Modeling of Cation Binding in Hydrated 2:1 Clay Minerals

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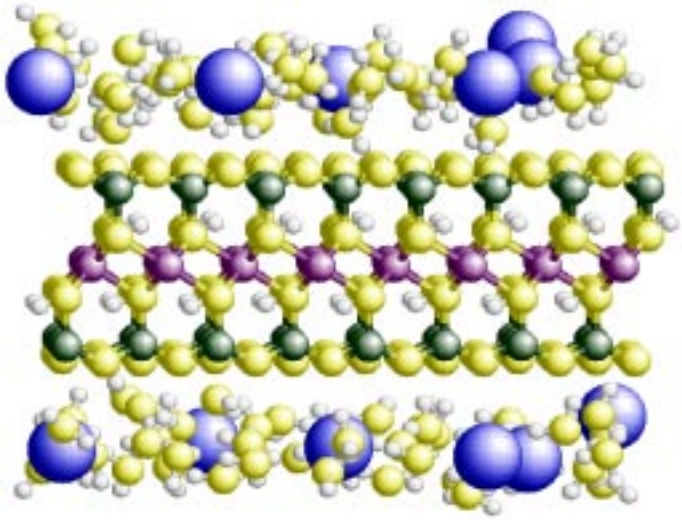


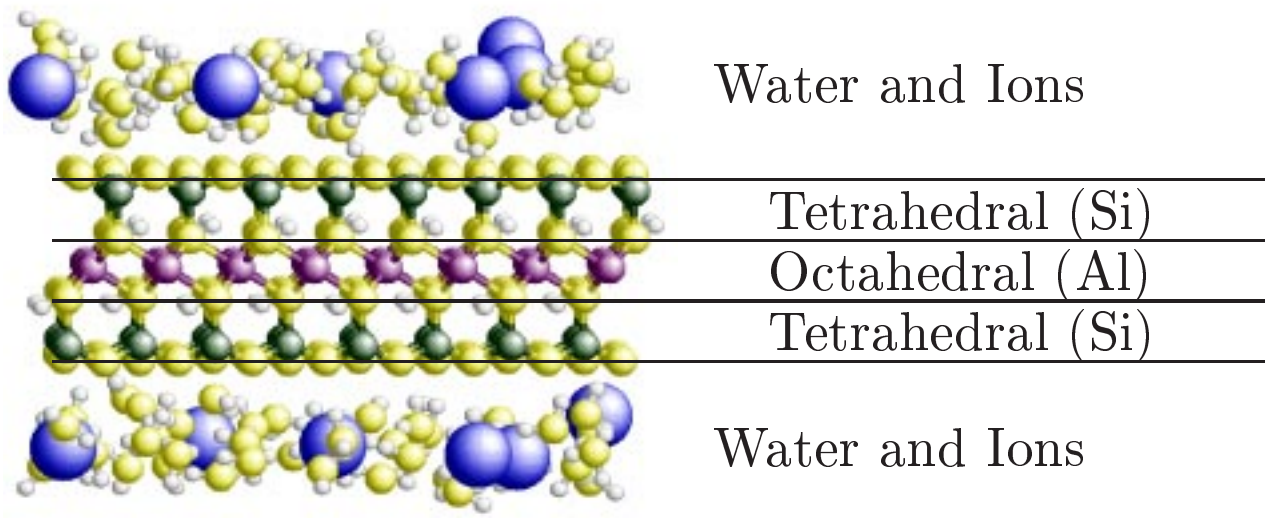
Objectives

The long-range objective of our research is the development of molecular models of ion exchange on clay minerals, with a view toward understanding the mechanisms of radionuclide transport through soils. The research involves the use of molecular simulation methods to correlate clay-ion binding strengths with interlayer structure and swelling properties.

Specific objectives of this presentation include:

- the description and validation of molecular modeling procedures applied to alkali-metal substituted montmorillonite clays.
- the characterization of swelling energetics for both Cs- and Na-substituted montmorillonites. Do simulations properly predict a discrete swelling mechanism and the preferential formation of monolayer hydrates for Cs-substituted clay minerals?
- the characterization of ion-clay binding structures, with a view toward understanding why cesium, of the alkali metal series, binds most favorably to clay minerals.
- the report of ion exchange free energies for alkali metals on a montmorillonite clay, and the description of modeling methods required for a complete ion exchange calculation.

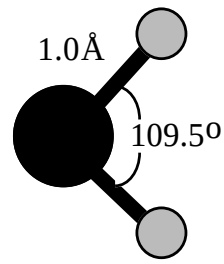
Hydrated 2:1 Clay Minerals



The ion exchange properties of 2:1 clay minerals result from isomorphic substitution for silicon, aluminum, or magnesium atoms in the tetrahedral or octahedral layers of the clay lattice. Typical substitutions (magnesium for aluminum, for example) lead to a net negative clay layer charge that in turn is balanced by interlayer cations, shown in blue above. Clays with moderate layer charge, such as montmorillonites, swell in the presence of water, allowing for exchange of interlayer ions.

