Modeling of Cation Binding in Hydrated 2:1 Clay Minerals

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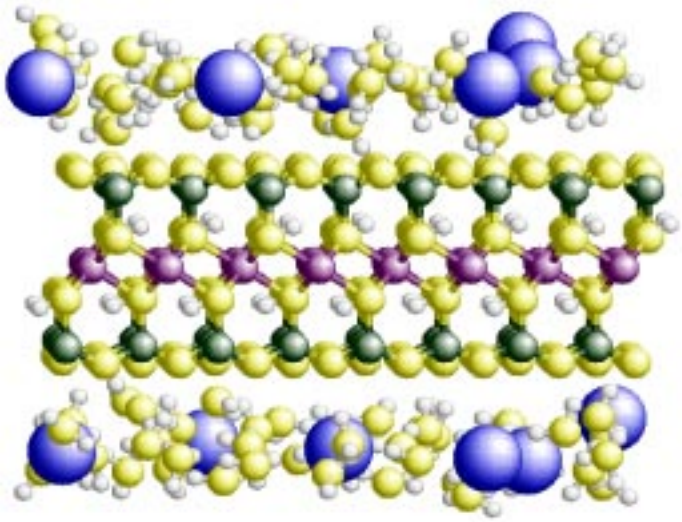


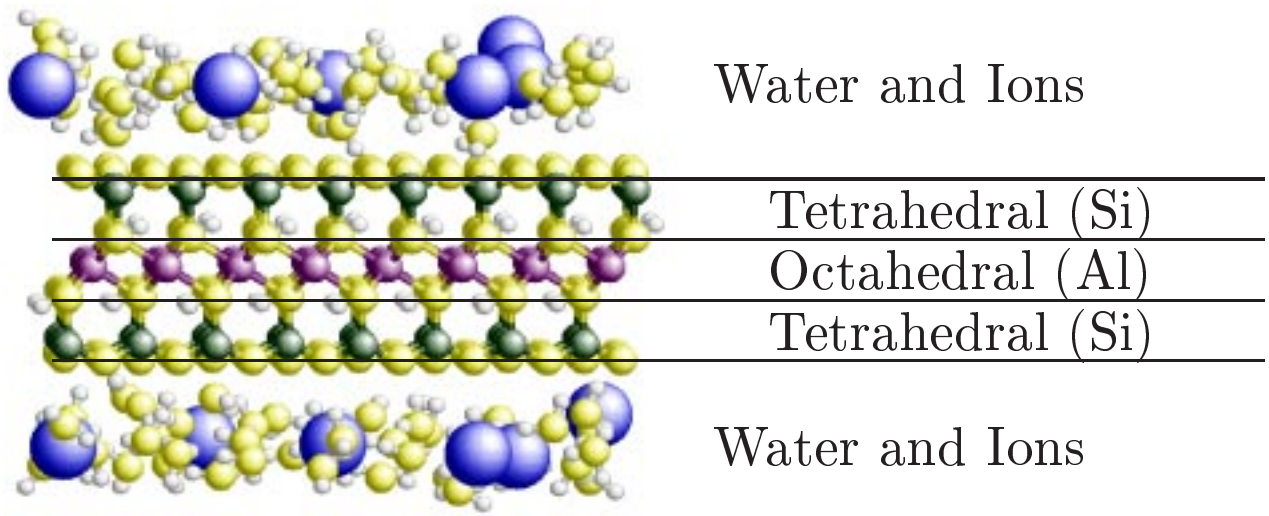
Objectives

The long-range objective of our research is the development of molecular models of swelling and ion exchange in 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 are:

- to describe procedures for molecular modeling of clay minerals including a recently-developed μVT-ensemble technique.
- to characterize swelling thermodyamics for Cs-, Na-, and Sr-substituted montmorillonites. What are the thermodynamic origins of discrete, crystalline swelling in clays? The effect of ion charge on the swelling mechanism will be described.
- to report ion exchange free energies for alkali metals on a montmorillonite clay and describe the 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.

Modeling: Overview

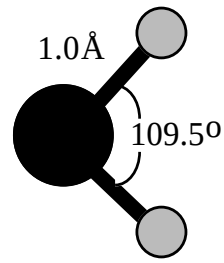
Molecular modeling of hydrated clay minerals is a relatively new field with most published work appearing within the last decade. The models used in the simulations reported here are fairly simple - a rigid clay lattice and well-characterized ion and water interaction potentials. Using this model, molecular dynamics simulations were performed under various thermodynamic constraints (ensembles):

- constant NpT: used to characterize immersion energies and swelling curves.
- constant NVT: used to investigate constant water content swelling transitions
- constant μVT: used to calculate swelling thermodynamics at fixed water chemical potential (μ)

The grand canonical ensemble (constant μVT) simulations are crucial for simulating clay minerals under environmentally relevant conditions where water content is determined by the water chemical potential (i.e. by the relative humidity or solution ionic strength).

