FINAL REPORT
U.S. Department of Energy

MODELING OF CATION BINDING IN HYDRATED 2:1 CLAY MINERALS

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Contents

1 Executive Summary

Hydrated 2:1 clay minerals are high surface area, layered silicates that play a unique role in determining the fate of radionuclides in the environment. This project consisted of developing and implementing computer simulation methods for molecular characterization of the swelling and ion exchange properties of these minerals. Project objectives included not only this characterization, but subsequent analysis and theoretical modeling with a view toward improving contaminant transport modeling as well as soil remediation and radionuclide containment strategies. Major accomplishments of the project include:

- development of simulation methods to treat clays under environmentally relevant conditions of variable water vapor pressure.
- calculation of clay swelling thermodynamics as a function of interlayer ion size and charge. Calculated quantities include immersion energies, free energies, and entropies of swelling.
- calculation of ion exchange free energies including contributions from changing interlayer water contents and layer spacings.

While this research has several potential implications for DOE environmental management problems, it has had little immediate practical impact. The project from its inception consisted mostly of 'broad fundamental research' rather than 'needs-driven' development. Potential practical applications of the research stem from the eventual development of improved theoretical models for swelling and ion exchange in clays. Development of these theoretical models is possible only after simulation methods are derived and implemented, and results fully collected. While significant progress was made, the project objectives in this respect were not fully achieved. This was due primarily to the inefficiency of a simulation approach that was attempted initially. A better, alternative approach was developed only in the last months of the project period. We will continue the research in the hopes that it may eventually have both the fundamental and practical impact initially envisioned.

Collaborative work on this project was restricted to student and postdoctoral researchers. One thesis (D.A. Young) is currently in preparation and should be available later this spring.

2 Research Objectives

Hydrated 2:1 clay minerals are high surface area, layered silicates that play an important and unique role in determining the fate of pollutants in the environment.[1–4] Ionic radionuclides may displace interlayer cations from the clay and bind, sometimes irreversibly, to the negative charge sites on the clay layers. Swelling of clay minerals upon contact with water also significantly impacts soil hydrodynamics and thus influences radionuclide transport and soil remediation processes.

While many qualitative or macroscopic aspects of ion-clay interactions are well characterized, the molecular nature of these systems is still poorly understood. This is in part due to the compositional complexity of the environmental clay minerals. This molecular complexity suggests a need for the development of molecular models of clay behavior. The specific objectives of this research involve using computer simulations to improve our molecular understanding of swelling and ion exchange, and to use information from simulations to begin developing improved theoretical models of these processes. Specific research objectives are given below.

2.1 Simulation model development and validation

Adequate first-generation simulation models for clay minerals already existed at the start of this research project.[5–7] Simulation objectives included adaptation of one of these models[7] for use with a molecular dynamics simulation code developed by the PI,[8] development of an efficient grand canonical ensemble (constant chemical potential) simulation model for use with clay minerals, and validation of the simulation model through comparison with experiment. This latter goal is most challenging due to compositional complexity and interference from external surface effects in the environmental clay systems.

2.2 Crystalline swelling: Simulations and theoretical modeling

This objective was not specified separately in the original proposal, but formed instead a key part of the ion exchange objective. At low water contents, in the 'crystalline' swelling regime, 2:1 clay minerals expand in a discrete fashion through the sequential formation of integer layer hydrates. This fact has been established experimentally,[9–13] but is not well understood on a molecular level beyond simple notions of solvent layering. Experimental investigations of crystalline swelling are difficult to interpret microscopically due to layer-charge inhomogeneities and external surface effects. As a result, existing models for clay swelling, reviewed recently by Laird,[14] generally neglect molecular aspects of the process that are directly related to the stepwise nature of clay expansion. Models of clay swelling could therefore benefit significantly from the incorporation of molecular information. Computer simulations provide a logical route for obtaining such information as they allow for complete control of clay composition, the elimination or explicit treatment of external surface effects, and complete information on molecular structure and dynamics. A primary objective of our simulations then was to characterize the molecular origins of crystalline swelling phenomena including how layer charge distributions and interlayer ion identity influence swelling. For example, why do Cs^+ and Na^+ respectively inhibit and enhance clay swelling? What is the origin of hysteresis in clay swelling? How does swelling affect interlayer ion diffusion? An

additional objective following characterization via simulations was to begin the development of improved theoretical models for swelling, models that might be used in codes for predicting contaminant transport.

2.3 Ion exchange: Simulations and theoretical modeling

Interlayer ion exchange on clay minerals provides a mechanism for substantial uptake of radionuclides in the environment. As with crystalline swelling, a great deal of macroscopic information about ion exchange phenomena is available,[15–17] but molecular details of the exchange process are not well characterized. Existing models of ion binding, reviewed recently,[15,18] are based either on simple electrostatic descriptions of ion-water and ion-clay interactions or upon empirical hard and soft acid and base concepts. They do not account explicitly for the intimate relationship between ion exchange and clay hydration, nor for hysteresis that is often observed in ion exchange measurements.[19,20] Development of improved models for ion exchange requires knowledge of clay layer-charge distributions, the structure of the ion-clay complexes, and how these correlate with exchange free energies. Two objectives of this research project were to generate this information from computer simulations, and to predict ion adsorption properties for any individual clay directly from its molecular structure. The hope is that, when completed, this will impact radionuclide transport modeling.