Interaction Potentials

- Water: 'SPC/E' Model



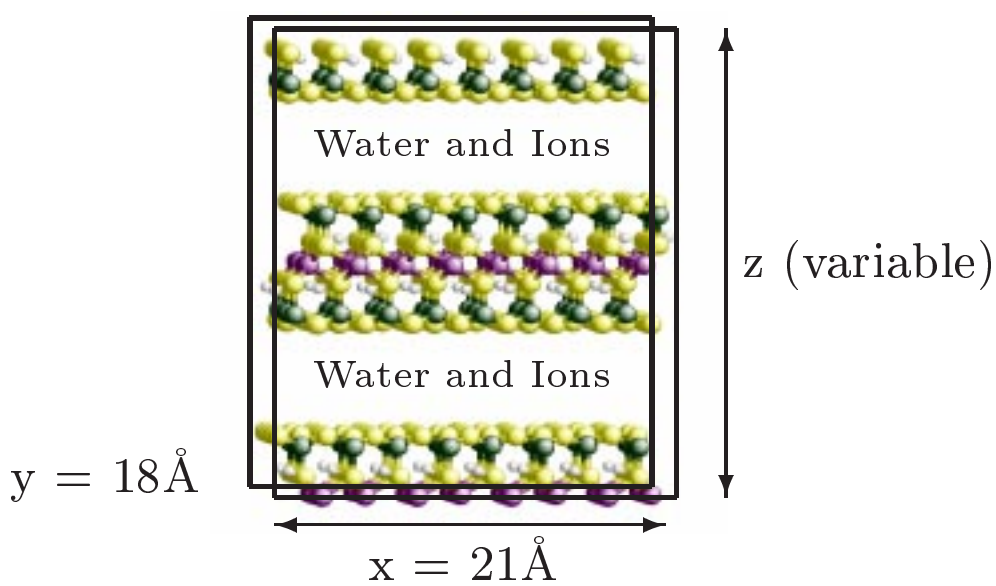
  - rigid
  - partial charges on each atom
  - Lennard-Jones (LJ) interaction centered on oxygen

$$U_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

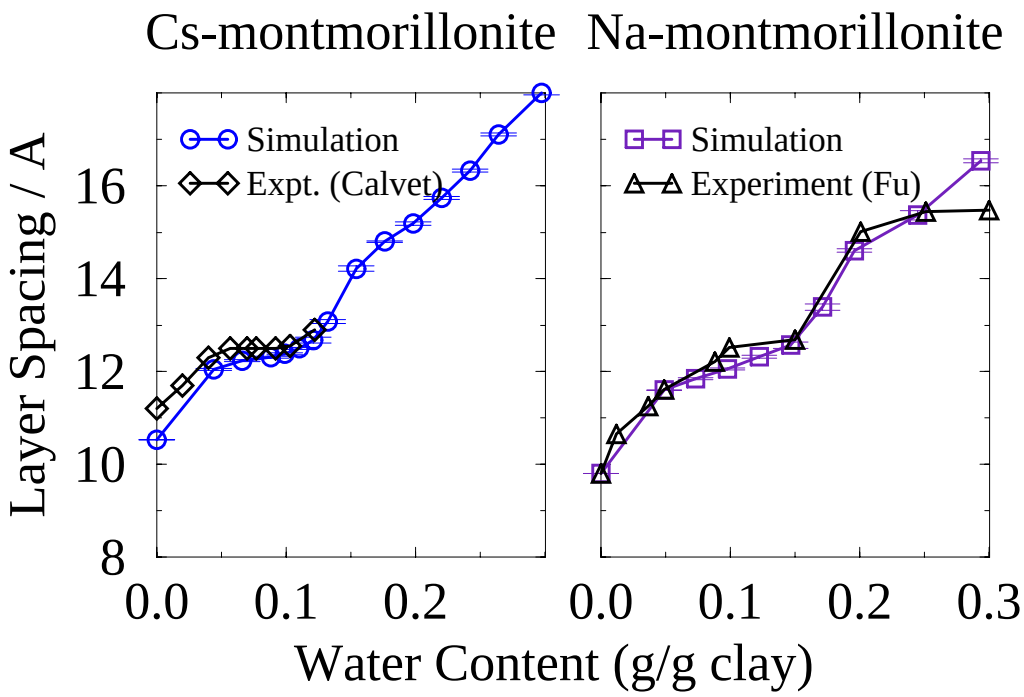
- Ions: Unit charge plus LJ interaction
- Clay: [Skipper, Chang and Sposito, Clays & Clay Minerals **43**, 285 (1995)]
  - rigid lattice
  - partial charges and LJ interactions

MD Simulation Methods

- Two clay sheets of 8 unit cells each, periodic boundary conditions
- $-0.75e$ charge per unit cell and a total of 12 charge-balancing cations
- Variable interlayer spacing
- Registry shifts allowed
- (NpT) ensemble, Ewald sums