Interaction Potentials

- Water: 'SPC/E' Model



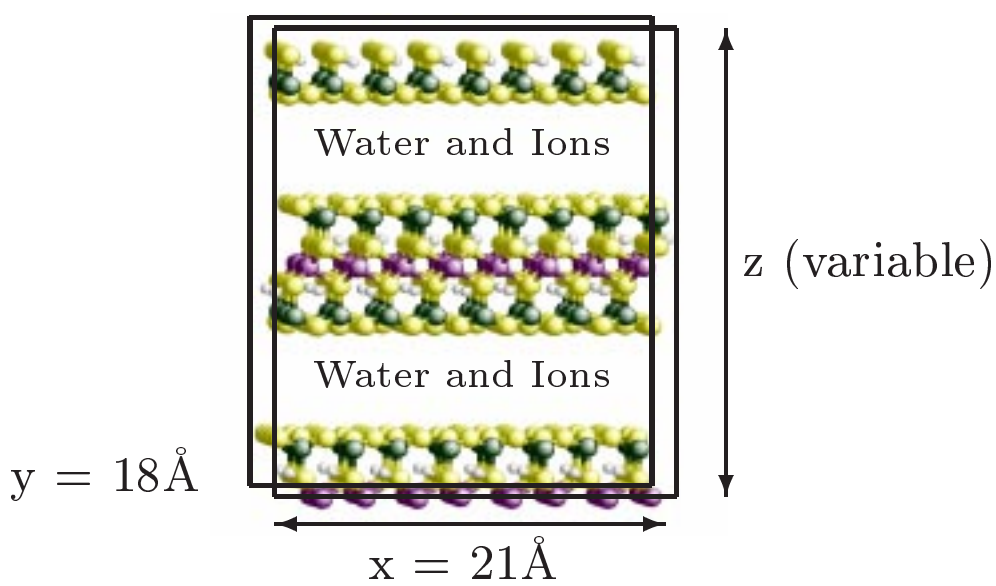
  - rigid
  - partial charges on each atom
  - Lennard-Jones (LJ) interaction centered on oxygen

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

- 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; Ewald sums
- $-0.75e$ charge per unit cell and a total of 12 charge-balancing cations; all charge in octahedral layer
- Variable interlayer spacing; registry shifts allowed
- NpT-, NVT-, and μVT-ensembles



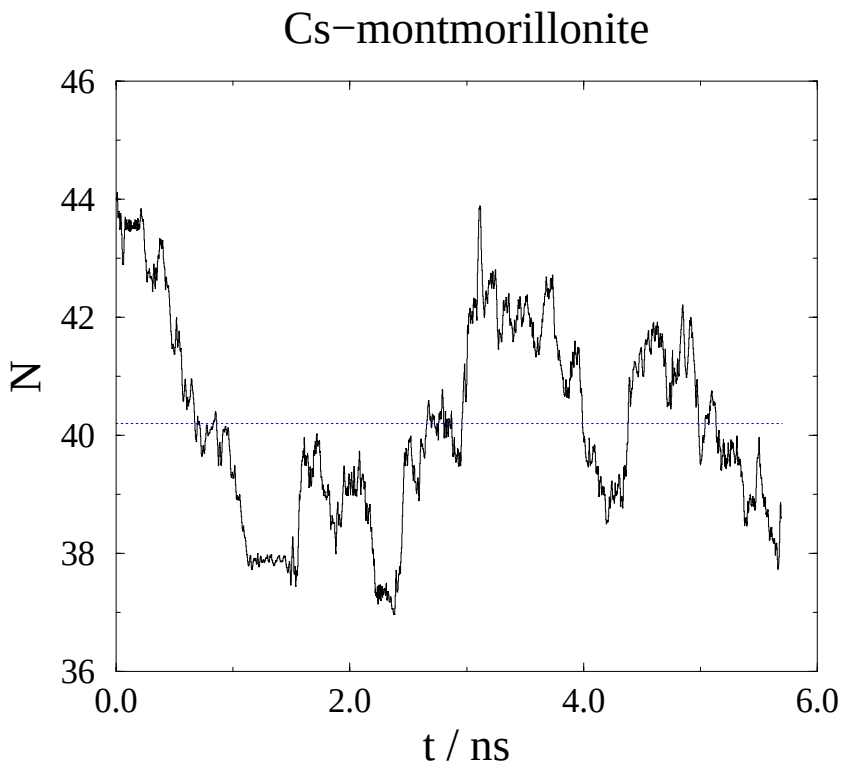
μVT-Ensemble: GMD

$$
\begin{aligned}
H^{\mu VT} &= \sum_i^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{q}) + \frac{p_s^2}{2Q} + gkT \ln s \\
&\quad + \frac{\mathbf{p}_f^2}{2m_f s^2} + U(\mathbf{q_f}) + \frac{p_\lambda^2}{2W} - (N+\lambda)\mu \\
&\quad - U_{bias}(\lambda)
\end{aligned}
$$

- In grand canonical molecular dynamics (GMD), motion of an extension variable λ yields fluctuations in N_w.[a]
- $U(\mathbf{q_f}) = \lambda U(\mathbf{q})$ couples the fractional particle to the system.
- U_{bias} improves efficiency.
- $< N_w >$ is determined by μ.

[a] R.M. Shroll and D.E. Smith, *J. Chem. Phys.*, **110**, 8295 (1999); **111**, 9025 (1999).