2.4 Interlayer ion mobility and binding sites

The residence times of cations bound to clay surfaces or in clay interlayer regions may be determined experimentally through the use of NMR and ESR techniques.[21,22] Diffusion in clay interlayers is quite slow and thus difficult to measure directly. Free energy simulation methods, however, provide an alternate route to this information. A final objective of this research then was to characterize lateral free energy profiles, and thus diffusion rates, for interlayer ions as a function of clay spacing and hydration.

3 Methods and Results

3.1 Methods

Simulation methods are described in full detail in two publications,[23,24] and will be summarized only briefly here. Most simulations were performed using a molecular dynamics (MD) code that was developed originally by the PI.[8] A few of the most recent calculations made use of a new Monte Carlo (MC) code developed in our group near the end of the project period. Water was represented by the extended simple point charge (SPC/E) model, with ions treated as charged Lennard-Jones (LJ) spheres. Solution simulation parameters are given in Table 1. The potential energy of the interlayer solution due to water-water and ion-water interactions is given by

$$U = \frac{1}{2}\sum_i \sum_j{}' \Big\{ 4\epsilon \Big[\Big(\frac{\sigma_{ij}}{r_{ij}}\Big)^{12} - \Big(\frac{\sigma_{ij}}{r_{ij}}\Big)^{6} \Big] + \frac{q_i q_j}{r_{ij}} \Big\}, \tag{1}$$

where the j summation is taken over all atoms except those in the same molecule as atom i. The ion-oxygen cross interaction terms in the LJ potential are generated using the usual combining rules:

$$\sigma_{ij} = \frac{1}{2}\Big(\sigma_i + \sigma_j\Big) \tag{2}$$

$$\epsilon_{ij} = \Big(\epsilon_i \epsilon_j\Big)^{1/2}. \tag{3}$$

Montmorillonite clay minerals were modeled as rigid layers following Skipper and co-workers.[5,7,25] Individual clay sites were represented by charge plus Lennard-Jones interactions, with parameters again given in Table 1.

Table 1: Solution and Clay Simulation Parameters

Solution				
	element	σ/Å	$\epsilon/kJ \cdot mol^{-1}$	q/e
	O	3.166	0.650	-0.848
	H	0.000	0.000	0.424
	Na	2.350	0.544	1.000
	Cs	3.830	0.418	1.000
	Sr	3.341	0.418	2.000
Clay				
Layer	element	σ/Å	$\epsilon/kJ \cdot mol^{-1}$	q/e
Tet.	O	3.166	0.650	-0.800
	Si	1.840	13.18	1.200
	Al	1.840	13.18	0.200
Apical	O	3.166	0.650	-1.000
Oct.	O	3.166	0.650	-1.424
	H	0.000	0.000	0.424
	Al	0.000	0.000	3.000
	Mg	0.000	0.000	2.000

Initial investigations involved a montmorillonite clay with 1/3 of its layer charge in the outer, tetrahedral sheet. The model for these tetrahedral substitution sites was later deemed to be inadequate,[26] and subsequent simulations treated clays with all octahedral layer charge.

Various simulations were performed in NpT, NVT, and μVT (grand canonical) ensembles, where the variables indicate the thermodynamic constraints. NpT-ensemble simulations allow the clay spacing at a given water content to vary depending upon the pressure applied perpendicular to the clay sheets. NVT-ensemble simulations were used to characterize swelling transitions in Sr-montmorillonite associated with partially-filled expanded states. Grand canonical ensemble runs most closely resemble experimental systems where the degree of clay hydration is variable depending on the chemical potential of the surrounding water. Considerable effort was devoted to developing reliable MD and MC methods for grand canonical ensemble simulations.[24]

3.2 Results: Swelling thermodynamics

Clay swelling thermodynamics have been characterized using a variety of calculated quantities including immersion energies[23] and free energies.[27] Immersion energies are calculated from NpT-ensemble simulations and may be compared qualitatively with experimental immersion enthalpies. Swelling free energies are calculated by integration of the pressure measured in μVT simulations as a function of clay spacing.

The simulated immersion energy, Q, is calculated from

$$Q = \left\langle U(N) \right\rangle - \left\langle U(N^\circ) \right\rangle - \left(N - N^\circ\right) U_{bulk}, \tag{4}$$

where $\langle U(N^\circ) \rangle$ is the average energy of the clay at a reference hydration state N°, to be specified, and $U_{bulk} = -41.4 kJ \cdot mol^{-1}$ is the mean interaction energy of bulk SPC/E water. Immersion energies have generally been found to exhibit oscillations indicative of stepwise swelling, i.e., swelling through the formation of discrete integer-layer hydrates. This is illustrated in Fig. 1.[26] Minima in the immersion energy curves correspond to energetically preferred states and may be identified, albeit approximately, with integer-layer hydrates. Inclusion of entropic contributions to swelling must be made for a quantitative determination of the water content associated with particular integer-layer states.

Several trends are evident in Fig. 1. The magnitude of the immersion energies at the smallest water content ($N = 24$) increases with increasing hydration energy ($Cs^+ < Na^+ < Sr^{2+}$). This is in qualitative agreement with experimentally measured immersion enthalpies for dry clays.[12,13] Also consistent with experimental measurements is the stability of the two-layer hydrate relative to the one-layer state. The two-layer hydrate is favored as hydration energy increases such that the one-layer state is preferred only for Cs-montmorillonite. Finally, the immersion energy minima shift outward in the same sequence. This suggests that the water content of a given integer-layer hydrate can depend significantly upon the interlayer ion identity. This behavior may be associated with a decrease in partial molar volume of the ions with increasing hydration energy,[28] thus increasing the number of water molecules required to form an integer layer.

