Supplemental Information for:

Protein-mineral interactions: molecular dynamics simulations capture importance of variations in mineral surface composition and structure

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1. Nonbonding parameters for Mn^{4+} and Mn^{3+} extension of ClayFF:

Nonbonding interactions, electrostatics and van der Waals, for ClayFF are of the form:

$$E_{ij} = \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad [1]$$

where the first term describes the pair-wise Coulombic interaction with q_i is the charge on atom i, e is the elementary charge of an electron, and ε_0 is the vacuum permittivity constant and the second term describes the van der Waals interaction with ε_{ij} and σ_{ij} as the well depth and collision parameter, respectively, of the Lennard-Jones potential energy.

Table S1: Nonbonding parameters for Mn^{4+} and Mn^{3+} (ref. 59) used with the "ob" O^{2-} nonbonding parameters of CLAYFF.

Species	Charge (e)	ε (kcal/mol)	σ(Å)
Mn^{4+}	2.100[a], 1.850[b]	19.9100	0.7751
Mn^{3+}	1.575[c], 1.850[b]	9.0265×10^{-6}	4.0697

[a]Charge applies to pure MnO_2 phases. [b]Charge applies to MnO_2 birnessite phase.[c] Charge applies to α-Mn_2O_3 (bixbyite-type) phase.

For CLAYFF, AMBER, and the simple point-charge models (SPC, SPC/E), the van der Waals parameter mixing scheme was used to supply missing parameters where:

$$\sigma_{ij} = \frac{\sigma_{ii}+\sigma_{jj}}{2} \quad [2]$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad [3]$$

2. Details of the Mineral Surface Sites

Table S2: Surface number density for all mineral systems considered in this work and surface charge densities for charged surfaces.

Sites	surface number density (nm^{-2})	surface charge density (C/m^2)
birnessite(001) Mn^{3+}	1.71	-2.74×10^{-1}
MMT(001) tetrahedral Al^{3+}	4.03×10^{-1}	-6.46×10^{-2}*
MMT(001) Mg^{2+}	4.03×10^{-1}	-6.46×10^{-2}*
kaolinite(001) surface H^{+}	1.30×10^{1}	
goethite(100) Fe^{3+}	7.21	
goethite(100) surface OH	7.21	

*For MMT(001), the total surface charge density is -0.129 (C/m^2).

3. Details of Analysis methods:

The electric dipole (e) is defined as:

$$\boldsymbol{\mu} = \sum_1^N q_i(\boldsymbol{r}_i - \boldsymbol{r}_{COM}) \quad [4]$$

Where q_i is the partial charge of atom i, $\boldsymbol{r_i}$ is the position of the Gb1 protein atom i, and $\boldsymbol{r}_{COM}$ is the center of mass of the Gb1 protein. The orientation of the dipole is defined as the angle, θ, between the protein dipole vector and the mineral surface normal.

Variation of the Gb1 protein structure from the initial Gb1 protein structure is measured using the root-mean-square-deviation (RMSD):

$$r_{RMSD}(\boldsymbol{r}, \boldsymbol{r}_0) = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\boldsymbol{r}_i - \boldsymbol{r}_{i,0})^2} \quad [5]$$

Where $\boldsymbol{r}$ is the current position of atom i and $\boldsymbol{r_{i,0}}$ is the initial position of atom i.

To quantify the amount of stretching or compression the Gb1 protein molecule undergoes, the radius of gyration, r_G, was calculated:

$$r_G = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\boldsymbol{r}_i - \langle\boldsymbol{r}\rangle)^2} \quad [6]$$

Where $\langle\boldsymbol{r}\rangle$ is the mean position of all Gb1 protein atoms.

The eccentricity, a measure of the shape of the protein, is defined as:

$$E_e = 1 - \frac{I_{ave}}{I_{max}} \quad [7]$$

Where I_{max} is the maximum principal moment of inertia of the Gb1 protein, I_{ave} is the average of the three principal moments of inertia of the Gb1 protein.

Tetrahedral order parameter, a measure of water molecules' order, is defined as:

$$q_{tet} = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\psi_{jk} + \frac{1}{3}\right)^2 \quad [8]$$

Where ψ_{jk} is the angle between bond vectors, $\boldsymbol{r}_{ij}$ and $\boldsymbol{r}_{ik}$. j and k are the four nearest neighbor atoms of the central ith water molecule oxygen atom.

4. Density Profiles:

The following density profiles compare the water-mineral surface systems with and without the presence of the GB1 at the mineral surface.