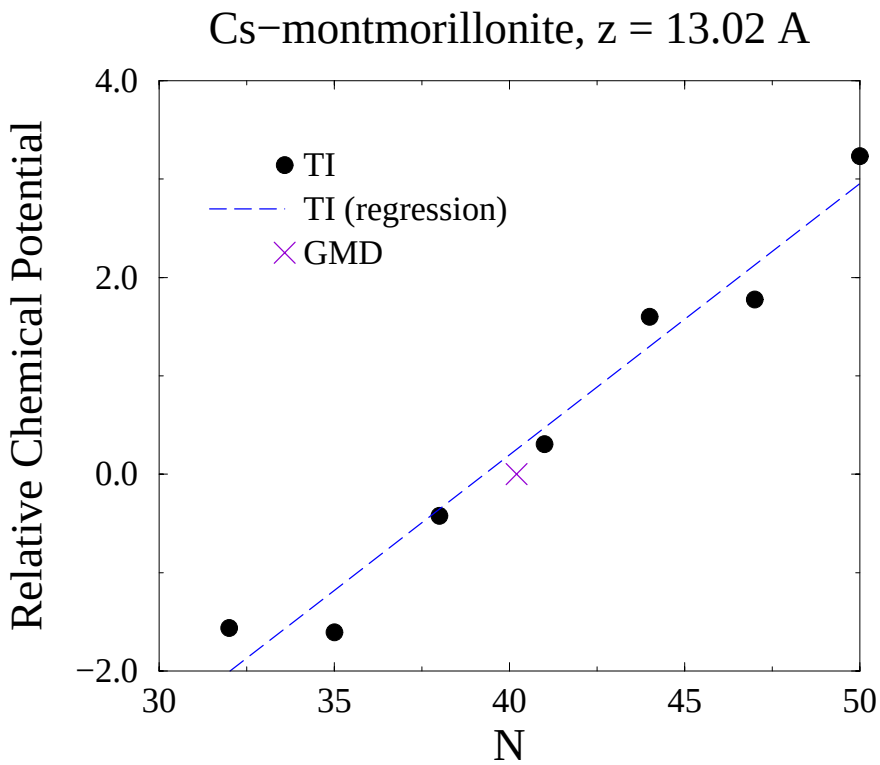
GMD Trajectory



- GMD trajectory yields water content fluctuations. For this graph, z = 13.02 Å and $\mu = \mu^o$, the bulk water chemical potential.

- Calculated water content: $< N_w > = 40.2$

GMD -vs- TI



- Results of thermodynamic integration (TI) calculations of the relative chemical potential, $\mu - \mu^o$, at various values of N_w are displayed in the graph.

- A value of $< N_w >$ determined from the GMD calculation at $\mu - \mu^o = 0$ is displayed for comparison.

- Agreement between the two methods is reasonable.

Swelling: Overview

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

The extent of swelling of clay minerals is affected significantly by interlayer ion identity. Large, low-charge ions such as cesium restrict swelling to a one-layer hydrate spacing. Na-substituted clays, in contrast, often swell macroscopically. Divalent ion substituted clays swell readily to two- or three-layer spacings, but do not swell macroscopically.

Computer simulations have been used to

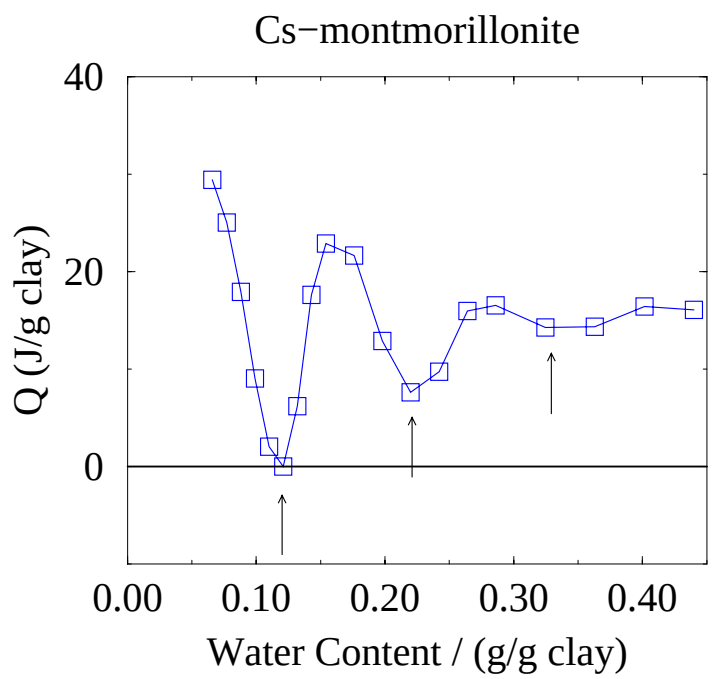
- reveal thermodynamic and structural origins of discrete swelling.
- identify two different swelling mechanisms for monovalent and divalent ion substituted clays.
- evaluate energetic and entropic contributions to swelling.

Immersion Energy

The existence of stable integer-layer states may be demonstrated through plotting the immersion energy, Q

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

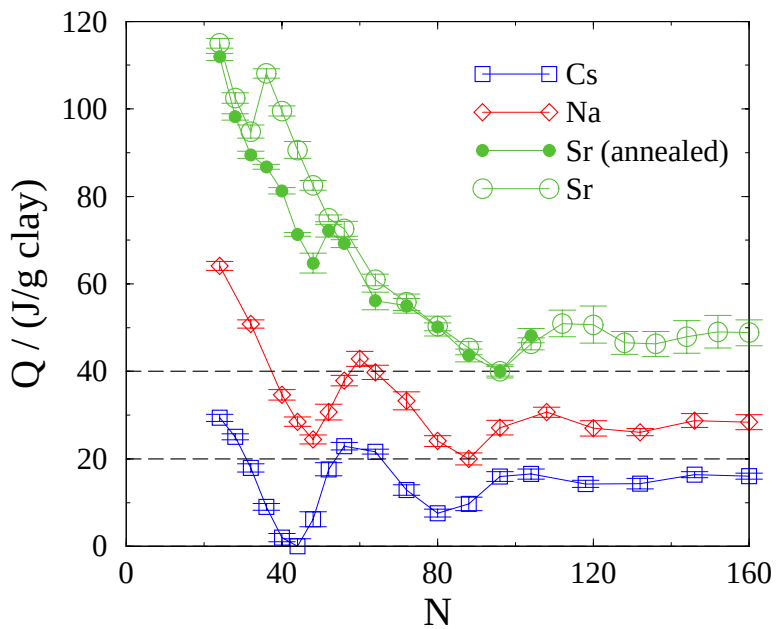
where N° is the one-layer hydrate water content.[a]



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

[a] D.E. Smith, *Langmuir* **14**, 5959 (1998).