The immersion energy for Sr-montmorillonite is unique in the one-layer hydrate region. The non-annealed Sr curve shows a discontinuous jump in Q at $N = 32$, whereas the annealed results show a similar jump at $N = 48$. The jumps correlate with a layer-spacing transition from $\sim$12.5Å to $\sim$14.5Å. The results indicate that there are two stable branches of the

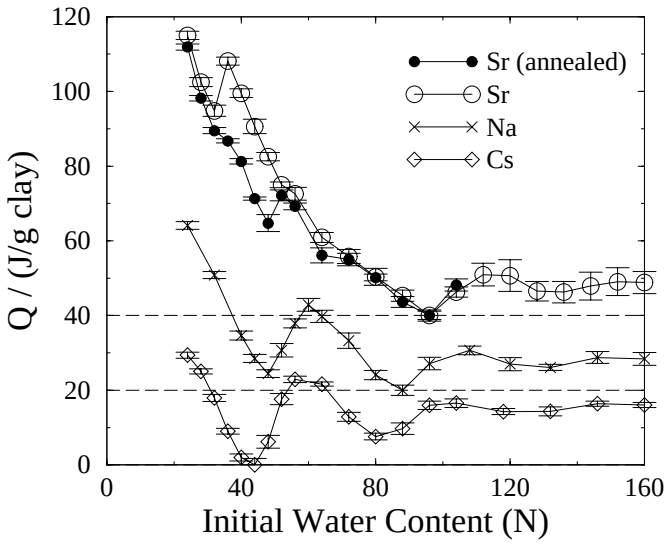

Figure 1: Immersion energies for Cs-, Na-, and Sr-montmorillonites. Curves for Na and Sr are displaced for clarity, with dashed lines corresponding to the curve minima. Error bars indicate 95% confidence limits.

immersion energy in the one-layer hydrate region. Hydration and dehydration processes occur discontinuously, as in a phase transition, through jumps between the two branches. The observed dependence upon annealing, reminiscent of hysteresis in experimental systems, results from trapping in a metastable portion of one or both branches around the equilibrium transition point. This behavior was investigated further through a series of NVT-ensemble simulations in which the swelling pressure of Sr-montmorillonite was measured as a function of clay spacing. Results are displayed in Fig. 2. The swelling pressure exhibits peaks that correlate clearly with increases in Sr coordination number. The outer peak extends well above the zero pressure line and allows for the formation of partially-filled expanded states. The inner and outer stable states, at 12.6 and 14.3 Å respectively, correspond to the two branches of the immersion energy discussed above. The large hydration energy for Sr^{2+} leads to the formation of hydrated Sr^{2+} 'pillars' that prop the clay open, and results in unique partially-filled expanded states for the Sr-clay.[26] A snapshot of one of these partially-filled states is displayed in Fig. 3. Similar partially-filled states were not observed for Cs- or Na-montmorillonite, suggesting that the mechanism for hydration and swelling of clay minerals is qualitatively different for monovalent and divalent ion substituted clays.

Although immersion energy and other fixed-N simulations reveal many interesting features of the clay swelling process, they cannot yield quantitative information on stable swelling states for clays. This is due both to the neglect of entropic effects and the unknown water chemical potentials in fixed-N simulations. Stable swelling states for a given clay model can be determined directly using grand canonical ensemble simulations.[27] In these calculations, the water chemical potential is set to its desired value (the bulk water value in the simulations described below) and P_{zz}, the pressure normal to the clay sheets, is measured as a function of clay spacing, s_z. The function $P_{zz}(s_z)$ is then integrated to yield the swelling

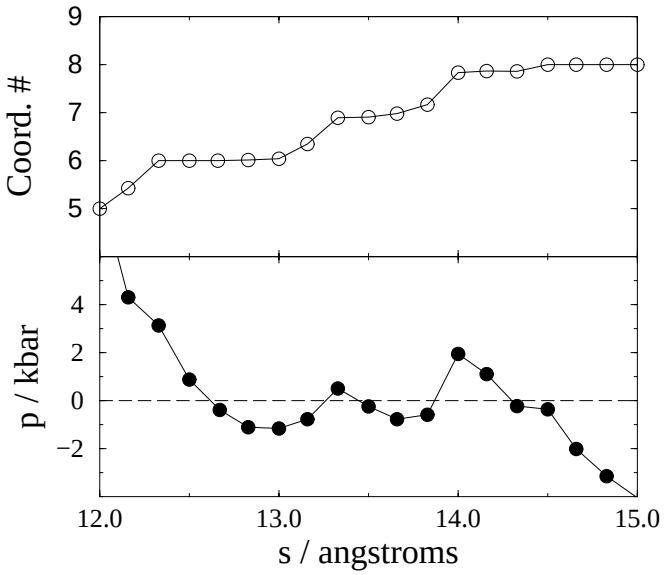

Figure 2: Swelling pressure for Sr-montmorillonite (lower plot), with a water content of N=48, measured as a function of layer spacing, s_z. Peaks in the swelling pressure are associated with changes in the Sr coordination number (upper plot). Mechanically stable states occur at spacings of 12.6, 13.4, and 14.3 Å.