Swelling Curves

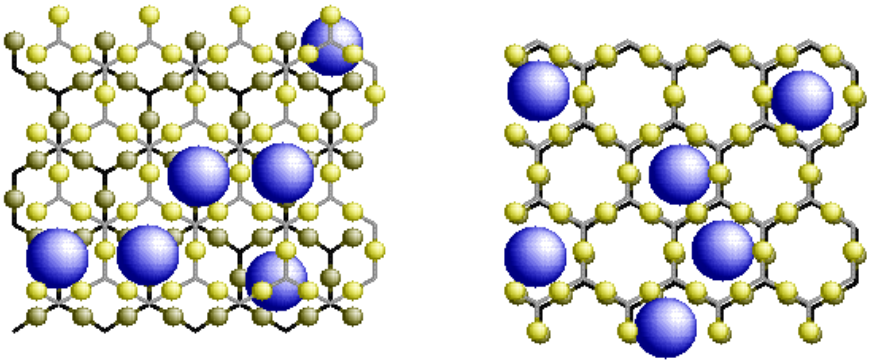


[Fu *et al.*, Clays & Clay Miner., **38**, 485 (1990)],

[R. Calvet, Ann. Agron. **24**, 77 (1973)]

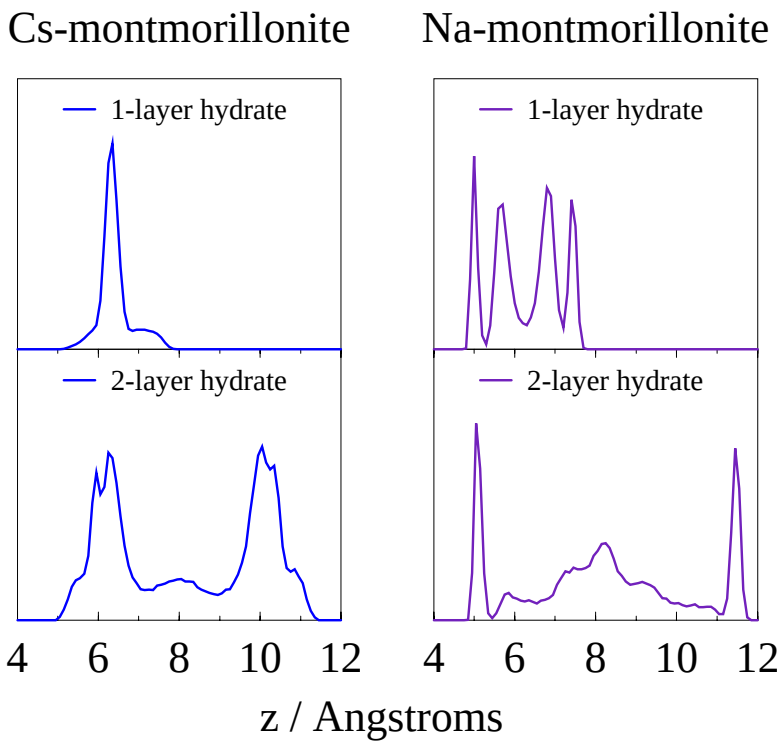
This 'Wyoming-type' montmorillonite has $\frac{1}{3}$ of its layer charge in the tetrahedral layers. The experimental and calculated curves all show plateau regions for monolayer water contents of $\approx 0.1\ g/g\ clay$. For Cs-montmorillonite, the multi-layer hydrates are inaccessible experimentally.

Mixed-layer States



Cs-NMR experiments suggest that dry Cs-smectites occur as a mixture of two registry-shifted states, each with differing cesium coordination to the clay basal surfaces. If such a mixed-layer state existed in the Cs swelling curve experiments, the measured layer spacing of 11.1Å would be an XRD average of the spacings of the two states. Two stable, dry-clay structures observed in our simulations are shown above. They have layer spacings of 10.5Å and 11.6Å, the average of which agrees well with the experimental dry-clay result.

Structure: Ion Density Profiles



'1-layer' and '2-layer' hydrate water contents are defined by the minima in the immersion energy plots shown later. Note that for the 2-layer hydrates, approximately $\frac{1}{3}$ of the sodium ions and approximately $\frac{2}{3}$ of the cesium ions are in contact with the clay surface. The monolayer structures are strongly ion dependent, due primarily to the difference in size between sodium and cesium. Further analysis of the ion structures will be given later.

Swelling: Expectations

It is known experimentally that the initial 'crystalline' swelling of hydrated clay minerals often occurs as a discrete process, through a discontinuous formation of integer-layer hydrates. At intermediate water contents, hydration may proceed through the formation of mixed-layer states with (most commonly) randomly interstratified stacks of differing integer-layer hydrates.