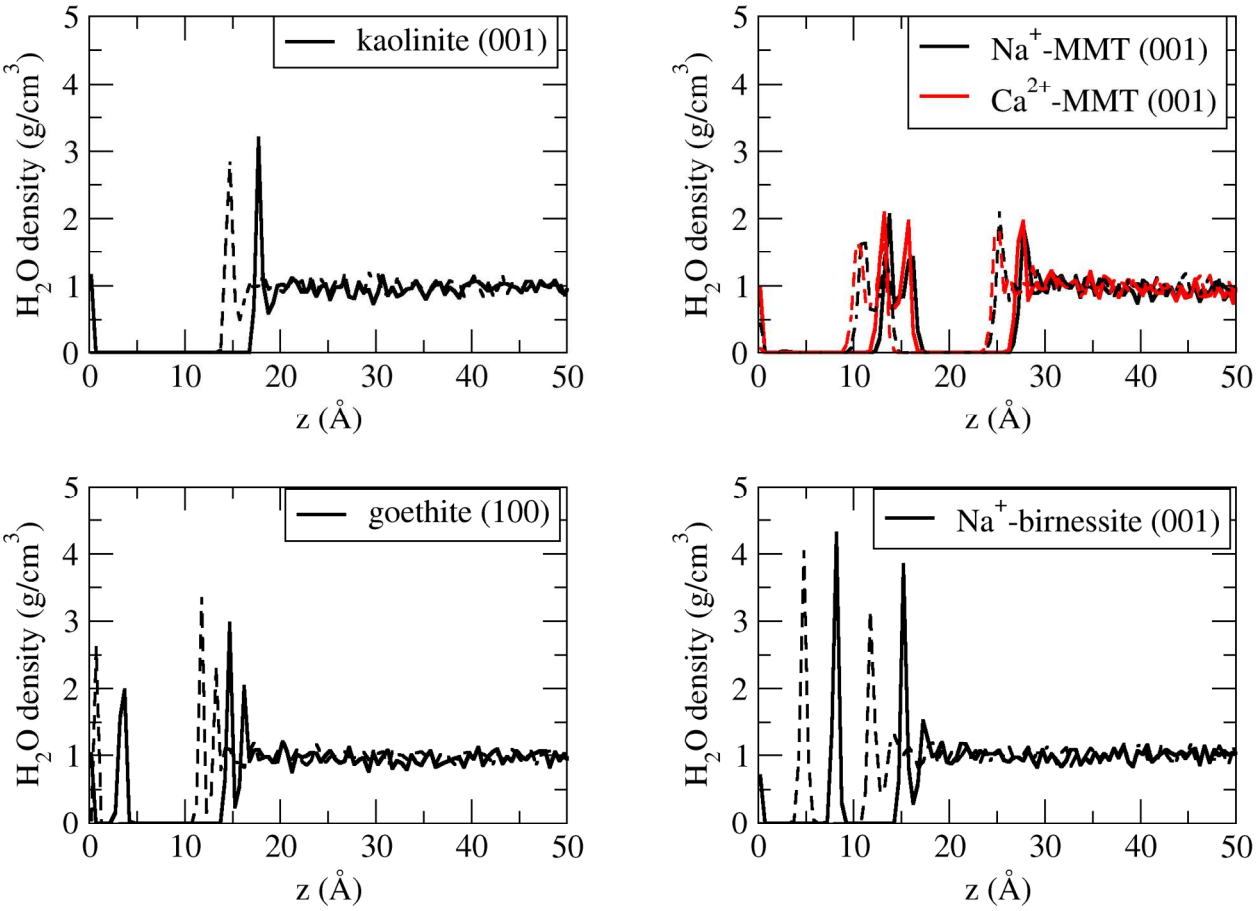


Figure S1: Water molecule density profiles along the z-axis for kaolinite(001) (top-left), Na^+/Ca^{2+}-MMT (001) (top-right), goethite(100) (bottom-left), and Na^+-birnessite(001) (bottom-right). The

solid lines indicate the presence of Gb1; the dashed lines indicate that no Gb1 was present (i.e., water-mineral system only). Dashed line offset by ~3 Å to show differences in Gb1-water-mineral and water-mineral-only water density profile peaks.