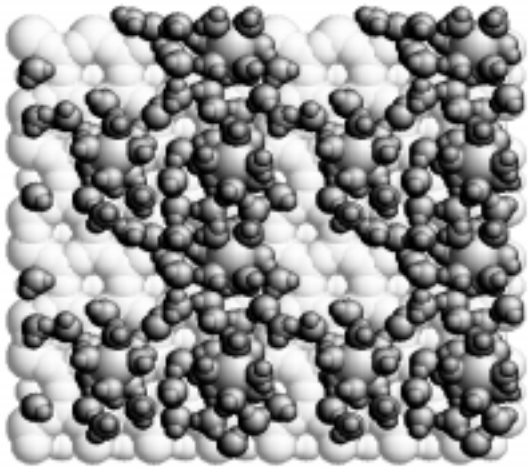

Figure 3: Snapshot of a partially-filled expanded state of Sr-montmorillonite. The perspective is looking down on the clay surface, with the upper clay sheet removed for clarity. Four periodically replicated images of the clay are displayed to more clearly reveal regions of filled and empty space. The eight-fold coordination of Sr^{2+} ions is also apparent.

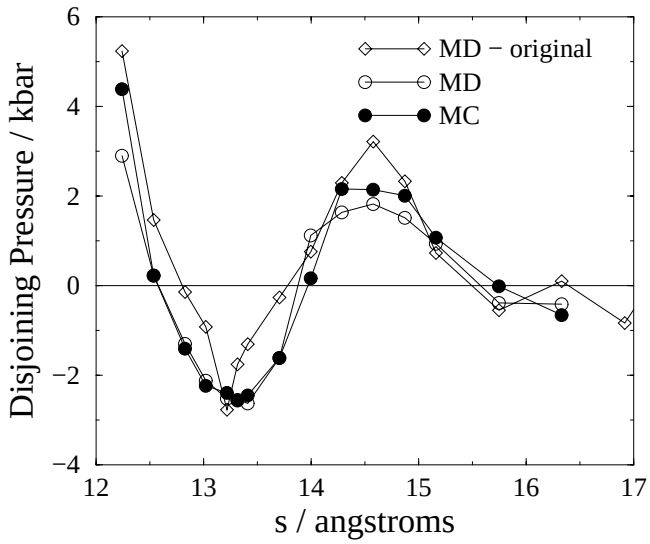

Figure 4: Disjoining pressure, Π, plotted as a function of clay layer spacing. Mechanically stable spacings with zero external pressure correspond to the crossing points, where the pressure is equal to the external pressure. The original MD run allowed free registry motion, while subsequent MD runs and MC runs restricted registry motion to a small area.[26]

free energy ΔX,

$$\Delta X = X(s_z) - X(s_z^o) = -A \int_{s_z^o}^{s_z} [P_{zz}(s_z') - P_{zz}^{app}]\, ds_z' \tag{5}$$

where A is the area of the clay sheet and P_{zz}^{app} is the sum of the external pressure applied perpendicular to the clay sheets and the bulk pressure p_b of the solution solution in contact with the clay. In the absence of any external pressure, this equation reduces to

$$\Delta X = -A \int_{s_z^o}^{s_z} \Pi(s_z') ds_z' \tag{6}$$

where $\Pi = P_{zz} - p_b$ is the 'disjoining pressure'. Disjoining pressures measured for a Cs-montmorillonite using both grand canonical MD and MC simulation codes are displayed in Fig. 4. All of the displayed curves show oscillations indicative of a stepwise swelling process that occurs through layer-spacing transitions. The 'original' data in the plot are from Shroll and Smith,[27] and were calculated allowing registry motions over a wide range of possible configurations. Registry motions are quite slow and were therefore restricted to a small area in subsequent simulations. This assures a more valid comparison between different clay systems. The registry restriction led to a small yet significant change in the measured swelling pressure. Results from the recently developed MC code performed under similar registry restrictions agree well with the MD data.

Disjoining pressures measured for a Na-montmorillonite using both grand canonical MD and MC simulation codes are displayed in Fig. 5. Registry motions were restricted for both of these systems. Unlike for Cs-montmorillonite, there is substantial disagreement between MD and MC results. Although this discrepancy is still being investigated, evidence in two

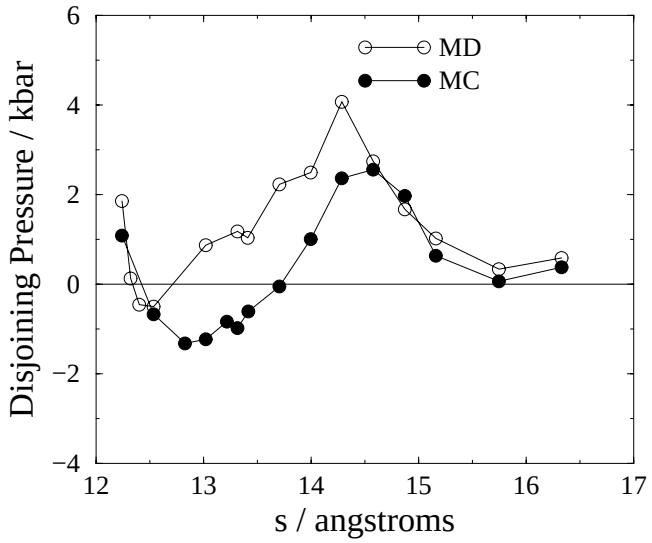

Figure 5: Disjoining pressure, Π, plotted as a function of clay layer spacing. Mechanically stable spacings with zero external pressure correspond to the crossing points, where the pressure is equal to the external pressure. Registry motions were restricted to a small area for both systems.

forms suggests that the MC results are more reliable. First, the MC method is significantly more efficient at approaching equilibrium and sampling particle number fluctuations around equilibrium. Second, as will be described below, ion exchange calculations are internally consistent only with the MC result. Our belief is that the MD method is more prone to trapping in metastable states far removed from equilibrium. Such states should be more prevalent in Na-montmorillonite than in Cs-montmorillonite due to the strong ion-water and ion-clay interactions in the Na clay. Discussion of grand canonical ensemble simulations will be restricted to MC results for most of the remainder of this report.