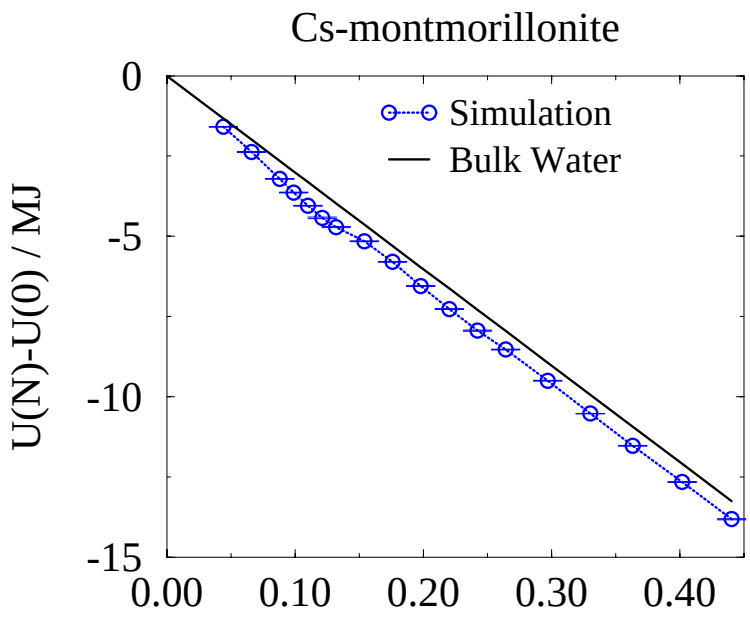
The extent of swelling of clay minerals is a function of clay layer-charge magnitude and location, and of interlayer ion identity. Large, low-charge ions such as cesium are swelling inhibitors. Cs-substituted clays typically form monolayer hydrates when in contact with water, while the same Na-substituted clays may form 2-layer hydrates or even macroscopically swollen states.

Questions: Do simulation thermodynamics

- predict discrete swelling?
- predict the formation of monolayer hydrates for Cs-substituted clays?

Integral Hydration Energy

Characterization of simulated swelling thermodynamics begins naturally with the integral hydration energy, $\Delta U = \left\langle U(N) \right\rangle - \left\langle U(0) \right\rangle$, which is the difference in the average potential energies of the hydrated and dry clays. This quantity is plotted below along with the corresponding bulk-water energy. Note that the hydrated clay is stable with respect to dry clay + bulk water for all water contents.



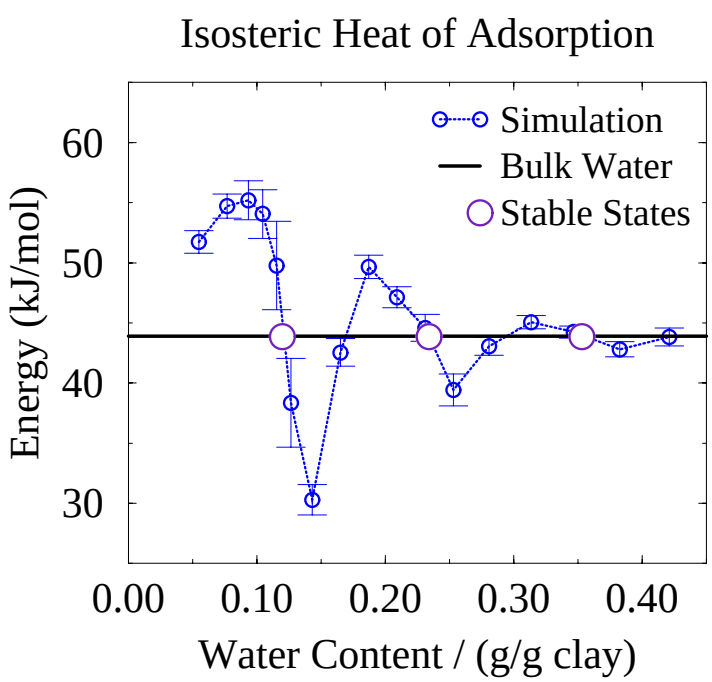
Driving Force for Swelling

For a clay at a given water content, the energetic driving force for hydration is given by the differential (partial molar) hydration energy of the clay q_d,

$$q_d = \left(\frac{\partial \Delta U(N)}{\partial N}\right)_{T,p},$$

which in turn is related to the experimental isosteric heat of adsorption, q_{st}, by