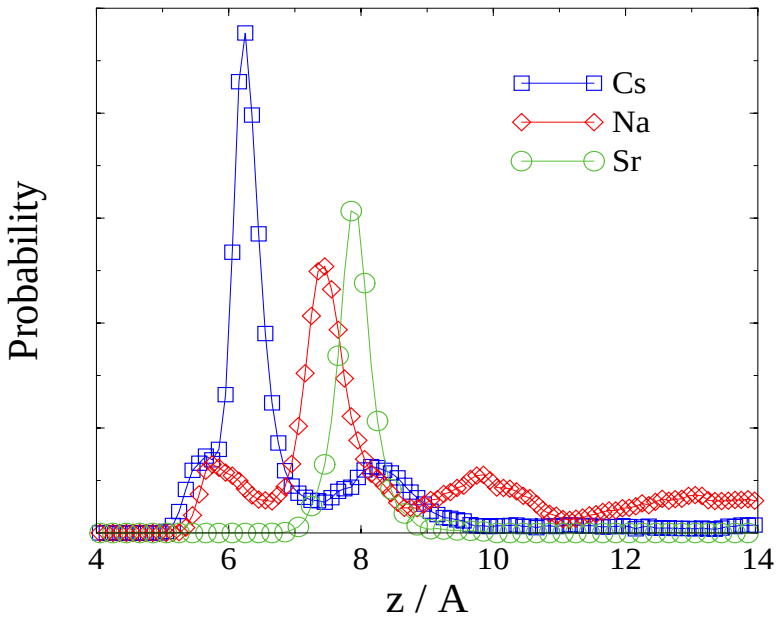
Immersion Energies: Cs, Na, and Sr



Immersion energies for all three clays show oscillations indicative of crystalline swelling. The one-layer hydrate is most stable for Cs-montmorillonite, while the two-layer hydrates are most stable for the other clays.

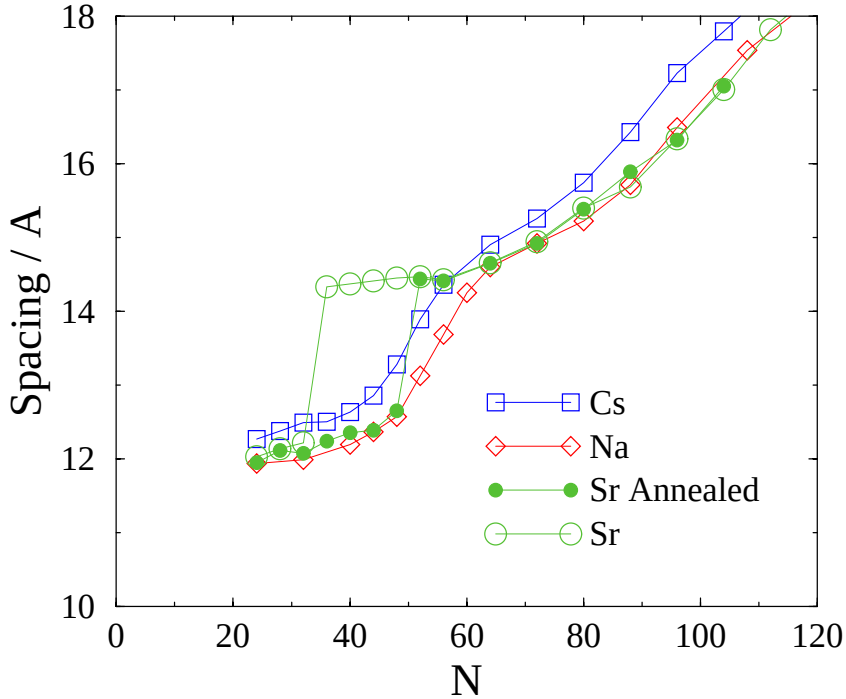
The Sr-montmorillonite curve is unique in the one-layer hydrate region, showing a discontinuous jump. Initial configurations for each point in the strontium immersion energy were generated by removing water molecules from a higher water content system followed by equilibration at 298K. The second Sr-curve was generated by annealing each starting configuration before collecting averages. This procedure yielded different results in the region of the discontinuity, suggesting that there are two stable branches to the immersion energy curve for some water contents.

Structure: Ion Density Profiles



Ion density profiles calculated for the three clays at a large interlayer spacing are displayed in this figure. The main peak for the Cs curve indicates that this ion preferentially forms an inner-sphere complex with the clay. This correlates with the energetic preference for the one-layer hydrate in Cs-clays discussed previously. Na ions most commonly form an outer-sphere complex but sometimes occupy inner-sphere states or diffuse layer configurations where the ion is dissociated !from the clay. It is thought that occupancy of diffuse-layer states provides a double-layer stabilization of osmotically swollen Na-substituted clays. Sr forms exclusively outer-sphere complexes.