Swelling free energies determined by integration of the MC disjoining pressures are displayed in Fig. 6. It is well-established experimentally that Cs^+ and Na^+ have an opposite influence on clay swelling, with Cs^+ inhibiting and Na^+ enhancing swelling.[12,29] The data displayed in Fig. 6 are consistent with this finding. The Cs-montmorillonite curve shows two distinct minima, of almost equal free energy, that correspond to one-layer and two-layer hydrates. The layer spacing of 12.5Å and water content of N=38 agree reasonably well with experimental measurements of hydrated Cs-montmorillonites.[12,29] In contrast, the one-layer hydrate minimum for the Na-montmorillonite is clearly less stable than the two-layer state, and swelling even beyond the two-layer state is likely.

Swelling free energies calculated from the simulations may be readily decomposed into energetic (ΔE) and entropic ($-T\Delta S$) components. Results of such a decomposition are displayed in Fig. 7. It is evident that the noise for the free energy is significantly smaller than for the energy and entropy. This is typical of free energy decompositions in simulations.[30] The energy curve rises sharply upon expansion to 14Å, while the entropy curve decreases. This suggests that expansion is entropically favorable even in this barrier region. While the free energy is continuous, there is a discontinuity of uncertain origin evident in both the energy and entropy curves between 14.0 and 14.3Å. This feature occurs in a similar,

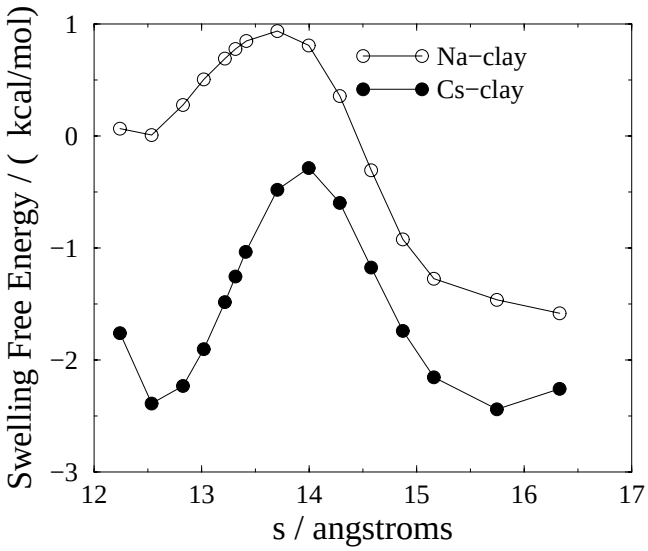

Figure 6: Swelling free energies, ΔX, plotted as a function of clay layer spacing. The free energy minima correspond to stable swelling states for the clays. The vertical placement of the curves is chosen for viewing convenience only as absolute values of the free energy are not known

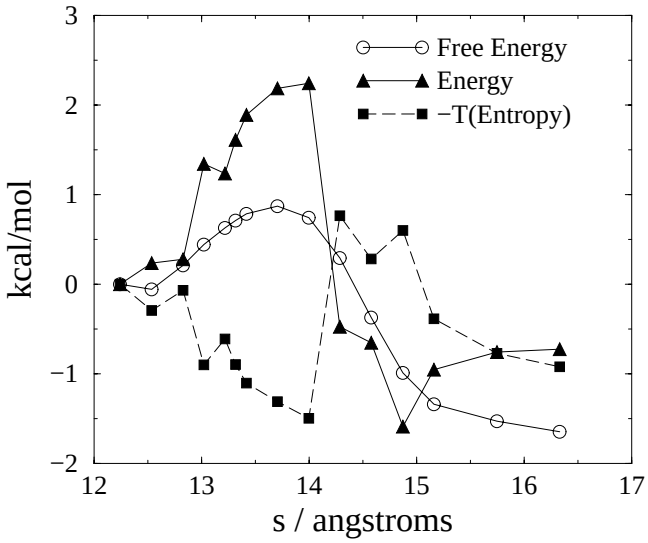

Figure 7: Decomposition of the swelling free energy, ΔX, for a Na-montmorillonite into its energetic and entropic components. The energy and entropy correspond to ΔE and -TΔS for the combined clay/solution system. All curves are set arbitrarily to zero at the smallest spacing.

albeit more subtle, fashion in the Cs-clay. Expansion is entropically driven beyond this spacing. Further analysis of these results is in progress and should yield new insights into the molecular origins of clay swelling behavior.

