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Water and ion adsorption to goethite

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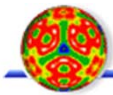


Office of Basic Energy Sciences

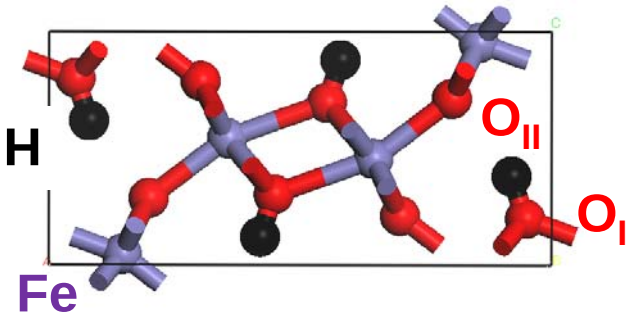
Objectives

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

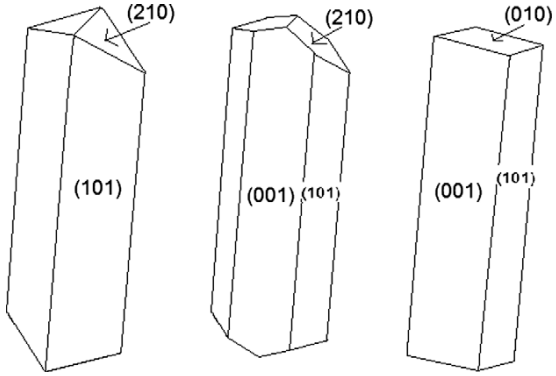
- To understand the properties of the electric double layer (EDL) at Fe-oxyhydroxide surfaces as a function of surface and solution properties

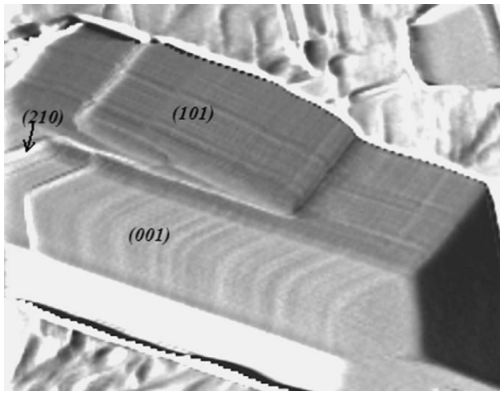
- Goethite (100) and (101) surfaces
  - Surface structure
  - Water structure
  - NaCl as a function of concentration
  - $MgCl_2$ and $BaCl_2$ (1 M concentrations).

Goethite: Predominant Surfaces and Surface Sites



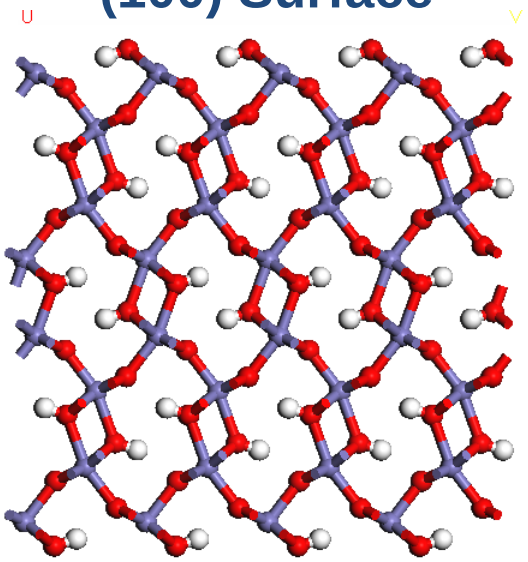
Goethite Unit Cell





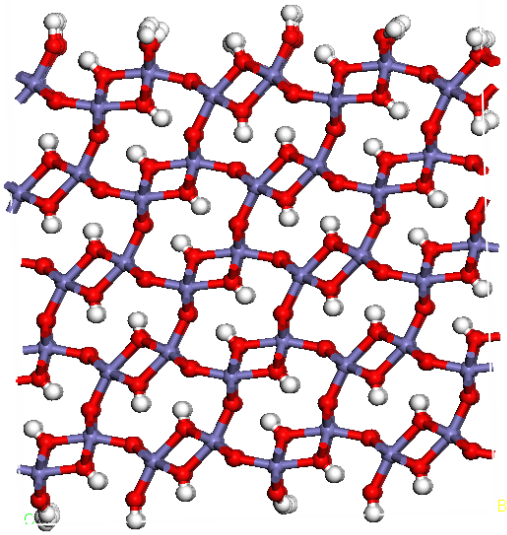
From Villalobos et al. (2009)

(100) Surface



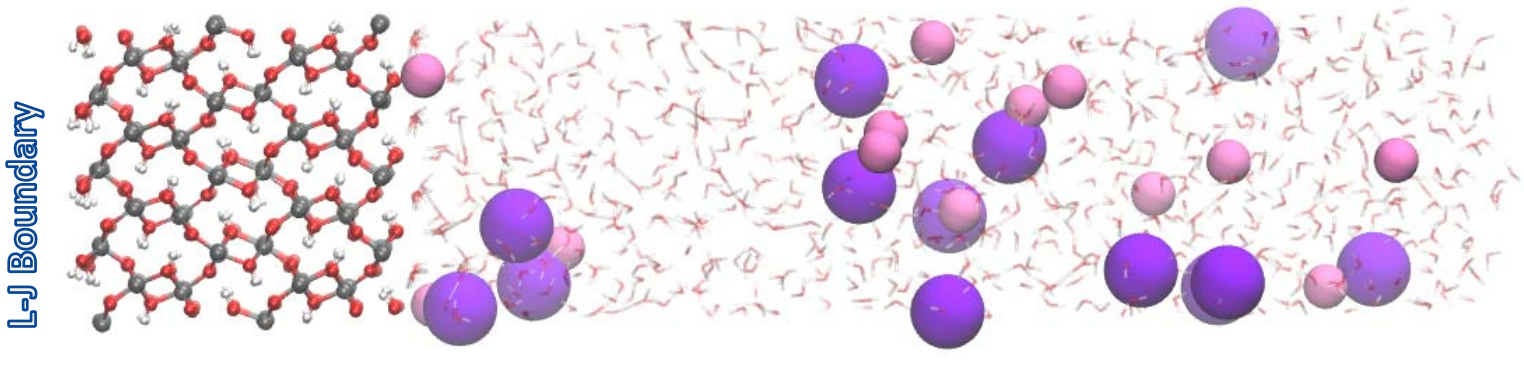
5-fold Fe
Fe_2O_IH
Fe_3O_{II}

(101) Surface



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

Computational Methods



Simulation Cell

192 FeO(OH) + 720 H_2O	768 FeO(OH)+2880 H_2O
NaCl: 0, 1, 4, 5 M	NaCl: 0, 0.1, 0.4, 1, 4 M
(100) Size: 18.1 Å x 18.5 Å x 92.0 Å	(100) Size: 36.1 Å x 37.0 Å x 100 Å
(101) Size: 21.9 Å x 18.1 Å x 92.0 Å	(101) Size: 43.9 Å x 36.1 Å x 90 Å

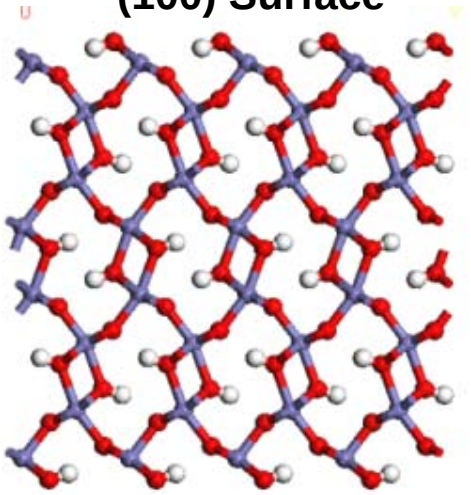
MD Simulation Method

Clayff Force Field (*Cygan et al.)*; LAMMPS MD code (*Plimpton et al*.)

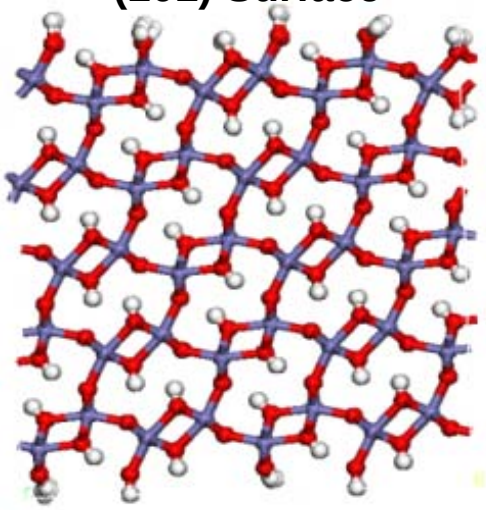
NVE equilibration	50 ps	50 ps
NVT equilibration	200 ps	1,950 ps
NVT production	10,000 ps	8,000 ps
Snapshots Stored	2,000 fs	2,000 fs

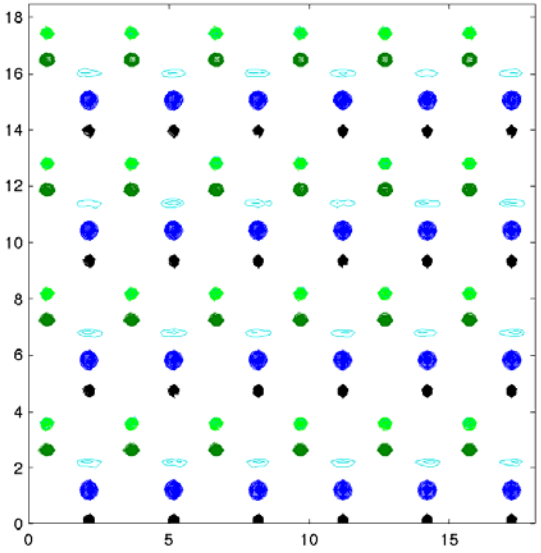
Classical Molecular Dynamics Simulations
Goethite (100) and (101) with H_2O