$$-q_d + RT = q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_{\Gamma}.$$



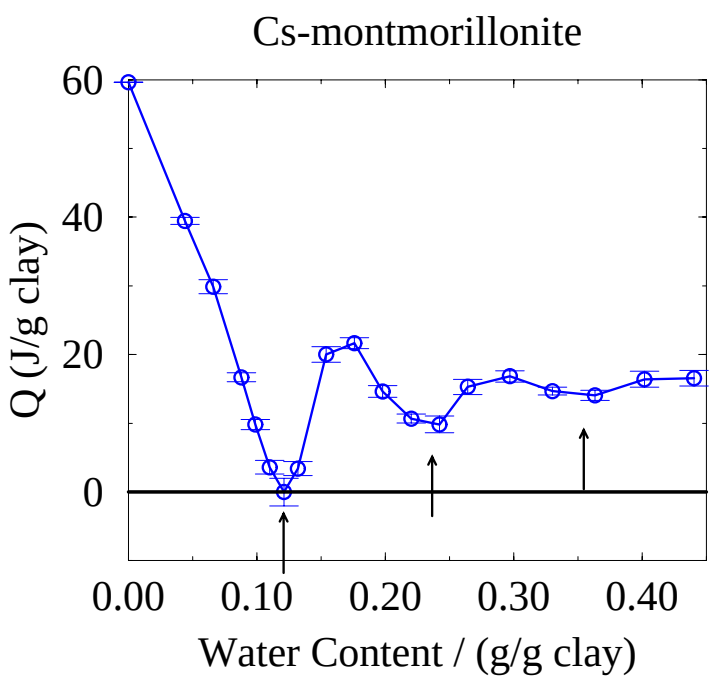
- Stable states occur for integer-layer hydrates.

Immersion Energy

The integer-layer, stable states shown above may be easily seen through plotting the simulated immersion energy, Q,

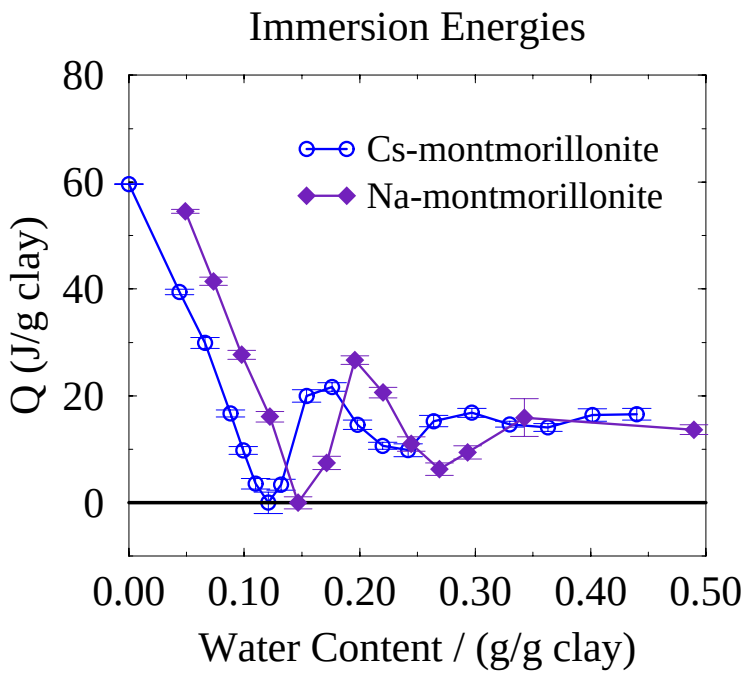
$$Q = \left\langle U(N) \right\rangle - \left\langle U(N^\circ) \right\rangle - \left(N - N^\circ \right) U_{bulk}$$

where N° is the monolayer hydrate water content.



Minima in this swelling-coordinate potential energy surface (indicated by arrows) are consistent with a discrete swelling mechanism and the preferential formation of a monolayer hydrate for Cs-montmorillonite.

Na-vs-Cs

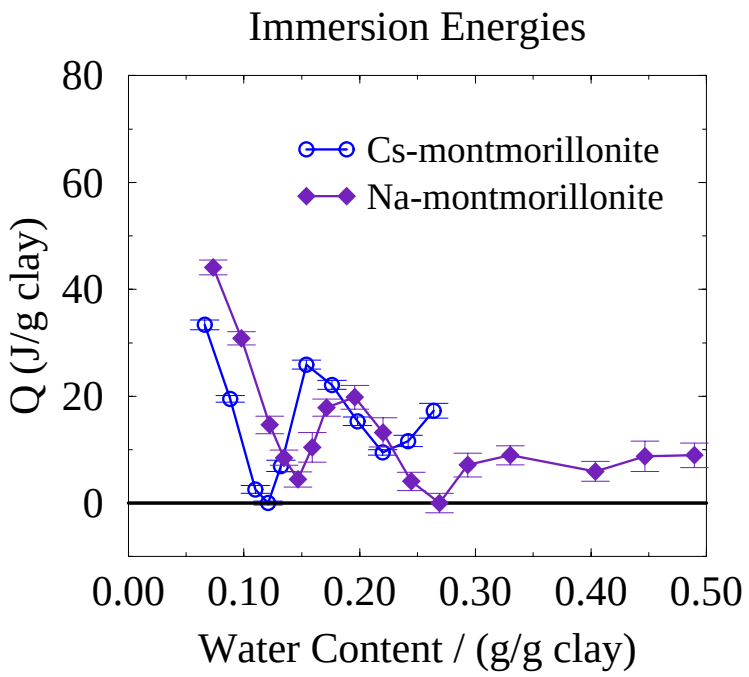


The calculated immersion energies for Na- and Cs-montmorillonite are qualitatively similar. The shift in minima position to the right for sodium is an insignificant artifact of the 'per gram clay' water content units.