3.3 Results: Ion exchange

Ion exchange processes in clays are complicated by the fact that interlayer water content and clay layer spacings depend significantly upon the interlayer ion identity. Traditionally, simulation methods use an NVT- or NpT-ensemble mutation approach to calculate free energy differences between ions in bulk water or aqueous solutions.[31] Such calculations provide one part of the three-part approach to ion exchange in clay minerals used here:

$$\Delta A_{tot} = \Delta A_{mut} + \Delta A_{wc} + \Delta X \tag{7}$$

Each of the three steps will now be discussed in more detail:

ΔA_{mut}**:** Beginning with Cs-montmorillonite at a selected layer spacing and its equilibrium water content at that spacing, a $Cs^+ \rightarrow Na^+$ mutation calculation is performed using the standard thermodynamic integration procedure:[31]

$$\Delta A_{mut}^{\text{clay}} = \int_0^1 d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda \tag{8}$$

where λ is a coupling parameter that changes the ion identity from Cs^+ to Na^+ as it varies from 0 to 1. The free energy for the opposite mutation, $Na^+ \rightarrow Cs^+$, in bulk water is added to the clay quantity to yield ΔA_{mut}. This completes the exchange process, except that the water content in the now Na-montmorillonite is not at its equilibrium value.

ΔA_{wc}**:** The free energy associated with the change in water content in Na-montmorillonite following exchange is calculated from

$$\Delta A_{wc} = \int_{N_{Cs}}^{N_{Na}} [\mu(N) - \mu_{\text{bulk}}]\, dN \tag{9}$$

where $\mu(N)$ is the water chemical potential in the Na-montmorillonite, μ_{bulk} is the bulk water chemical potential, N is the clay water content, and N_{Cs} and N_{Na} are the equilibrium water contents for the Cs- and Na-clays, respectively. The function $\mu(N)$ is determined for Na-montmorillonite using a grand canonical ensemble simulation.

ΔX**:** Swelling free energies such as displayed in Fig. 6 are then used to determine the swelling contribution to the exchange free energy. Each clay can be transformed to its equilibrium spacing (and water content) by moving along the swelling free energy curve to its minimum.

The absolute values of the swelling free energies displayed in Fig. 6 are unknown. The calculations of ΔA_{mut} and ΔA_{wc} determine the relative swelling free energies of the two curves at a given spacing. If these calculations are repeated at two or more spacings, the

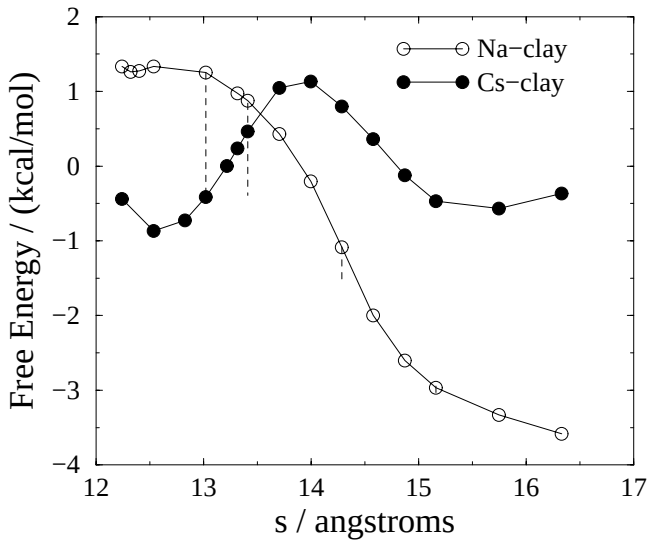

Figure 8: Solid lines correspond to MD swelling free energies, ΔX, plotted as a function of clay layer spacing. Dashed lines correspond to $\Delta A_{mut} + \Delta A_{wc}$ calculated from and MD simulations at each spacing. The dashed line at $s_z = 15.16$Å is only 0.1 kcal/mol in length, and is thus difficult to see. Note the the dashed lines do not consistently bridge the free energy curves, indicating a thermodynamic inconsistency in the MD calculation.

data provide an internal consistency check on the calculations. That is, the free energy difference between the two swelling free energy curves should correspond, within statistical uncertainty, to $\Delta A_{mut} + \Delta A_{wc}$ at *every* spacing. This follows from a fundamental property of thermodynamic state functions asserting that the change in value of a state function for any cyclical process must be zero.

NVT-ensemble mutation calculations were performed at spacings of 13.02, 13.41, 14.28, and 15.16Å. Water contents were chosen to match the equilibrium water content for Cs-montmorillonite as determined from the grand canonical MD simulation. ΔA_{wc} was determined for the Na-montmorillonite at the same spacings. Results are displayed in Fig. 8, with the dashed lines giving $\Delta A_{mut} + \Delta A_{wc}$ at each spacing. The solid curves correspond to $\Delta X(s_z)$ calculated from the MD runs. The absolute value of the ΔX curves are adjusted such that the dashed line exactly bridges the two curves at 13.02Å. It is evident that this calculation is not internally consistent as the dashed lines do not bridge the two curves at the larger spacings. Since statistical uncertainties should be < 0.5 kcal/mol, the calculations clearly contain some error. This was the status of these calculations approximately one year ago. Since that point, the ion exchange portion of the project has been on hold pending identification and elimination of this error.