Swelling Curves



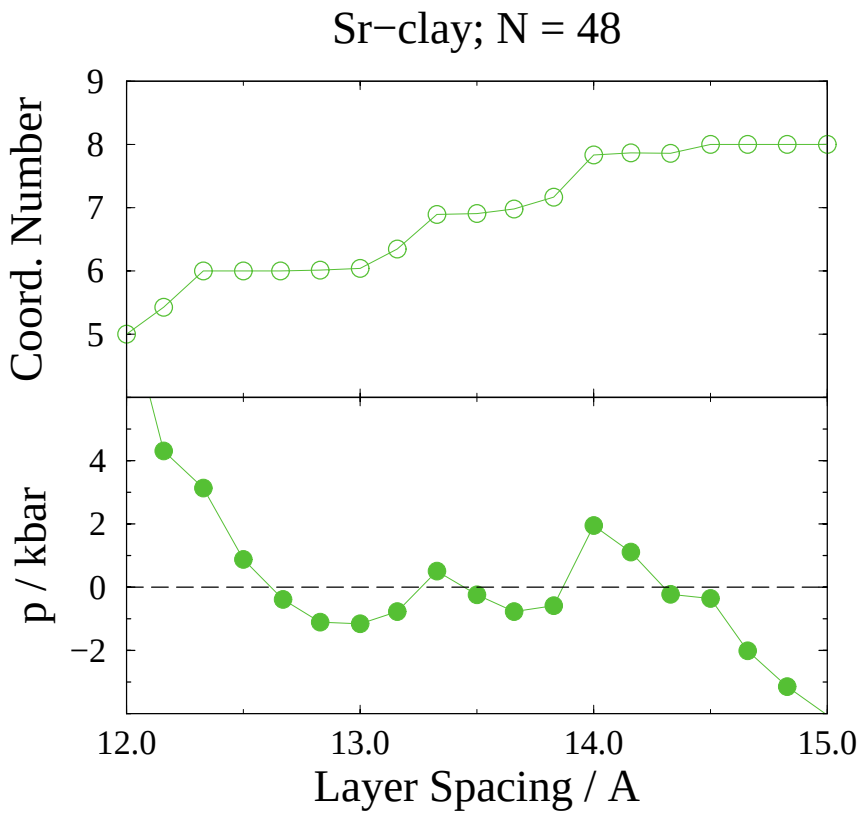
- NpT-ensemble; $p = 1$ bar; $T = 300$K

Swelling curves give a measure of the clay layer spacing, at constant pressure, for a given water content. The swelling curves shown here each show a plateau in the one-layer hydrate region. Layer spacings for the Na- and Sr-clays are smaller than for the Cs-clay at most water contents.

The Sr-clay opens up discontinuously to a two-layer spacing at N=48 (annealed) and N=36 (not annealed). The jump in spacing corresponds to the discontinuity in the Sr-clay immersion energy shown previously.

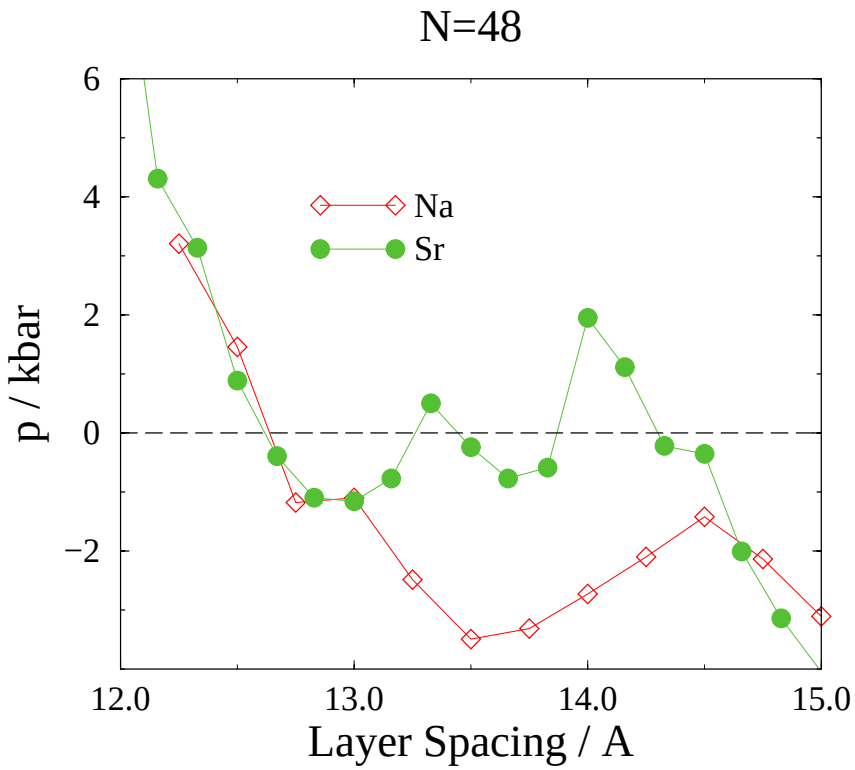
The hydration mechanism for the Sr-clay involves partially-filled expanded states and is thus different from the hydration mechanism for the monovalent ion substituted clays.

PV Isotherms



Pressure-volume isotherms are calculated at constant volume and water content. Stable states are located where the measured pressure is equal to the pressure applied normal to the clay layers. The plot indicates that, in the absence of any external pressure, there are multiple stable states at this water content. The peaks in the isotherm are clearly correlated with the strontium coordination number, also shown in the plot. The inner peak appears as the coordination number rises to 7, and the outer peak when an 8-coordinate complex is formed. Stable states at 12.6 and 14.3 Å correspond to the two branches of the immersion energy plot shown previously.