The simulations predict an energetically preferred monolayer state for *both* clays when in contact with bulk water. For sodium-montmorillonite, this conflicts with numerous experimental measurements, including the immersion enthalpy measurements discussed below, and likely indicates a flaw in the simulation model.

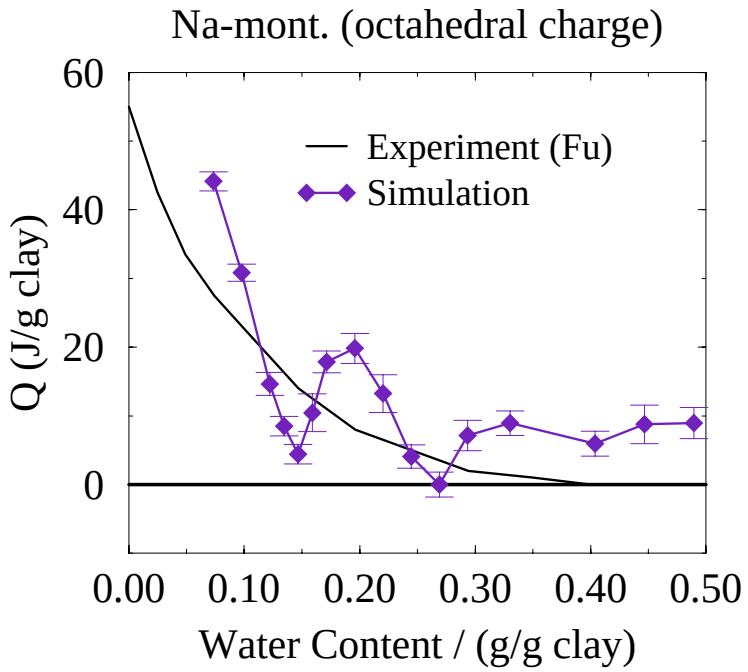
Layer-Charge Location

The following immersion energy plot is for Na- and Cs-montmorillonites with the same layer-charge magnitude as before but with *all charges located in the octahedral layer.*



The result for the Cs-clay is essentially unchanged. In contrast, for the Na-clay, the plot shows an energetic minimum for the 2-layer hydrate, now in qualitative agreement with experimentally-based expectations. This layer-charge location dependence may indicate the model flaw is associated with tetrahedral-layer substitution sites.

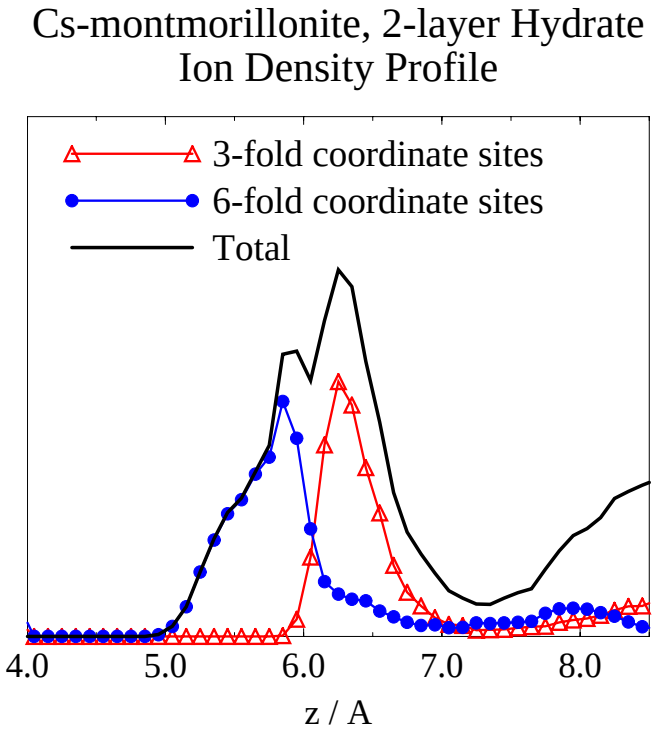
Comparison with Experiment



[Fu *et al.*, Clays & Clay Miner., **38**, 485 (1990)]

The simulation cell contains two interlayer regions that are constrained to have identical water contents, precluding the formation of mixed-layer states. The simulation thus calculates single-layer hydration thermodynamics. The oscillatory shape of the simulation curves is, nevertheless, indicative of the formation of mixed-layer states in the unconstrained bulk system. For example, a simulated state with an average 1.5-layer water content could minimize its energy by forming an equal mixture of 1- and 2-layer states. The bulk immersion energy for the unconstrained system would *not* show oscillations but would instead resemble the experimental curve.