(100) Surface



(101) Surface



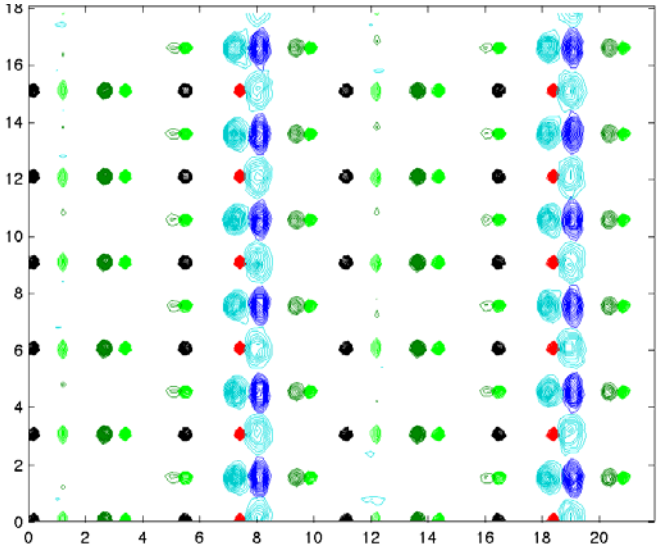


Fe

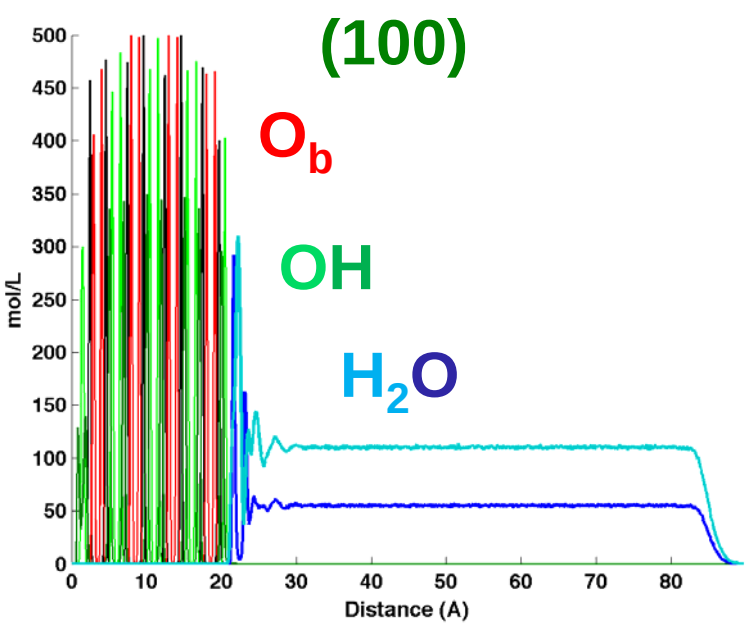
O_b

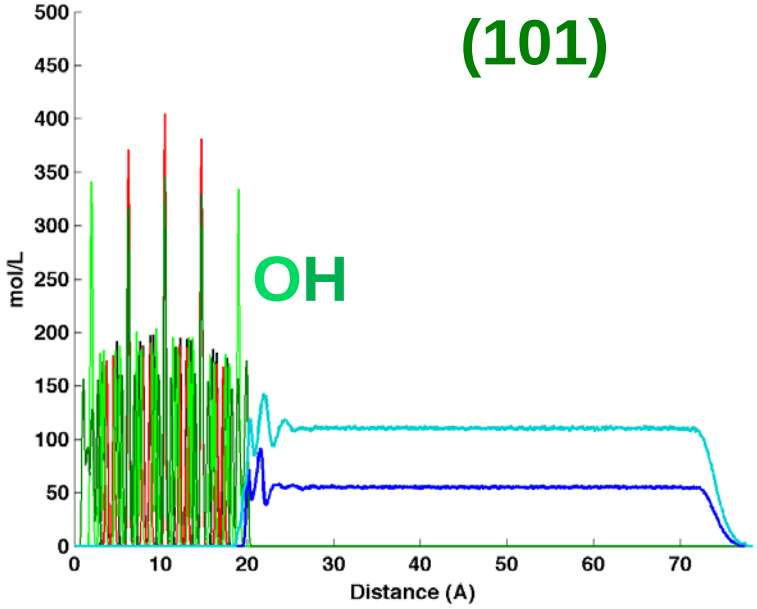
OH

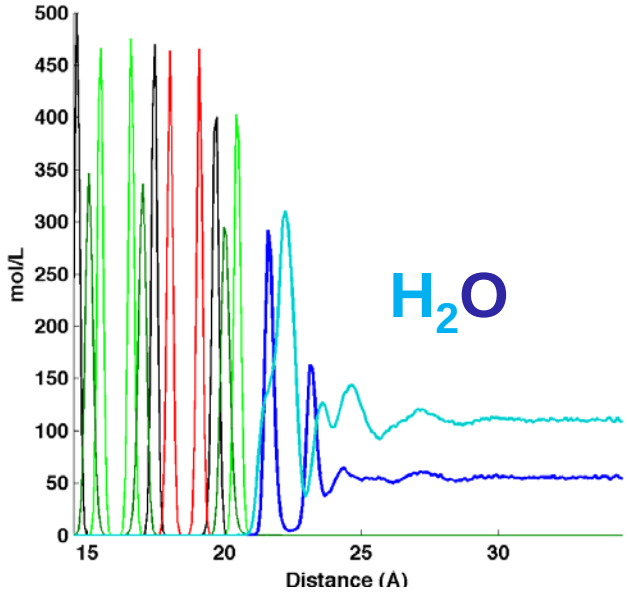
H_2O

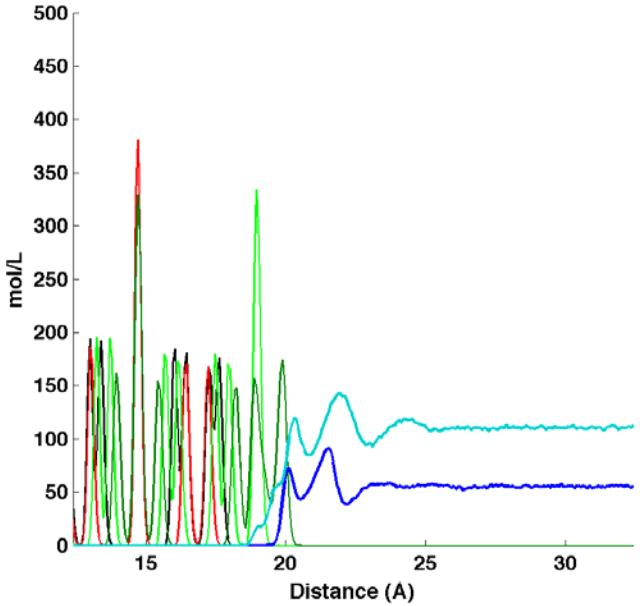


Goethite Surfaces with H_2O



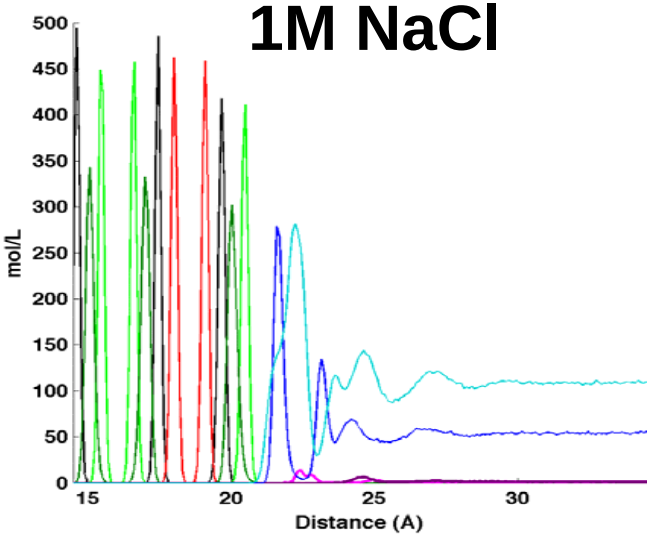


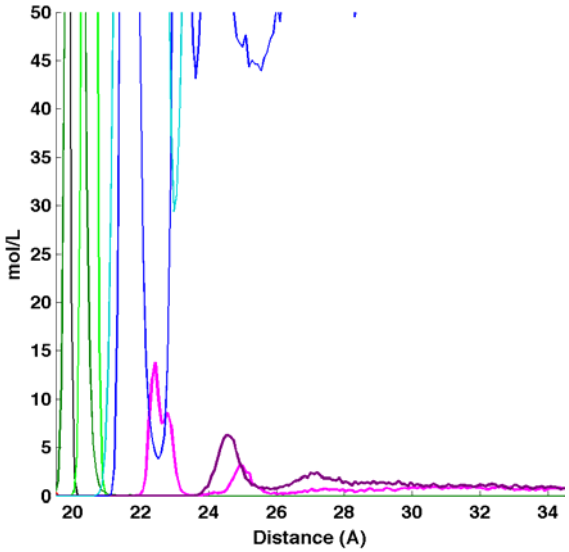




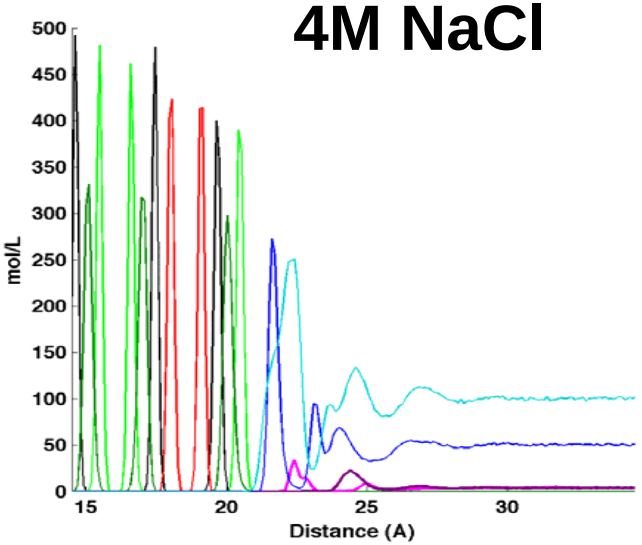
Goethite (100) with NaCl Solution

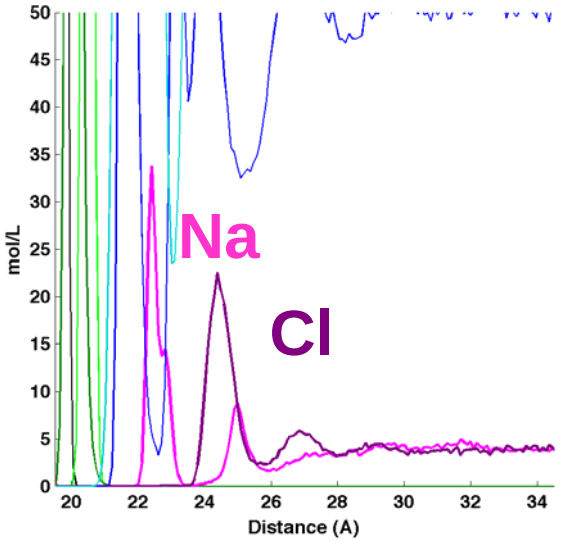