Sr -vs- Na Isotherms



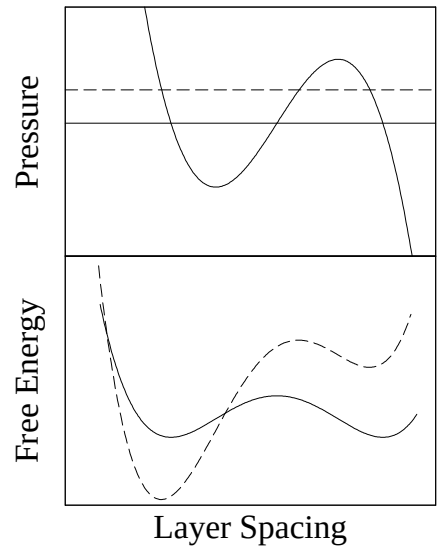
PV isotherms for Na and Sr are similar in that both curves show peaks associated with increasing ion coordination number as the clay expands. The peak for the Na isotherm at 14.5 Å does not, however, extend above the zero pressure line. As a result, partially-filled expanded states are not stable for the Na-clay. The isotherms are consistent with the immersion energy and swelling curve calculations where discontinuous expansion was observed only in the Sr-clay among those studied.

The contrasting behavior of the Na- and Sr-clays likely results from differences in ion hydration energies. As the clay expands, a larger hydration energy allows the Sr^{2+} ions to acquire full hydration shells more quickly than Na^{+} ions.

Grand Canonical Simulations

- NPT- and NVT-ensemble simulations have been used to characterize:
  - an energetic origin of discrete swelling.
  - swelling and hydration mechanisms.
- μVT-ensemble simulations are required for:
  - ion exchange calculations.
  - analysis of swelling free energies and their entropic components.
  - comparison with experimental adsorption isotherms (including hysteresis).
  - characterization of swelling phase diagrams.!

Swelling Free Energy



Thermodynamics (fixed μ_w, P_z^{ext}, T, shear):[a]

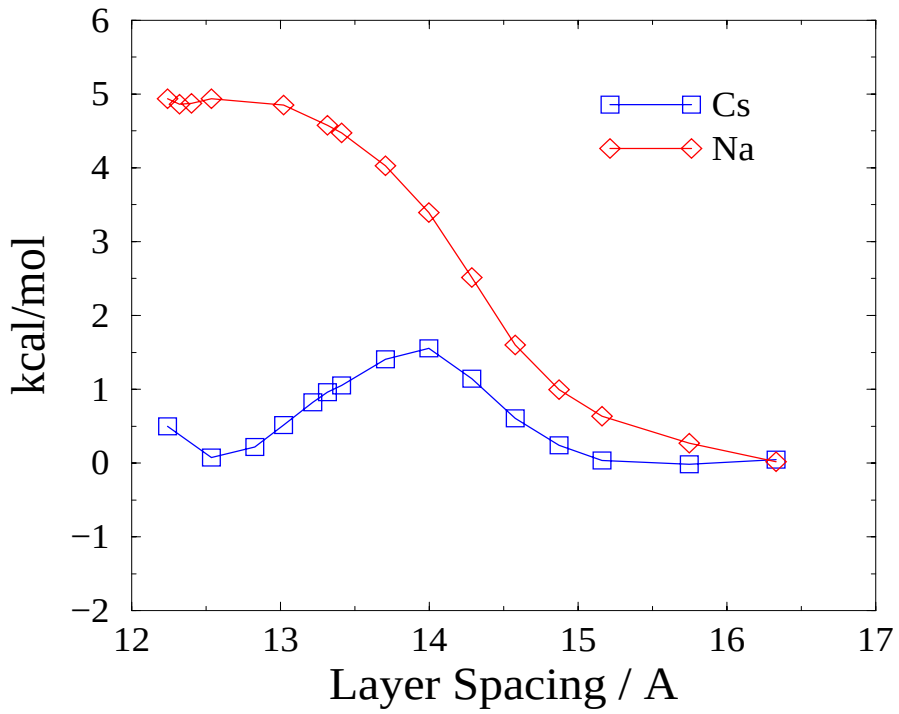
$$\Delta X(z) = -A \int \left[\Pi(z') - P_z^{ext} \right] dz'$$

$X(z)$ = 'Grand Isoforce Potential' (free energy)
Disjoining pressure: $\Pi(z) = P_z(z) - P_b(T, \mu)$

Multiple stable states result from oscillations in the P -vs- layer spacing isotherms.