Cs-montmorillonite Structure



Cesium binds favorably to two clay surface sites.

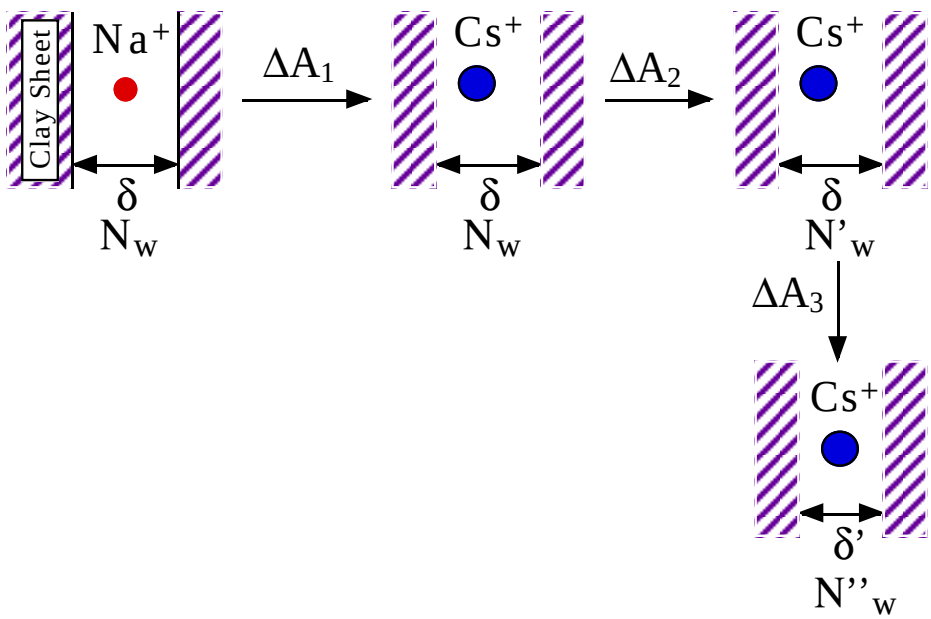
- First site (blue): ions reside in the pseudo-hexagonal holes *adjacent* to tetrahedral substitution sites.
- Second site (red): ions occupy positions directly above tetrahedral-layer silicon atoms, and are 3-fold coordinated with clay basal oxygens.

Swelling: Conclusions

- All clays studied show hydration thermodynamics consistent with a discrete swelling mechanism.
- The monolayer hydrate is favored for both Cs-substituted clays studied, and (incorrectly) for a sodium-montmorillonite that contains a fraction of tetrahedral-layer charge.
- The two-layer hydrate is favored for the octahedrally-substituted Na-montmorillonite.
- The preferential formation of monolayer hydrates is correlated with the formation of inner-sphere ion-surface complexes. The only clay without a stable clay-surface complex is the octahedrally-substituted Na-montmorillonite.

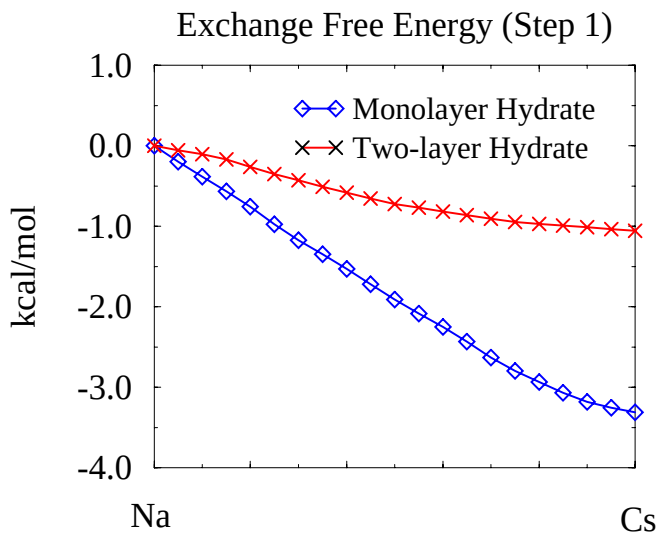
- Future calculations of swelling free energies will help elucidate the role of entropy in discrete swelling processes.