1M NaCl





4M NaCl

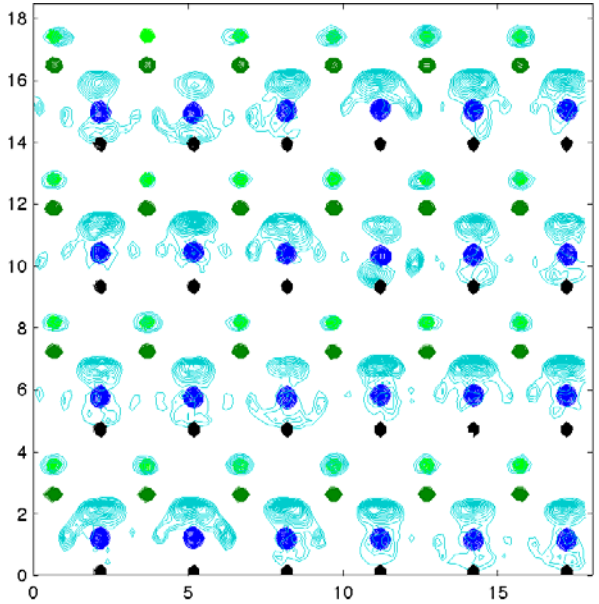


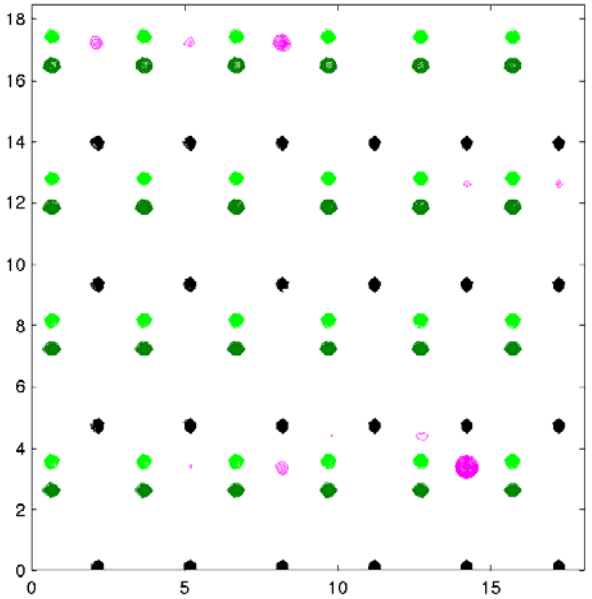


Goethite (100) with 1 M NaCl Solution

Layer 1

H_2O

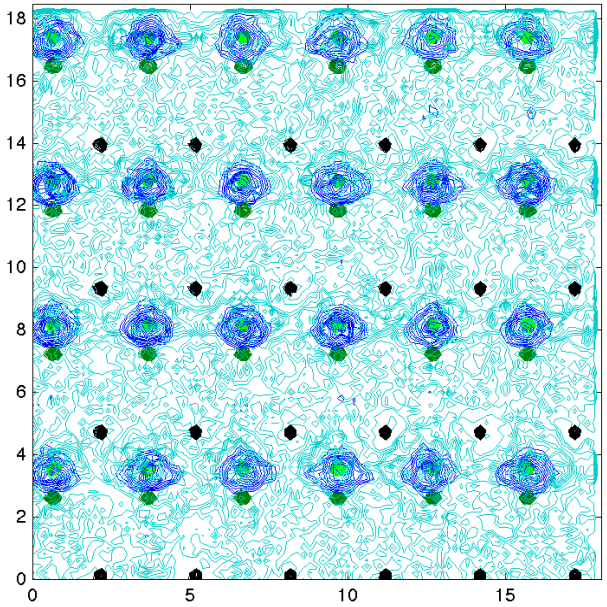


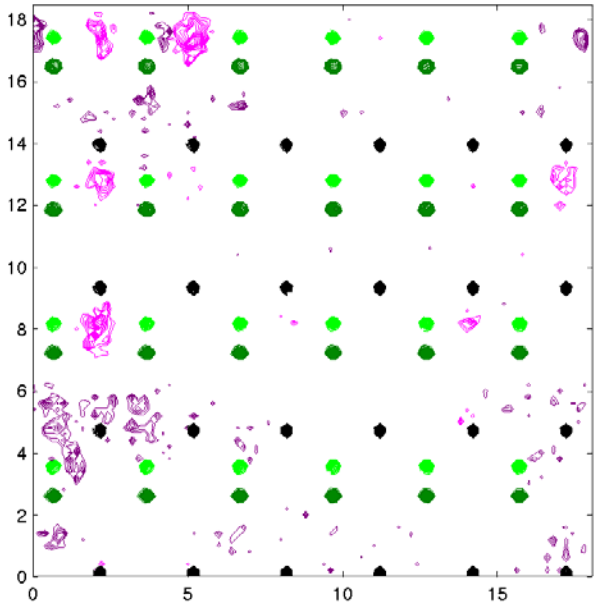


Fe

Na

Layer 2





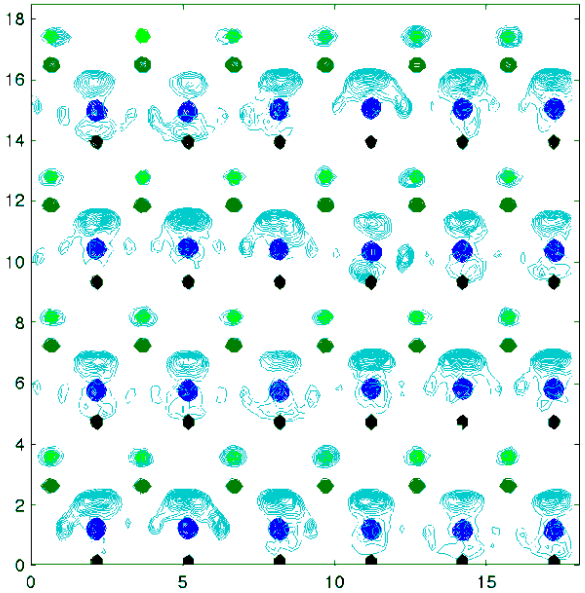
OH

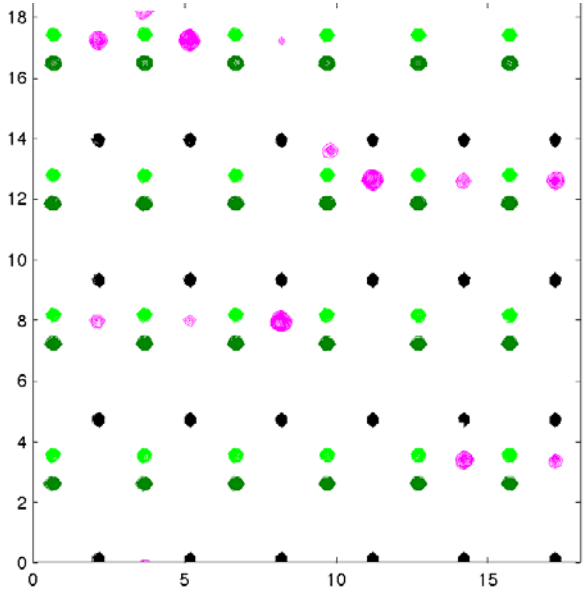
Cl

Goethite (100) with 4 M NaCl Solution

Layer 1

H_2O

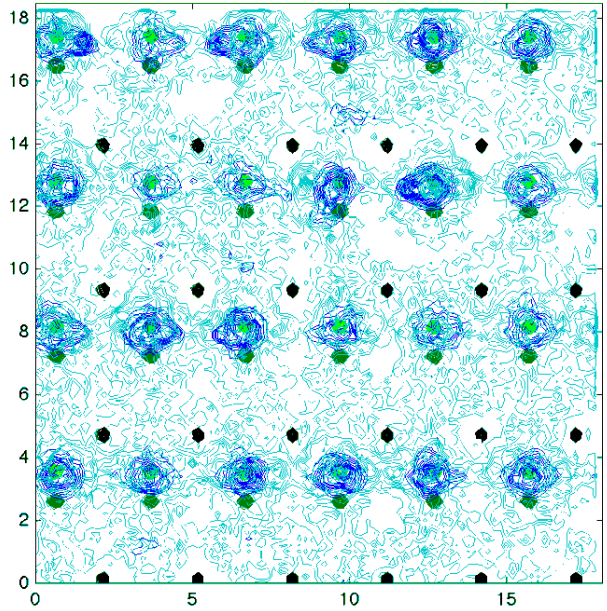


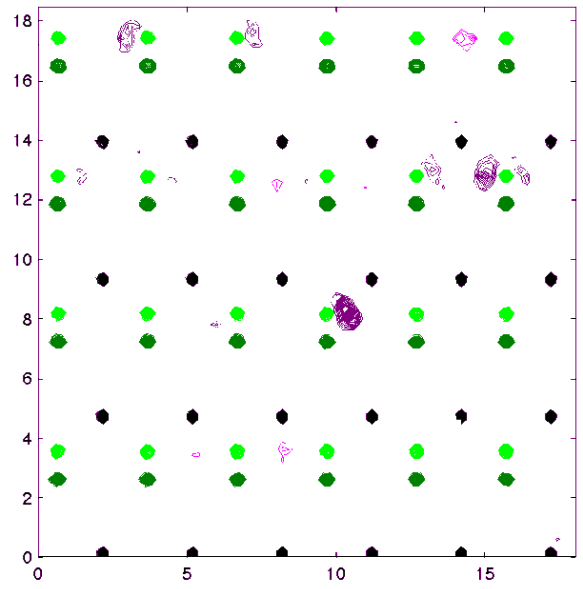