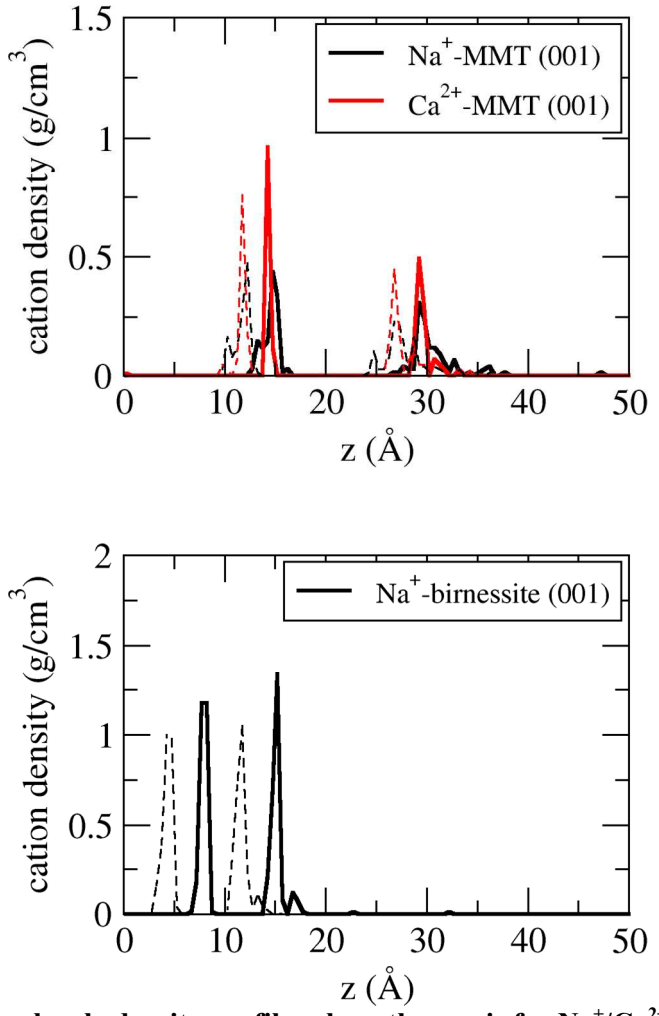
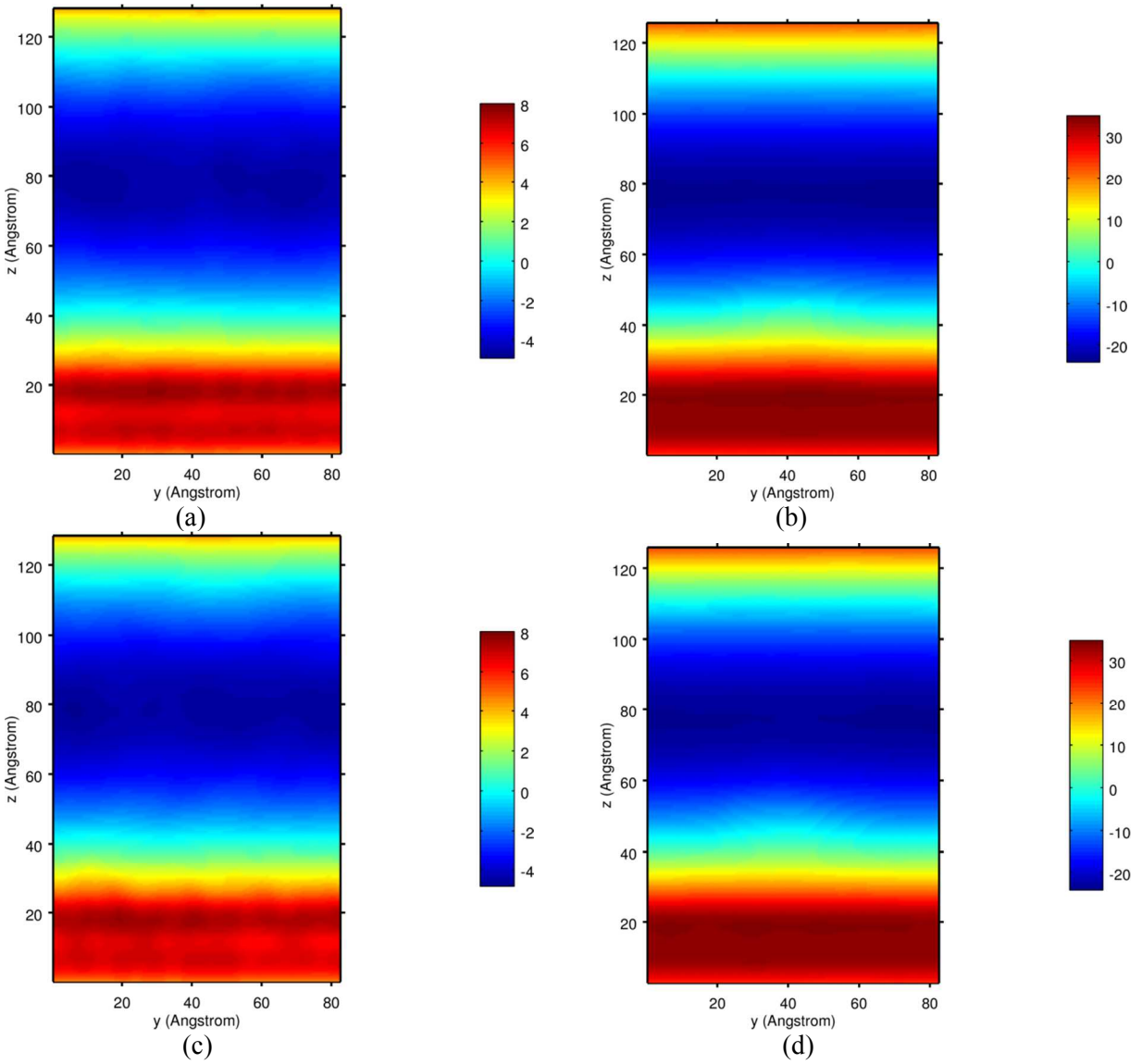
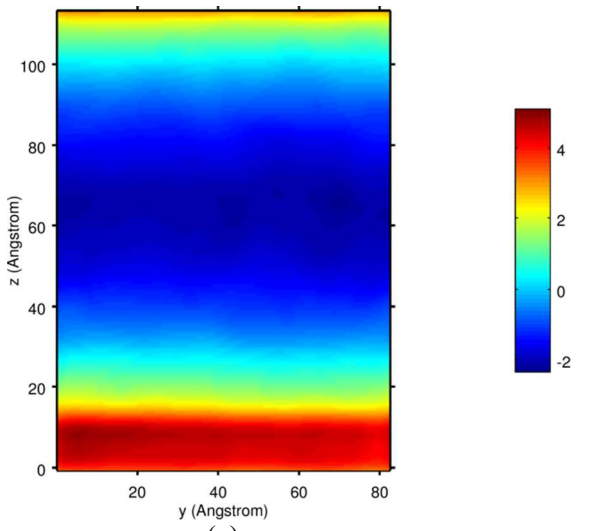