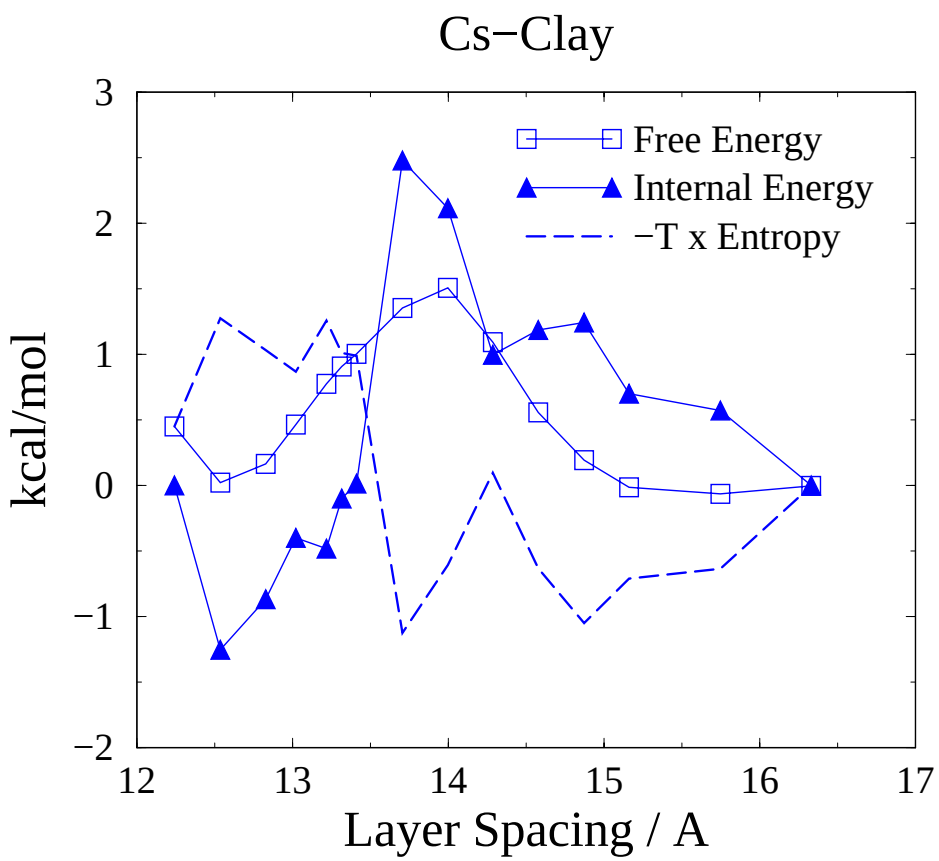
[a] D.J. Diestler *et al.*, *J. Chem. Phys.* **100**, 9140 (1994).

Swelling Free Energy



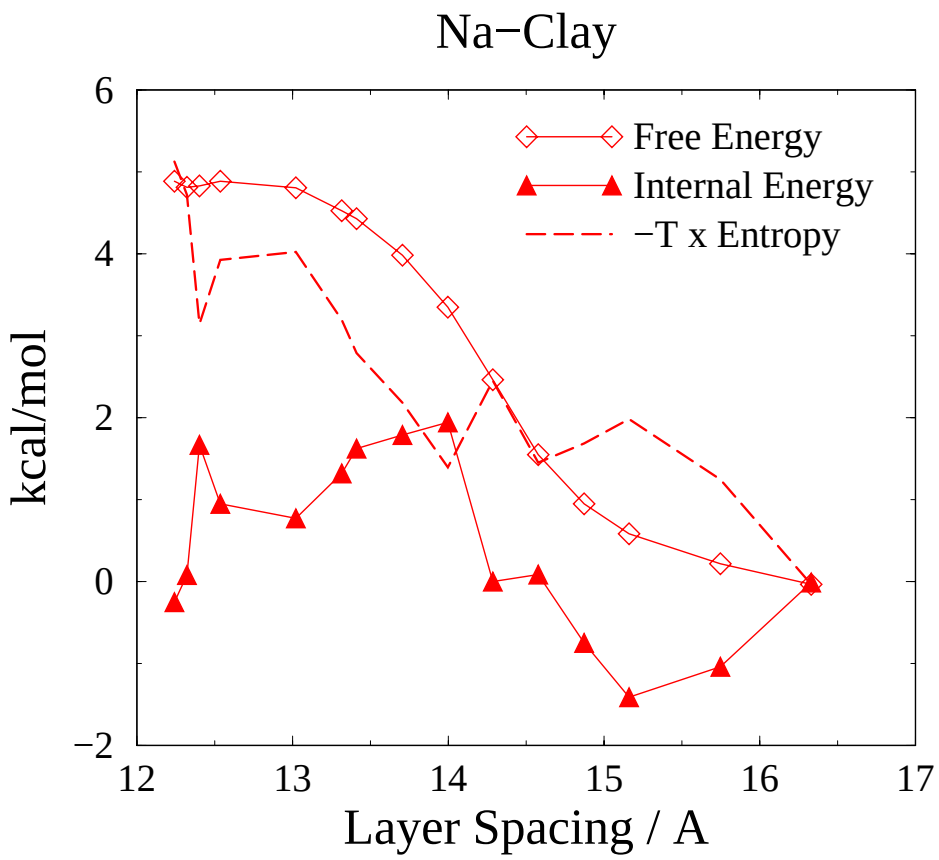
- Minima or plateaus at integer-layer spacings
- Two-layer and one-layer spacing equally favored for Cs
- $>$ two-layer spacing favored for Na
- Qualitatively consistent with experimentally observed spacings

Swelling Entropy and Energy



- Composite system (clay + external solution) quantities are reported.
- Energy favors the one-layer spacing.
- Entropy favors the two-layer spacing