We now believe that inefficiencies of the grand canonical MD algorithm account for the thermodynamic inconsistency of the MD ion exchange calculation. Preliminary results for the analogous grand canonical MC calculation are displayed in Fig. 9. ΔA_{mut} values discussed above were used without modification as the NVT-ensemble MD runs are likely accurate. The ΔA_{wc} terms have not yet been calculated but are likely small and similar for each spacing. Thus they have been neglected here. Results show clear internal consistency, lending support to our assertion that, for grand canonical simulations, the MC method

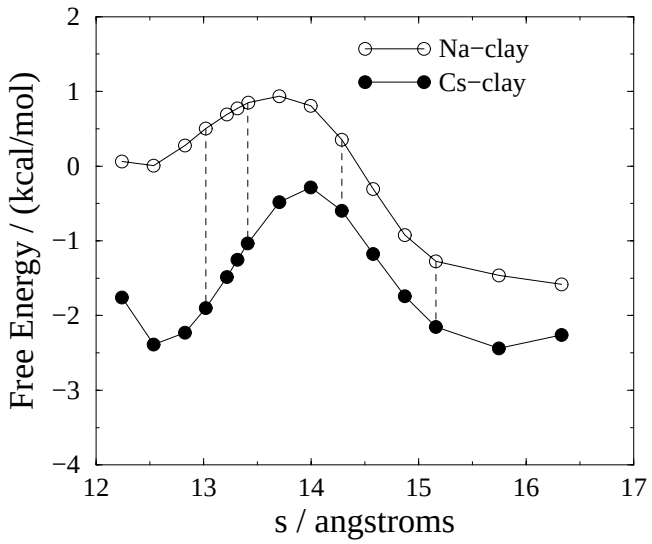

Figure 9: Solid lines correspond to MC swelling free energies, ΔX, plotted as a function of clay layer spacing. Dashed lines correspond to ΔA_{mut} calculated from and NVT-ensemble MD simulation at each spacing. Note the the mutation lines effectively bridge the free energy curves at each spacing.

are more accurate than MD. This preliminary result will be completed shortly with the determination of ΔA_{wc} values. Assuming continued thermodynamic consistency, this will allow for the thorough investigation of ion exchange processes envisioned at the start of this project.

Experimental measurements have been analyzed to yield relative contributions of tetrahedral and octahedral substitution sites to ion exchange selectivity coefficients in clay minerals.[17] For the clay modeled here, this analysis yields a Na $\rightarrow$ Cs exchange free energy of approximately -0.7 kcal/mol. This is in good agreement with our exchange free energy obtained by assuming a two-layer hydrate starting configuration for the Na-clay ($s_z = 15-16$Å) and a one-layer equilibrium configuration for the Cs-clay ($s_z = 12.5$Å).

4 Relevance, Impact and Technology Transfer

This research has potential impact on modeling of contaminant transport in soils and on the development of soil remediation and radionuclide containment strategies. Unfortunately, the research has had little immediate impact on these DOE environmental management problems. There are two reasons for this. First, the project from its inception consisted mostly of 'broad fundamental research' rather than 'needs-driven' development. Potential practical applications of the research stem from the eventual development of improved theoretical models for swelling and ion exchange in clays. Second, development of these theoretical models is possible only after simulation methods are derived and implemented, and results fully collected. While significant progress was made, the project objectives in this respect were not fully achieved. This was due, most notably, to the inefficiency of the grand canonical MD approach that was attempted initially. Now that an alternative simulation approach has been implemented, we will continue the research in the hopes that it may eventually

have both the fundamental and practical impact initially envisioned.

5 Project Productivity

Project productivity for each of the four objectives outlined in Section 2 is outlined here.

5.1 Simulation model development and validation

The model of Skipper and co-workers[7] was successfully modified to use a Lennard-Jones nonbonded form and incorporated into the PI's existing MD code. A grand canonical ensemble MD code was successfully developed and applied to simulations of bulk water[24] and Cs-montmorillonite.[27] This method was found to be too inefficient for use with Na-montmorillonite and, by implication, other clays with small or multivalent interlayer ions. A grand canonical ensemble Monte Carlo method was developed successfully as a replacement, and is currently generating results for several clay systems. Qualitative validation of the simulation models was achieved through comparison with experimental immersion enthalpies and adsorption isotherms. The simulation model was found to be adequate in its representation of octahedral substitution sites but not for tetrahedral sites. Quantitative validation of the model is still incomplete but should be facilitated by the new MC code described above.

5.2 Crystalline swelling: Simulations and theoretical modeling

Immersion energy calculations for Na-, Cs-, and Sr-montmorillonites were successfully completed and revealed several interesting swelling trends with ion size and charge including different swelling mechanisms for monovalent and divalent substituted clays. Grand canonical simulations for Na- and Cs-montmorillonites were also completed, revealing stable swelling states for these clays in contact with bulk water. Characterization of swelling properties as a function of clay composition and water chemical potential were not completed due to the inefficiency of the grand canonical MD method. The additional objective of developing improved swelling models has also not yet been achieved due due to the lack (until recently) of a reliable simulation method for identifying stable swelling states under conditions of controlled water chemical potential.

5.3 Ion exchange: Simulations and theoretical modeling

Objectives related to ion exchange were generally not met, although some significant progress toward the goal of simulation characterization is evident. A first, complete ion exchange calculation (none are published by anyone to date) was nearly complete at the end of the third year of the project, but with a thermodynamic inconsistency that invalidated the results. Only recently has the origin of this error been identified and corrected. Additional calculations will be performed as described in the 'Future Work' section.

5.4 Interlayer ion mobility and binding sites

Ion binding sites were identified and characterized graphically for Cs-montmorillonite.[23] Lateral free energy profiles were not measured. These should be measured at the equilibrium water content for a particular clay, as determined by a grand canonical ensemble simulation. Development of a reliable grand canonical code was deemed a higher priority than calculating these functions for the few clays for which the equilibrium water content was known.