Figure S2: Counterion molecule density profiles along the z-axis for Na^+/Ca^{2+}-MMT (001) (top), and Na^+-birnessite(001) (bottom). The solid lines indicate the presence of Gb1; the dashed lines indicate that no Gb1 was present (i.e., water-mineral system only). Dashed line offset by ~3 Å to show differences in Gb1-water-mineral and water-mineral-only counterion density profile peaks.

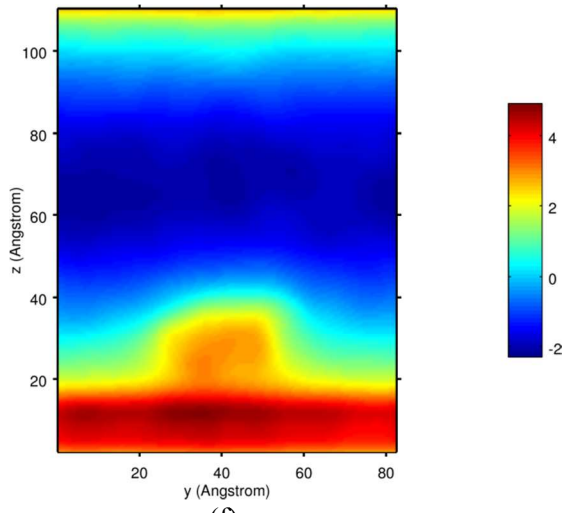
5. Electrostatic Potential Profiles:

Calculations were performed with PMEPot module of the VMD software package.[1] Postprocessing of the OpenDX grid data generated by VMD's PMEPot module was performed with the GNU Octave software package.




z (Angstrom)
y (Angstrom)
0
20
40
60
80
100
-2
0
2
4

(e)


z (Angstrom)
y (Angstrom)
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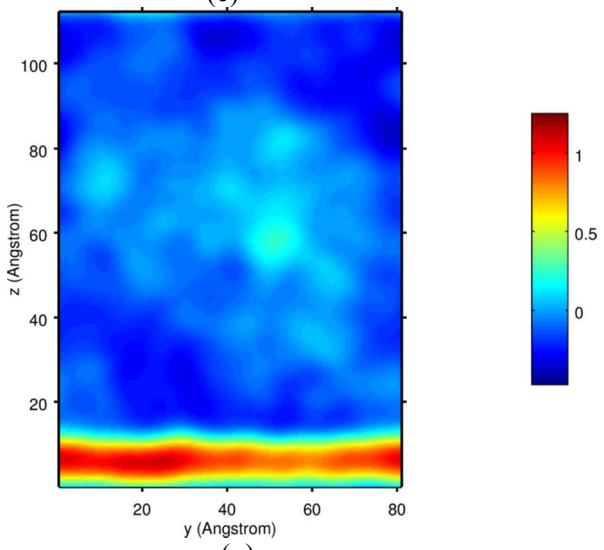
40
60
80
100
-2
0
2
4