Swelling Entropy and Energy

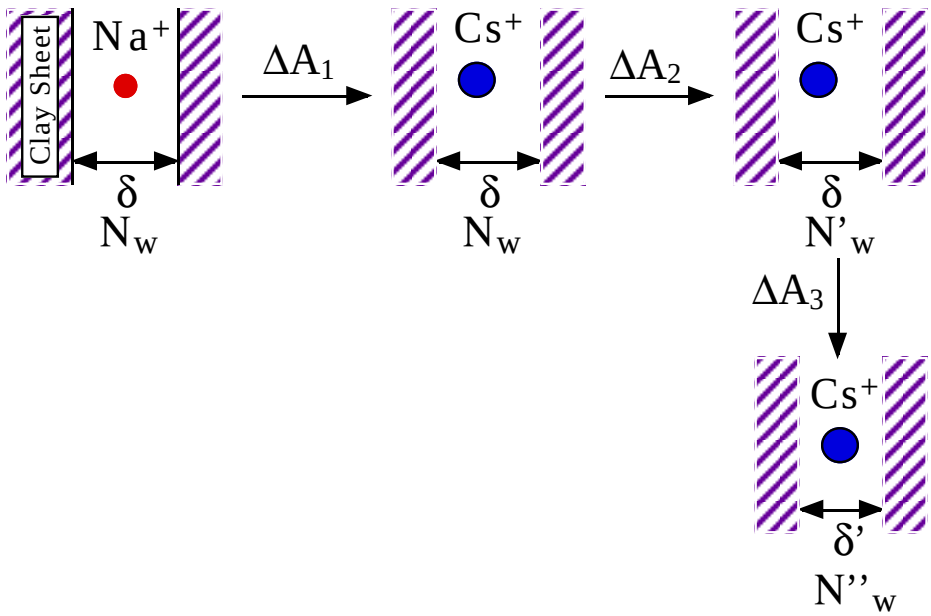


- Composite system (clay + external solution) quantities are reported.
- Entropy favors larger spacings and dominates the energy term.

Swelling: Conclusions

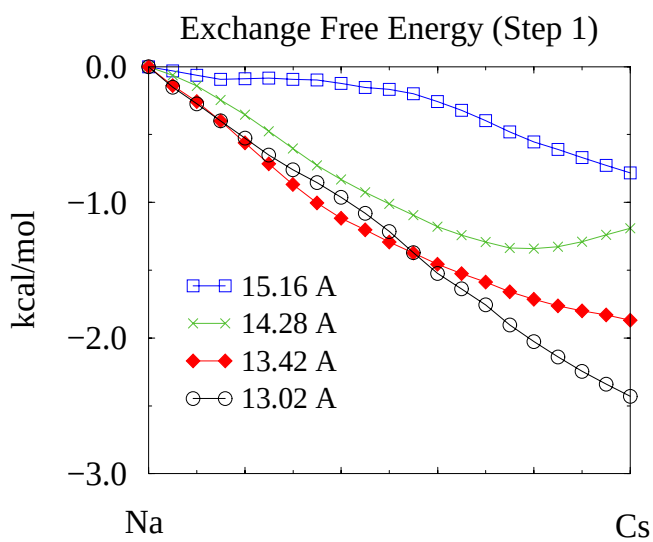
- All clays studied show hydration thermodynamics consistent with a discrete swelling mechanism.
- Simulations of the interlayer ion size and charge dependence of swelling have revealed two hydration mechanisms. Swelling and hydration are concurrent processes for monovalent ion substituted clays. For Sr-montmorillonite, in contrast, partially-filled expanded states are observed.
- For clays in contact with bulk water, entropy provides the driving force for clay expansion.
- Simulation results should be useful in the development of better predictive models for discrete clay swelling.

Exchange: Approach



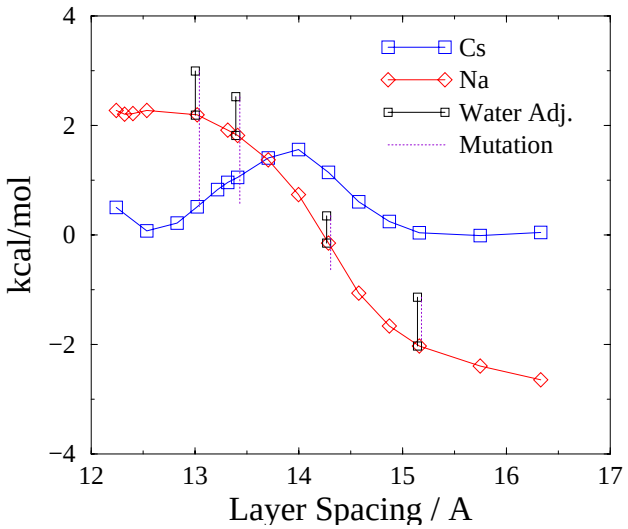
- ΔA_1: Standard thermodynamic integration technique of mutation at constant layer spacing and water content. Subtraction of $\Delta A_{1,bulk}$ is required.
- ΔA_2: 'Water adjustment' term associated with the different equilibrium water contents in the Na- and Cs-clays, calculated using a μdN integral. This step may be performed before mutation (with the Na-clay) if the mutation calculation is performed at the proper water content for the Cs-clay.
- ΔA_3: 'Swelling work' - a pdV integral if simulations are performed at $\mu = \mu^o$.

Exchange: ΔA_1



The Na→Cs exchange free energy at *fixed layer spacing and water content* is displayed above. The water content in each run was chosen to equal the equilibrium water content for Cs-montmorillonite at that spacing. The magnitude of the exchange free energy increases as the layer spacing is decreased, consistent with the preferential formation of a one-layer hydrate for Cs-montmorillonite.

Exchange: Total



- Water adjustment and mutation terms should connect the two swelling free energy curves.
- Absolute values of the free energy curves are adjusted to achieve connection at 13.02 Å spacing.
- Curves do not match up well at other spacings, indicating an error is present in at least one step of the total exchange calculation.

Exchange: Summary

Molecular simulations of ion exchange on clay minerals will assist in developing our understanding of the mechanism of radionuclide transport through soils. Simulations provide a variety of information that 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. The relative contributions of mutation and swelling to overall ion exchange free energies may also be determined and used to predict or explain ion exchange hysteresis. Calculated thermodynamic values can also be correlated directly with structural feature such as ion binding geometry or interlayer charge distribution. This information may then be used to develop improved models of ion exchange in swelling clay minerals.

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- Christina Del Rio (undergraduate)

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- Dr. Huang Shiping

Reprints, preprints, and references are available from the PI at davsmith@nmsu.edu.