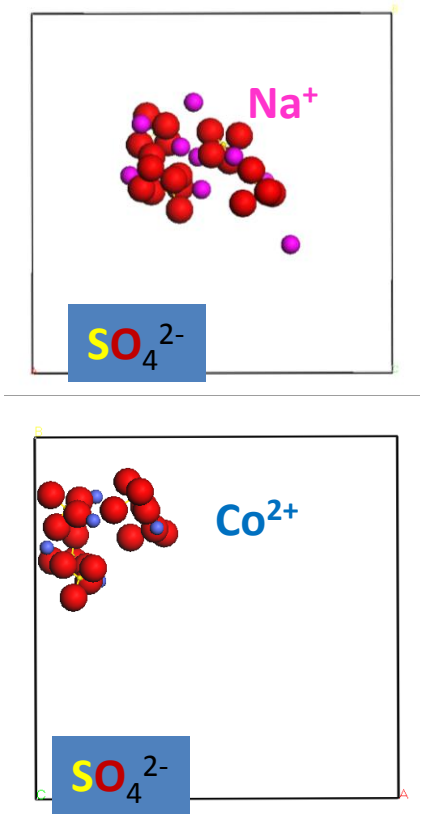


Modeling Na_2SO_4 Adsorption with Classical Force Field Models



- Na_2SO_4 Concentrations
  - 0.46 molal
  - 1.00 molal
  - 1.46 molal
  - **BELOW Na_2SO_4 Solubility**
- L-J potential at top
- 3 vacuum boxes above
- Simulation cell 18.06 A x 18.48 A x 66.77 A (for H_2O)
- 50 ps equilibration NVE
- 10 ns production NVT at 300K

Cation-SO_4 Pairing in Aqueous Solution



25A x 25 A x 25 A
< 0.5 m Na_2SO_4 or $CoSO_4$
5 SO_4 in each box

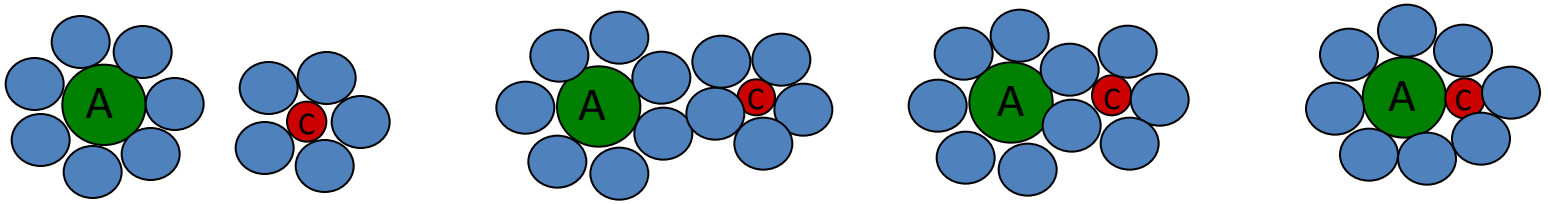
Water	Sulfate	Sodium	Persistant Clusters
SPC/E	1-6	1	yes
SPC/E	2	2	excessive pairing
TIP4P/ 2005	2	1	solvated ion clusters
SPC/E	2p	1p	yes
POL3	2(p)	1(p)	no
Dang-Chang	2	1	no

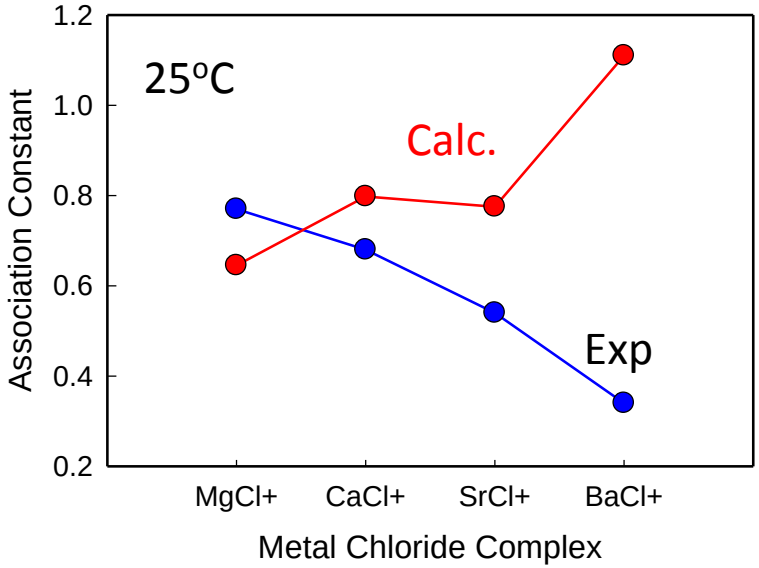
After Wernersson and Jungwirth (2010)
Different combinations of SO_4, Na, and H_2O models considered.
Polarizability of H_2O critical.
More SSHIP and SSIP than CIP

Need for Polarizable Water Model?

$$A + C \Leftrightarrow A \| C \Leftrightarrow A | C \Leftrightarrow AC$$

free ions | SSIP | SSHIP | CIP





*Majer and Stulik (1982)

$$A:C \equiv SSIP + SSHIP + CIP$$

$$K_a = \frac{a_{A:C}}{a_A a_C} = 4\pi \int_{R_L < r < R_U} g_{AC}^{\infty}(r) r^2 dr$$

$$W_{AC}(r) = -kT \ln g_{AC}^{\infty}(r)$$

Stability of complexes
$MgCl^+ > CaCl^+ > SrCl^+ > BaCl^+$

Larentzos and Criscenti (2008)

Summary and Conclusions

- H_2O is more structured on (100) surface than on (101) surface of goethite.
- NaCl pairing w/ Na^+ as IS evident on (100) at high NaCl concentrations
- Na^+ and Cl^- adsorption does not impact water structure on (100), but Na^+ does impact H_2O structure on (101). Therefore electrolyte anions will have a larger impact on the EDL on the (101) surface.
- Heavy metal force field of Matthew and Naidoo (for Co^{2+}) does not predict heavy metal adsorption properly.
- Both alkaline earth metal-chloride and cation-sulfate complexation in solution suggest that polarizable H_2O model is required to model ion-pairing in solution (and hence surfaces).

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