Fe

Na

Layer 2

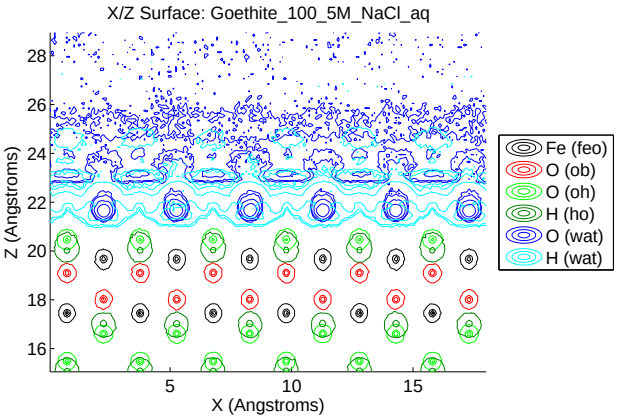


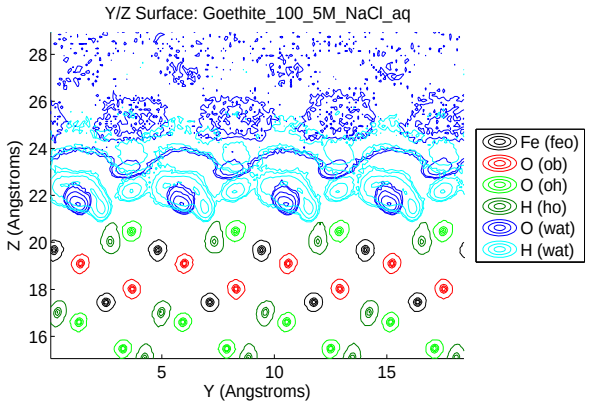


Cl

OH

Goethite (100) with 5 M NaCl

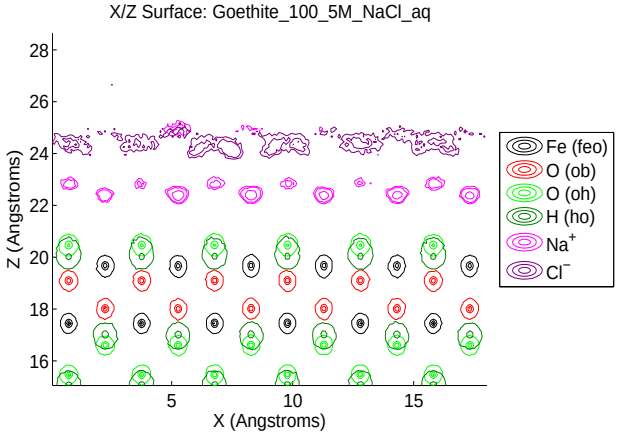


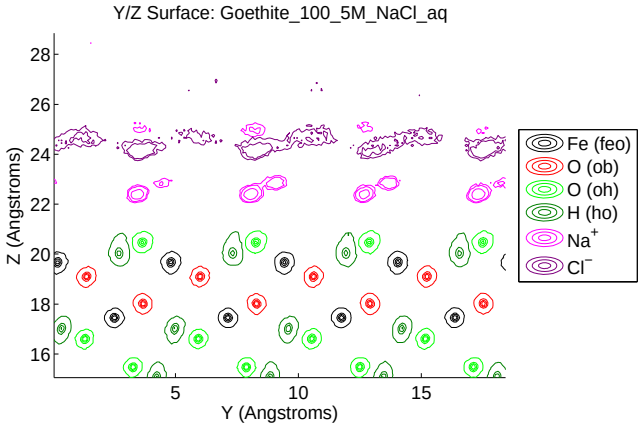


H_2O

OH

O_b



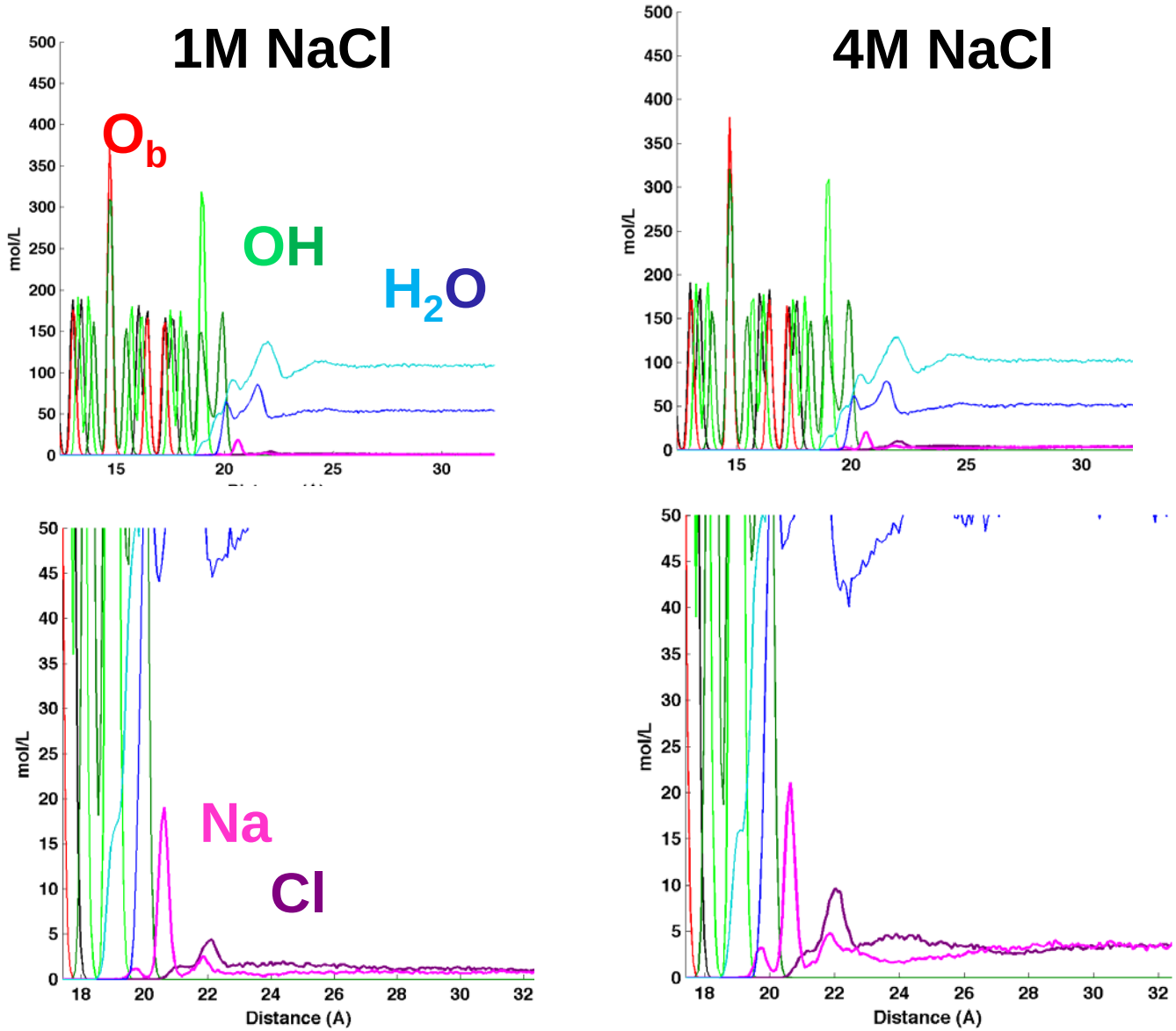


Cl

Na

Fe

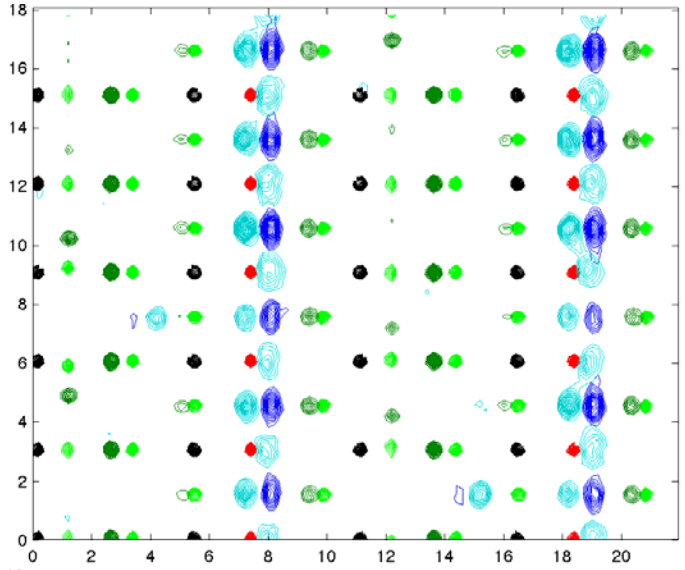
Goethite (101) with NaCl Solution

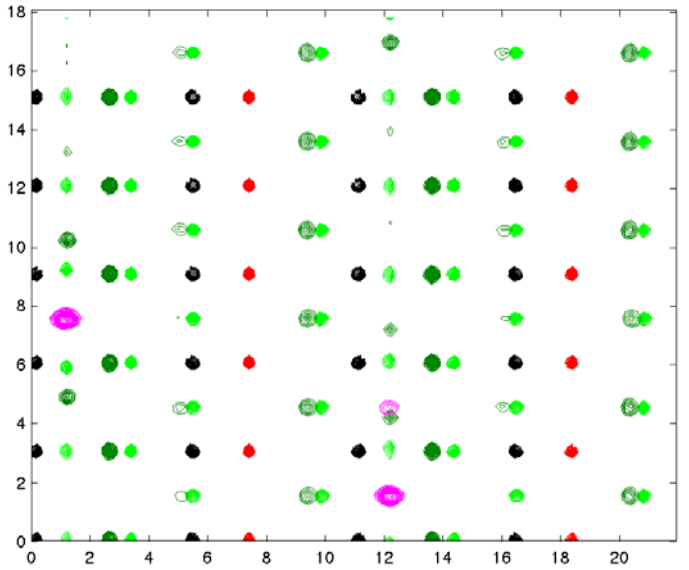


Goethite (101) with 4 M NaCl Solution

Layer 1A