(f)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y (Angstrom)
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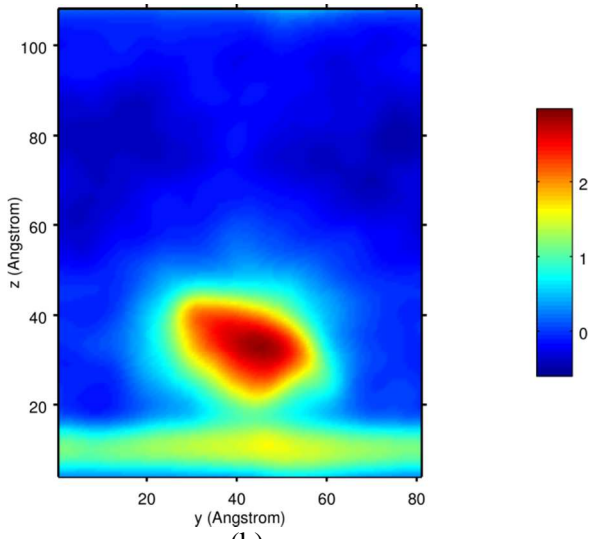
40
60
80
100
0
0.5
1

(g)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y (Angstrom)
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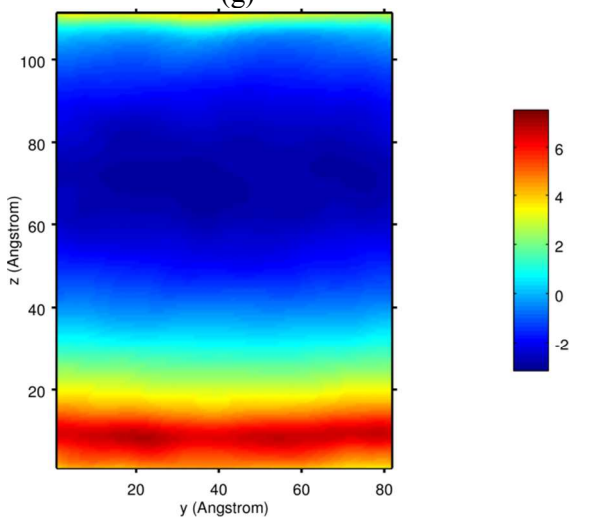
40
60
80
100
0
1
2

(h)


z (Angstrom)
y (Angstrom)
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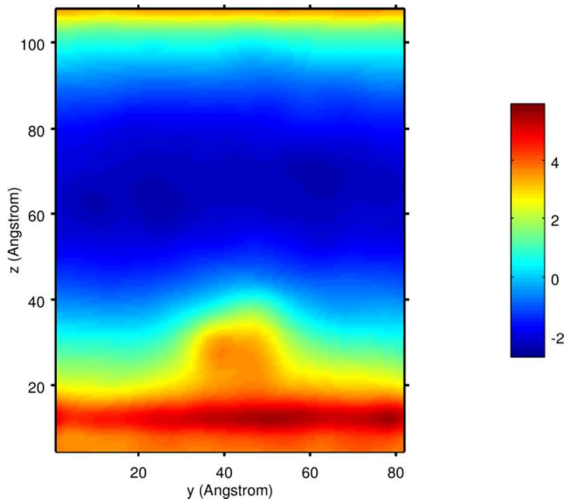
40
60
80
100
-2
0
2
4
6

(i)


z (Angstrom)
y (Angstrom)
20
40
60
80
100
-2
0
2
4

(j)

Figure S3: Electrostatic potential profile slices for hydrated (a) Na^+-MMT(001) only, (b) Gb1-Na^+-MMT(001), (c) Ca^{2+}-MMT(001) only, (d) Gb1-Ca^{2+}-MMT(001), (e) kaolinite(001) only, (f) Gb1-kaolinite(001), (g) goethite(100) only, (h) Gb1-goethite(100), (i) Na^+-birnessite(001), and (j) Gb1-Na^+-birnessite(001). Color scheme is in volts.

References:

1. Aksimentiev, A.; Schulten, K., "Imaging alpha-hemolysin with molecular dynamics: Ionic conductance, osmotic permeability and the electrostatic potential map," *Biophysical Journal*, **2005**, *88*, 3745-3761.