Exchange: Approach



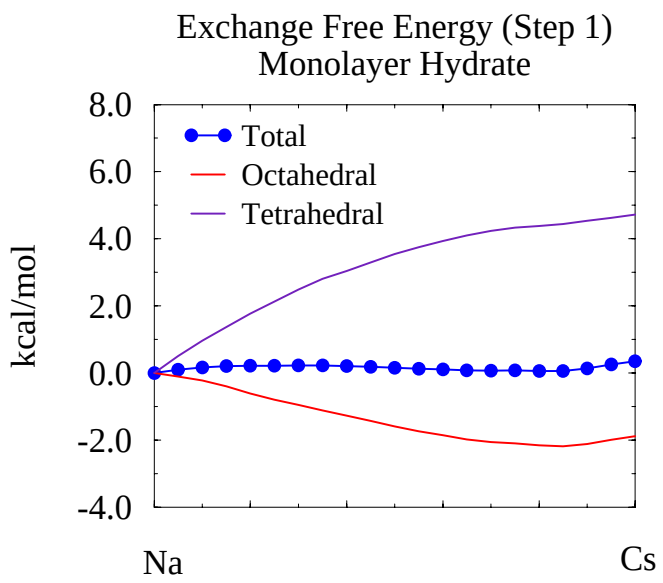
- ΔA_1: Standard thermodynamic integration technique of mutation at constant layer spacing and water content. Subtraction of $\Delta A_{1,bulk}$ required.
- ΔA_2: 'Mass work' associated with change in water chemical potential upon exchange. $\mu_{water} dN$ integral.
- ΔA_3: 'Swelling work' - just a pdV integral if simulations are performed at $\mu_{water} = \mu_{water}^{bulk}$.

Exchange: ΔA_1



The Na→Cs exchange free energy at *fixed layer spacing and water content*, calculated for a clay with all octahedral-layer charge, is displayed above. The results are in qualitative agreement with experiments that universally report favorable cesium exchange free energies. [Xu and Harsh, Clays & Clay Miner., **40**, 567 (1992), and references therein.] The $> 2.0 kcal/mol$ difference in exchange free energy for the two plots suggests that the swelling contribution (Step 3) to exchange is significant. The results are also consistent with a preferential formation of the monolayer hydrate for Cs-montmorillonite and the two-layer hydrate for Na-montmorillonite.

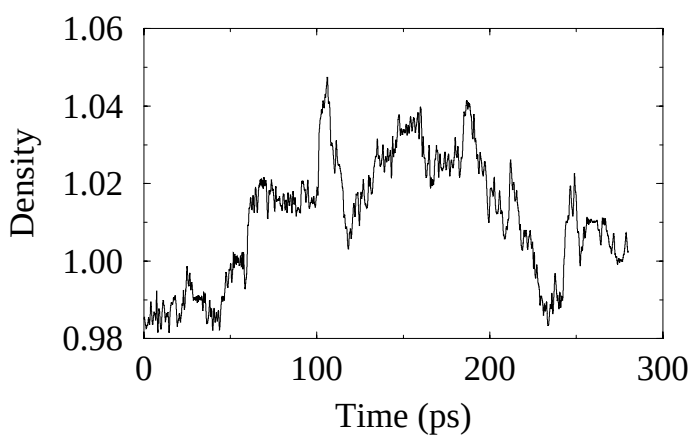
Exchange: ΔA_1



The Na→Cs exchange free energy for a montmorillonite with $\frac{1}{3}$ tetrahedral-layer charge was found to be approximately zero. The simulated free energy may be decomposed into contributions of ions associated with tetrahedral- and octahedral-layer charges. While the 'octahedral' result is in qualitative agreement with the previous plot and with experimental measurements, the 'tetrahedral' result is not. This again indicates a flaw in the simulation model associated with tetrahedral substitution sites. A model reparameterization based upon DFT calculations of ion-clay interactions is currently underway in collaboration with Dr. Randy Cygan of Sandia National Laboratories.

Grand Canonical Molecular Dynamics

Grand canonical (GC) simulation methods are required to determine the ΔA_2 and ΔA_3 contributions to the exchange free energy. Traditional GC Monte Carlo methods are often inefficient, particularly in constrained environments such as a clay interlayer. We have incorporated a molecular dynamics (MD) algorithm, modified from Pettitt's GCMD methods.[Lynch and Pettitt, J. Chem. Phys. **107**, 8594 (1997)]. The method treats the water particle number as a dynamical variable in such a way that GC ensemble averages are produced. Preliminary results of our method applied to bulk SPC water are shown below. For a target excess chemical potential of $-5.7 kcal/mol$, the density fluctuates around $\approx 1.0 g/cc$, as expected for this water model. Applications of the method to hydrated clays are currently underway.



Exchange: Summary

Molecular simulations of ion exchange free energies on clay minerals will assist in developing our understanding of the mechanism of radionuclide transport through soils. A variety of information available in the simulations is inaccessible or difficult to obtain experimentally. For example, individual ion and single interlayer contributions to exchange thermodynamics may be determined for comparison with 'bulk' experimental measurements. Calculated thermodynamic values can also be correlated directly with structural features such as ion binding geometry or interlayer charge distribution. This information may then be used to develop improved theories of ion exchange on swelling mineral surfaces.

Ongoing work:

- Completion of alkali-metal ion exchange calculations for comparison with existing exchange theories.
- Extension of swelling and exchange work to include strontium and uranium.

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- Dwarakanath Vijayaraghavan (graduate)
- Russel Waymire (undergraduate)

Postdoctoral:

- Dr. Robert Shroll

Further information and an complete reference list is available in preprint form from the author (e-mail: davsmith@nmsu.edu)