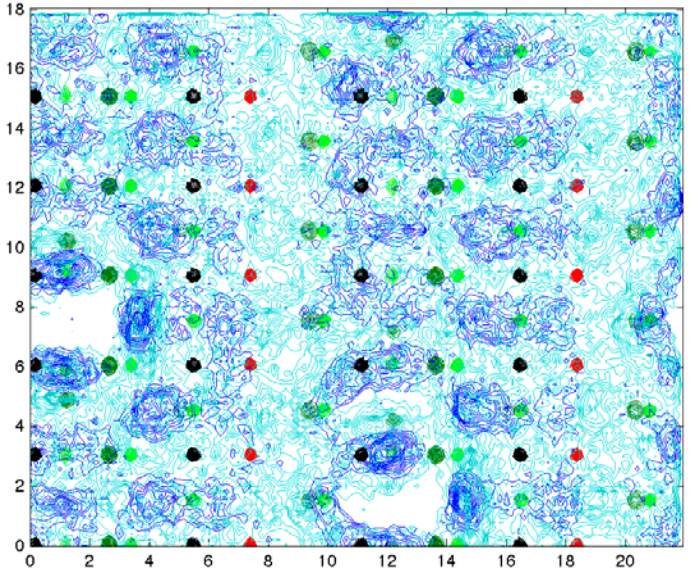
Layer 1B

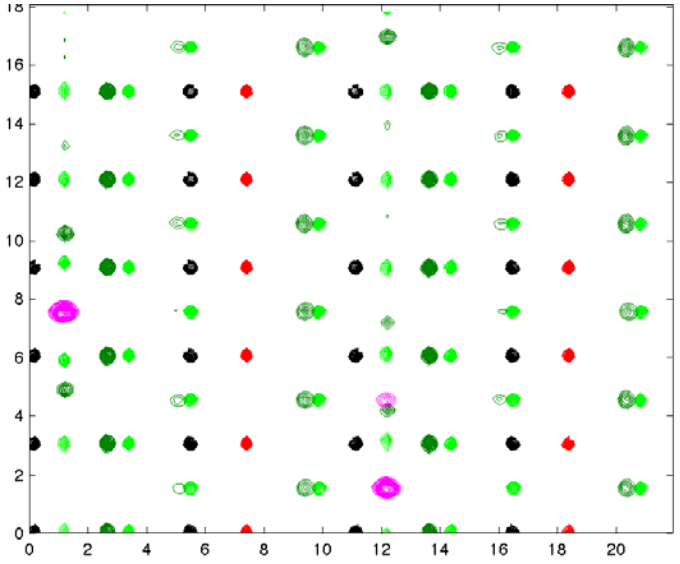




O_b

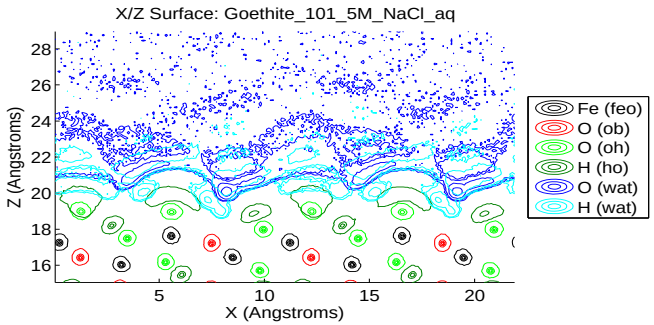
OH

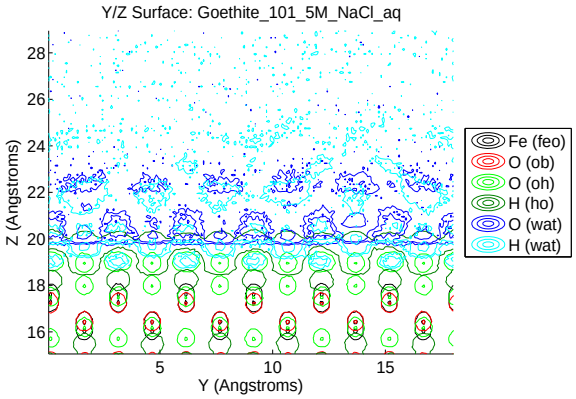




Na

Goethite (101) with 5M NaCl Solution

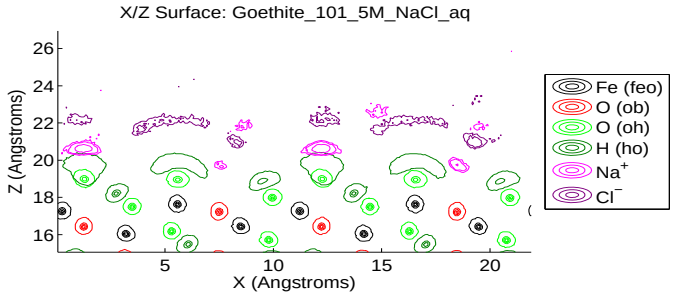


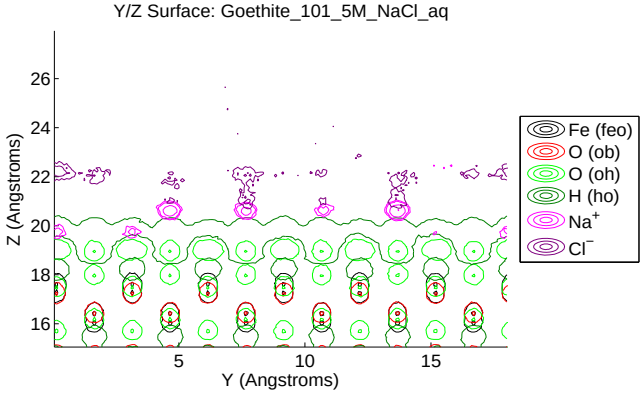


H_2O

OH

O_b





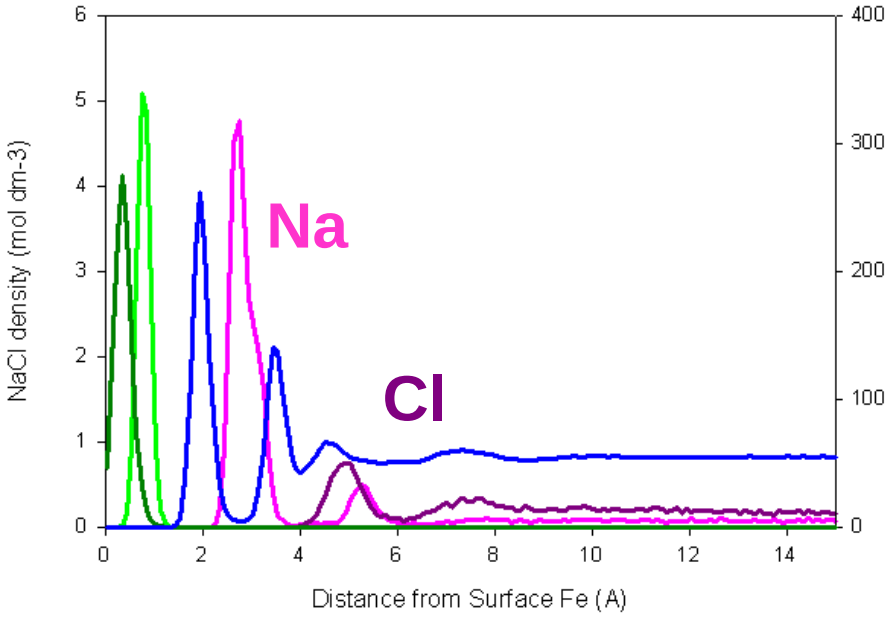
Cl

Na

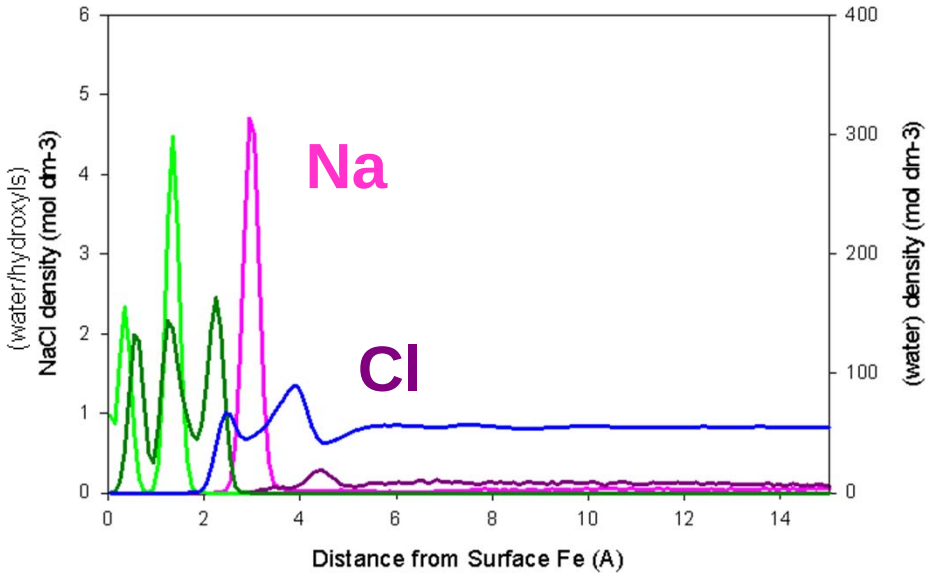
Fe

0.1 M NaCl Atomic Density Profiles

(100) Surface

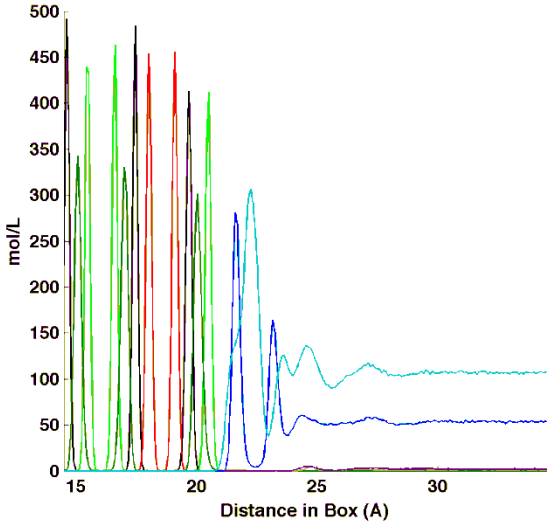


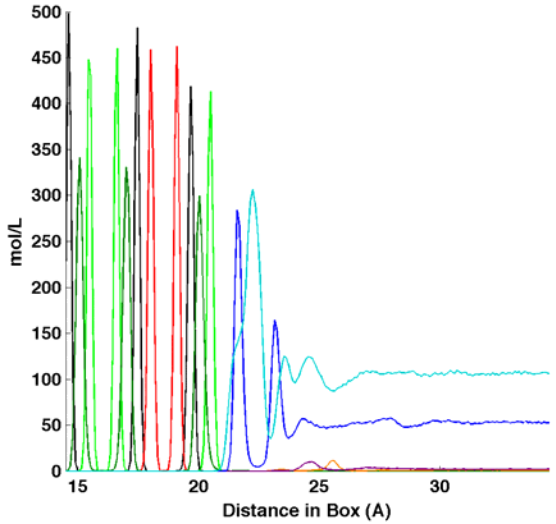
(101) Surface

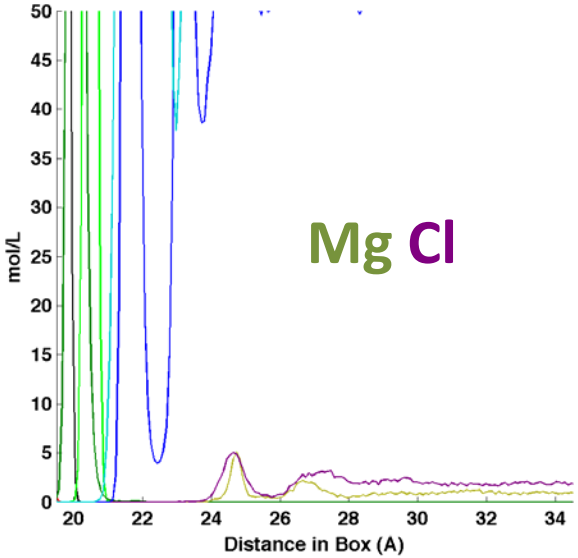


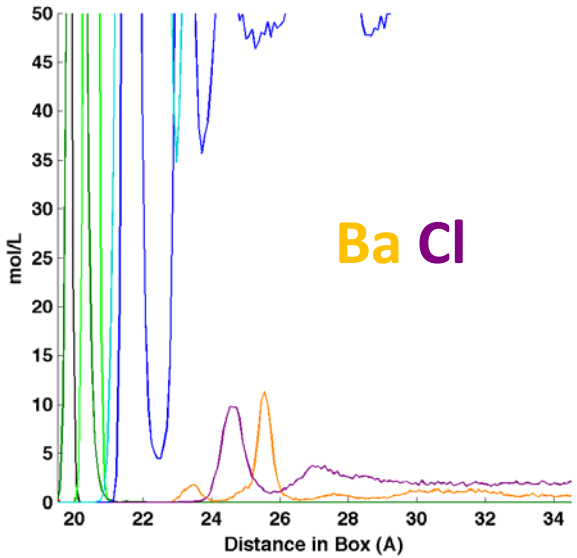
- Larger cell simulations and longer time frames (20 ns) required for low ionic strength calculations.
- No Na^+ observed in same layer as "ligand water" on (100) surface; but most Na^+ adsorbs directly to this water and is closer to the surface than Cl^-.
- On (101) Na^+ is inner-sphere; Cl^- is outer-sphere.

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





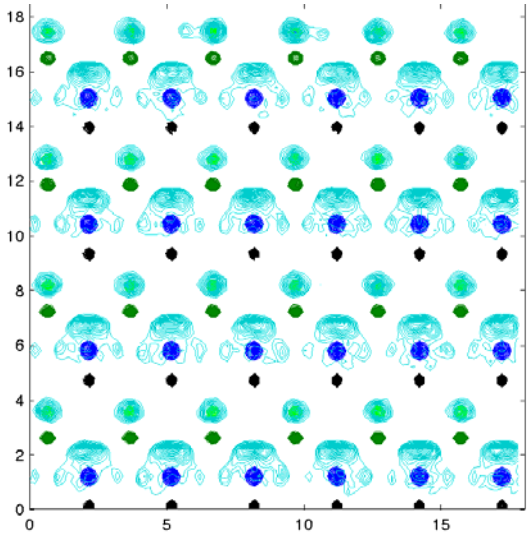


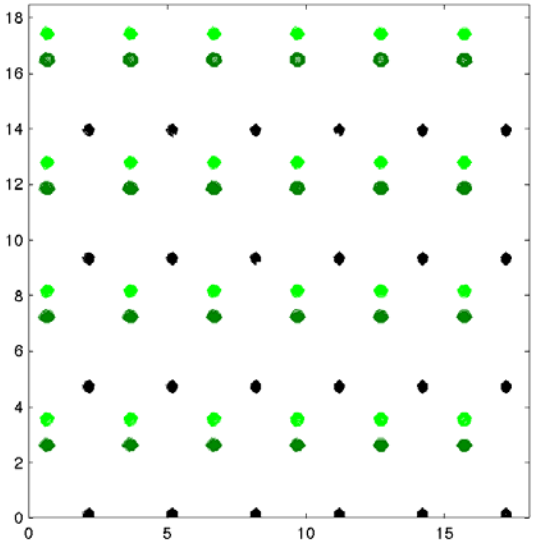


Consistent with Katz et al. (JCIS, 2012) for gibbsite basal surface

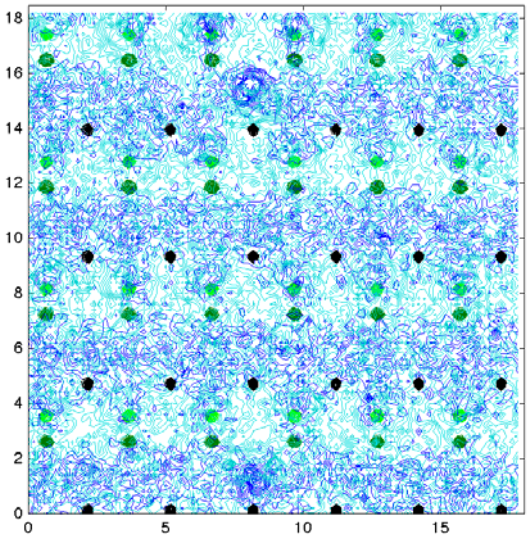
Goethite (100) 1 M $MgCl_2$

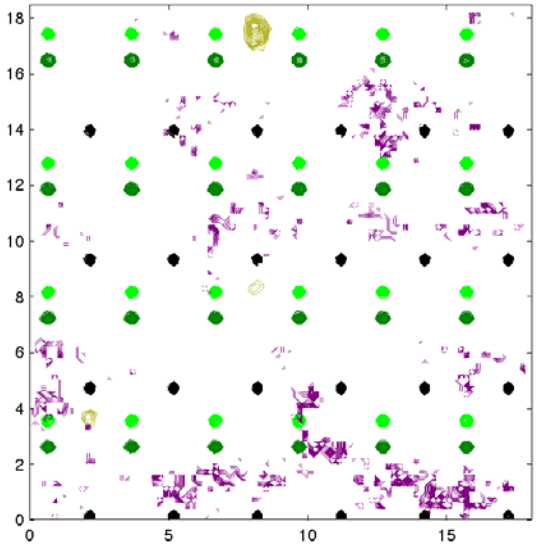
Layer 1





Layer 2



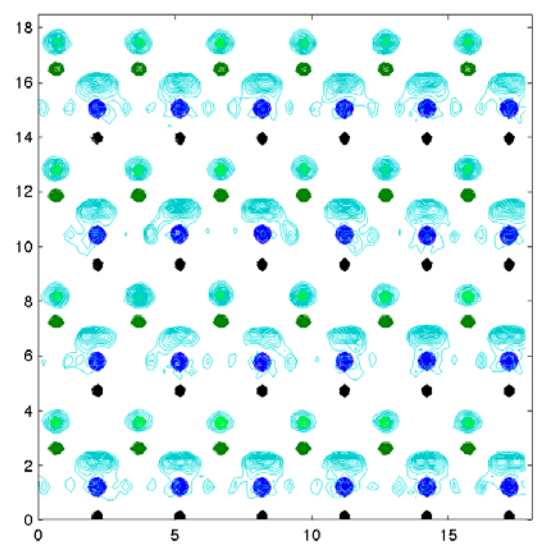


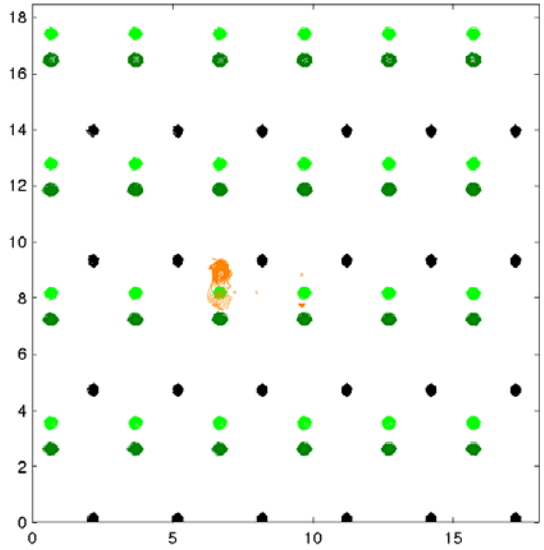
Mg Cl

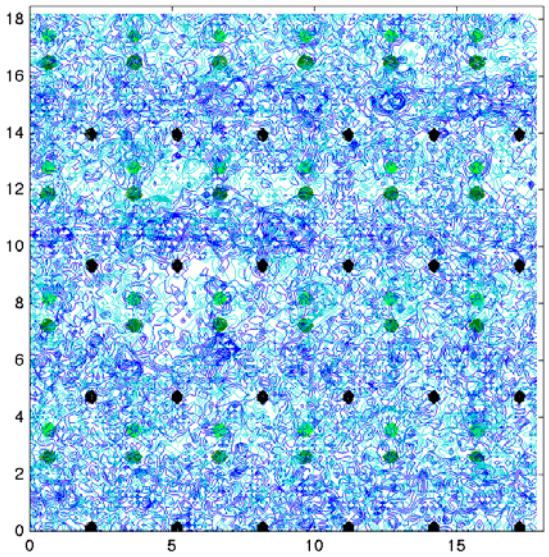
Goethite (100) 1 M $BaCl_2$

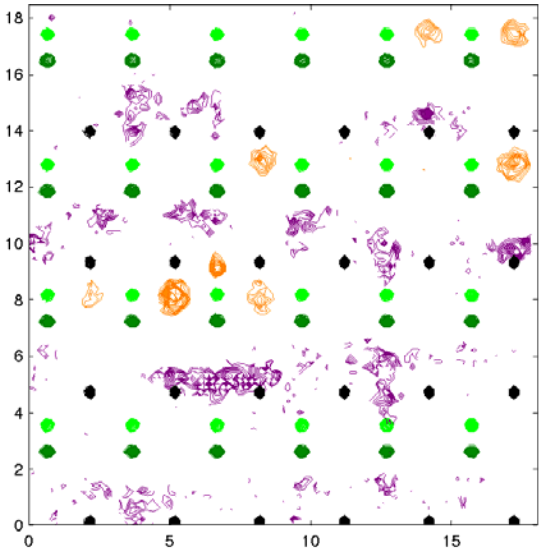
Layer 1

Layer 2



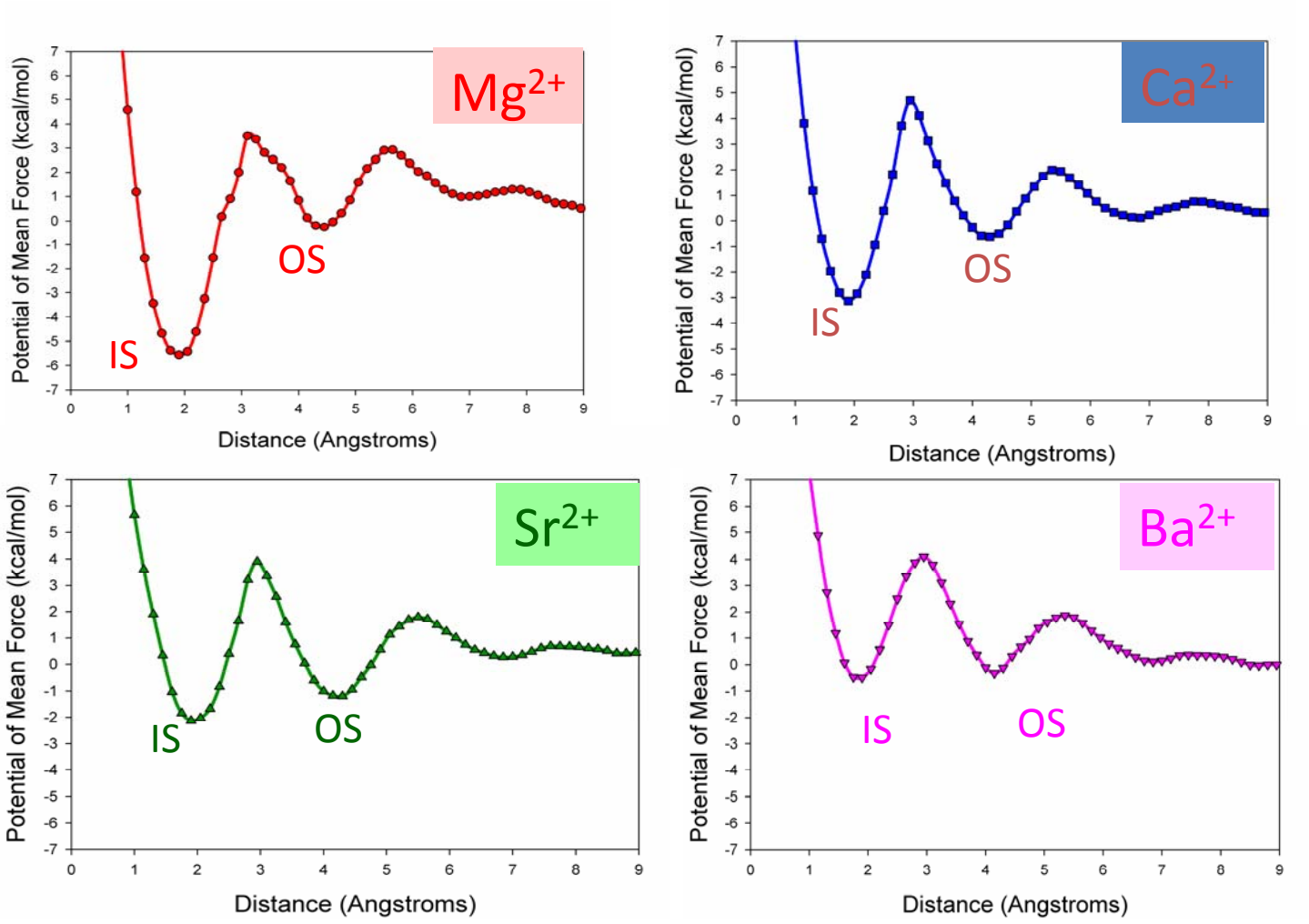






Ba Cl

Surface Potential of Mean Force on Gibbsite

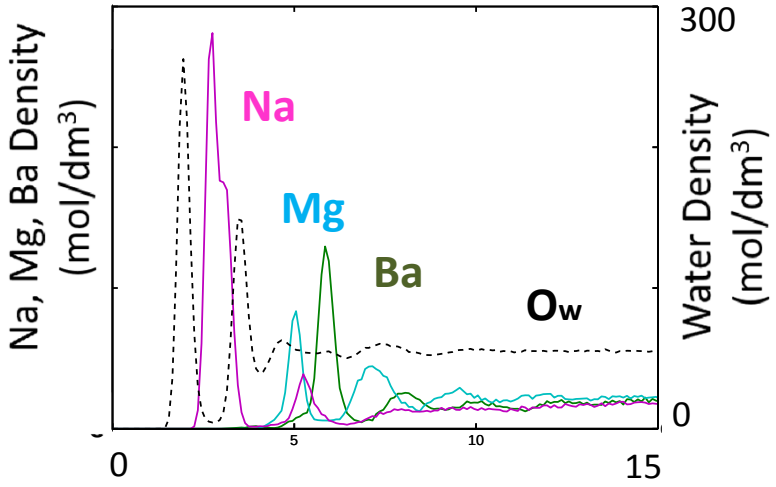


Katz, L.E., Criscenti, L.J., Chen, C.C., Larentzos, J.P., and Liljestrand, H.M. 2012. *Journal of Colloid and Interface Science,* http://dx.doi.org/10.1016/j.jcis.2012.05.011

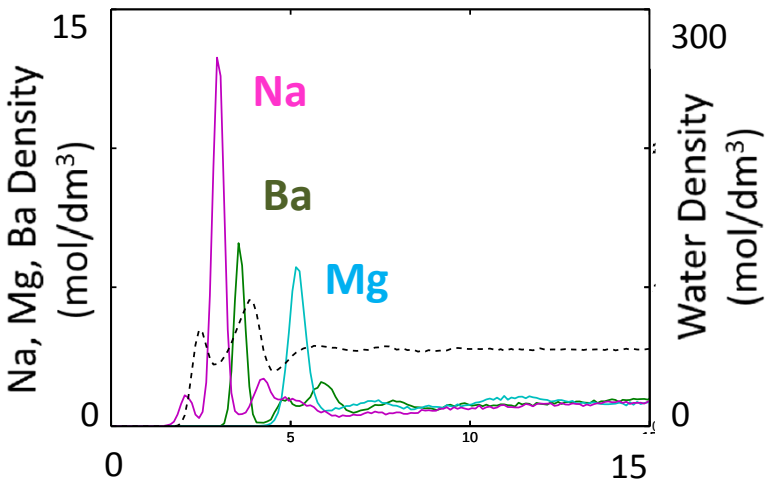
Comparison of 1 M NaCl, $MgCl_2$, and $BaCl_2$ Adsorption

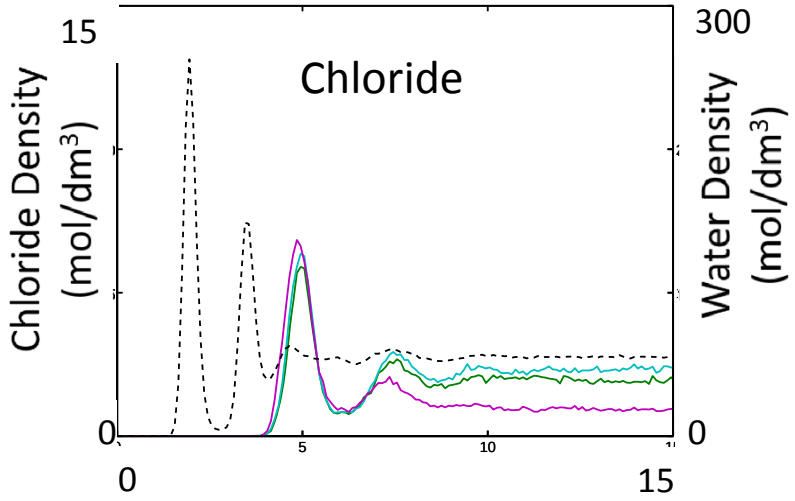
Large Simulations, 20 ns

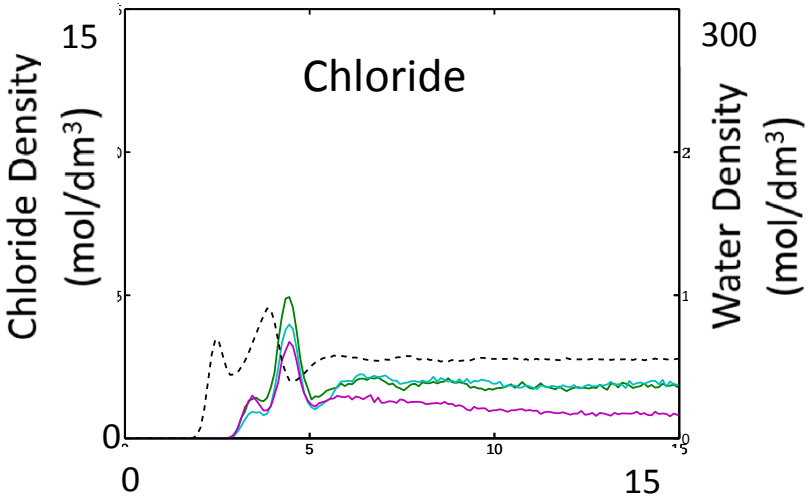
(100)



(101)

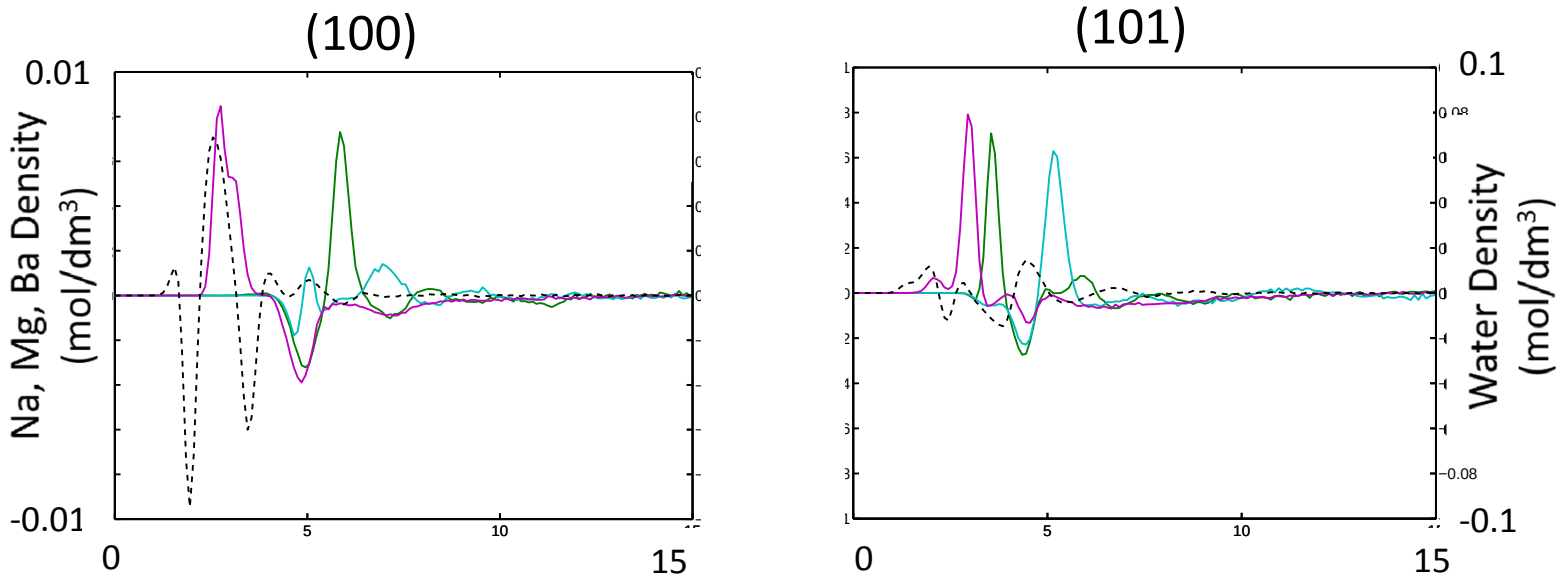






Charge Density Due to Ions and Water

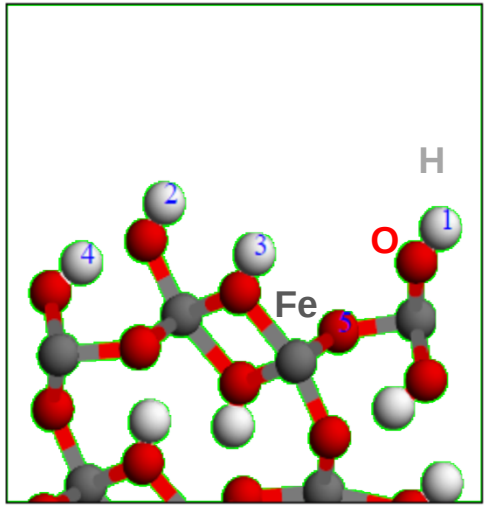
1 M NaCl, $MgCl_2$, and $BaCl_2$

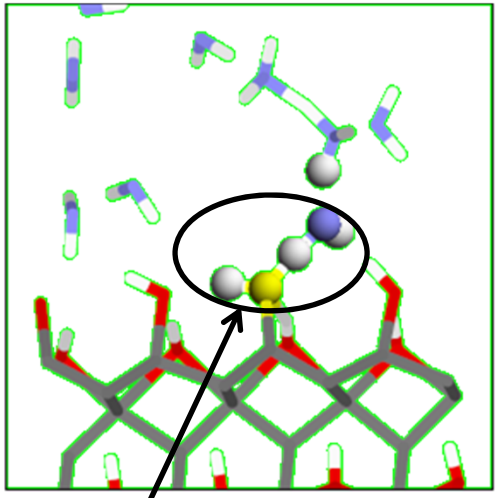


Ion adsorption on the (101) surface makes a significantly larger contribution to the overall EDL charge than at the (100) surface.

Predicting the pK_a of a Goethite Hydroxyl Group from First Principles

(101) FeOOH surface





Transfer of H^+ from $FeOH_2^+$ to form H_3O^+

- Five types of hydroxyl groups are defined on (101) FeOOH surface according to:
  - O_IH is structural OH group; $O_{II}H$ exists at surface only
  - # of Fe atoms the O is attached to
  - Fe_3O_IH (types 3 and 4) are defined as *different* because of inter-hydroxyl H-bonding of type 4. ***Inter-hydroxyl bonding is not considered in bond valence models***.

- Calculate pK_a for $FeO_{II}H_2^+ \rightarrow FeO_{II}H + H^+$ for Type 2 surface group
  - *Ab initio* Molecular Dynamics (AIMD) + Potential of Mean Force Technique
- Results:
  - Calculated **pK_a = 7.0**; 2 inter-hydroxyl H-bonds present throughout PMF calculation, and 1 H-bond to H_3O^+
  - Bond Valence Models:
    - **MUSIC pK_a = 7.7**; 2 H-bonds to H_2O
    - Gaboriaud and Ehrhardt (2003) pK_a is 3.2, 7.7, or 11.7 based on 3, 2, or 1 H-bond to H_2O
- Leung and Criscenti *(J. Phys. Condensed Matter, 24,* doi: 10.1088/0953-8984/24/12/124105*).*

Summary and Conclusions

- H_2O is more structured on (100) surface than on (101) surface of goethite.
- Cl^- always adsorbs as an Outer-Sphere complex; Na^+ adsorbs predominantly as an Inner-Sphere complex.
- NaCl pairing w/ Na^+ as IS is evident at high NaCl concentrations
- Preliminary results suggest that large alkaline earth metals such as Ba^{2+} may adsorb IS on the (101) surface and OS on the (100) surface.
- The influence of ion adsorption on the charge of the EDL is on the same order of magnitude as the water dipole orientations for the (101) surface and of lesser consequence on the (100) surface.

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