6 Personnel Supported

1. Faculty PI: Dr. David E. Smith received summer salary support from this grant for years 1996-2000.

2. Postdoctoral Fellow: Dr. Robert M. Shroll was supported entirely by this grant from July, 1997 through July, 1999. He is the co-author of two papers and one manuscript in preparation.

3. Postdoctoral Fellow: Dr. Huang ShiPing was supported entirely by this grant from March, 2000 through September, 2000. He is the co-author of one manuscript in preparation.

4. Graduate Student: Dwarakanath Vijayaraghavan received support in the form of an RA for portions of the 1996-1997 academic year. He worked on the initial mutation calculations.

5. Graduate Student: Daniel Young received support in the form of summer and academic year RA's for portions of 1997-1999. He is the co-author of one paper.

6. Graduate Student: Dong Su received support in the form of an RA during the summer of 2000. He participated in the grand canonical MC code development and some swelling free energy calculations.

7. Undergraduate Student: Russell Waymier received support for undergraduate research early in the grant period.

8. Undergraduate Student: Christina Del Rio received support for undergraduate research during the 1999-2000 academic year. She is the co-author of two manuscripts in preparation.

9. Undergraduate Student: Heather Whitley received support for undergraduate research during the 1999-2000 academic year. She is the co-author of two manuscripts in preparation.

7 Publications

The following four published journal articles stemmed at least in part from this research:

1. "Molecular Computer Simulations of the Swelling Properties and Interlayer Structure of Cesium Montmorillonite", D.E. Smith, Langmuir **14**, 5959 (1998).

2. "Molecular Dynamics Simulations in the Grand Canonical Ensemble: Formulation of a Bias Potential for Umbrella Sampling", R.M. Shroll and D.E. Smith, J. Chem. Phys. **110**, 8295 (1999).

3. "Molecular Dynamics Simulations in the Grand Canonical Ensemble: Application to Clay Mineral Swelling", R.M. Shroll and D.E. Smith, J. Chem. Phys. **111**, 9025 (1999).

4. "Simulations of Clay Mineral Swelling and Hydration: Dependence upon Interlayer Ion Size and Charge", D.A. Young and D.E. Smith, J. Phys. Chem. B **104**, 9163 (2000).

Several additional manuscripts are in preparation.

8 Interactions

The following conference/workshop/colloquium presentations covered research supported directly by this grant.

1. September 1997: American Chemical Society Fall National Meeting in Las Vegas, NV. Contributed talk: "Computer Simulations of Cesium Adsorption on Hydrated Clay Minerals."

2. Fall 1997: Computational Sciences and Engineering Workshop in Las Cruces, NM. Invited talk: "Simulations of Clay Minerals."

3. April 1998: New Mexico State University Environmental Chemistry Symposium in Las Cruces, NM. Contributed poster: "Molecular Simulations of the Swelling Properties and Interlayer Structure of Cesium Montmorillonite."

4. June 1998: National Meeting of the Clay Minerals Society in Cleveland, OH. Contributed talk: "Simulations of the Swelling Thermodynamics of Cesium Montmorillonite."

5. July 1998: US-DOE Environmental Management Science Program Workshop in Chicago, IL. Invited poster: "Modeling of Cation Binding in Hydrated 2:1 Clay Minerals."

6. November 1998: New Mexico State University Department of Mathematics Colloquium. "Extended System Methods in Molecular Dynamics Simulations."

7. February 1999: 3rd Annual Mesilla Chemistry Workshop in Las Cruces, NM. Invited talk: "Swelling and Ion Exchange in Clay Minerals."

8. February 1999: University of Texas, El Paso Department of Chemistry. "Crystalline Swelling and Ion Exchange in Clay Minerals."

9. June 1999: National Meeting of the Clay Minerals Society in West Lafayette, IN. Contributed talk: "Crystalline Swelling Phase Transitions in Montmorillonites: A Grand Canonical Ensemble Computer Simulation Study." Contributed poster: "Crystalline Swelling in Montmorillonites: Ion Size and Charge Dependence of Simulated Immersion Energies."

10. October 1999: Southwest and Rocky Mountain Regional ACS Meeting in El Paso, TX. Invited talk: "Crystalline Swelling Phase Transitions in Clay Minerals: A Grand Canonical Ensemble Simulation Study."

11. October 1999: New Mexico Institute of Mines and Technology Department of Chemistry. Colloquium.

12. November 1999: University of California, Santa Cruz Department of Chemistry. Colloquium.

13. January 2000: University of Arizona Department of Soil and Water Sciences. Colloquium.

14. February 2000: University of Houston Department of Chemistry. Colloquium.

15. April 2000: EMSP National Workshop in Atlanta, GA. Invited poster: "Modeling of Cation Binding in Hydrated 2:1 Clay Minerals."

16. June 2000: Fourteenth Symposium on Thermophysical Properties in Boulder, CO. Invited Talk: "Grand Canonical Simulation Methods for the Simulation of Hydrated Clay Minerals."

9 Transitions

This research is basic in nature and has yet to be used in any direct technological application.

10 Patents

None.

11 Future Work

The development of an apparently reliable grand canonical MC code during the final months of this project opens up several avenues for future work related directly to unmet objectives of this project.

1. Model validation and development. It is difficult to validate simulation models for clay minerals due to compositional inhomogeneities and external surface effects in the related experimental systems.[23,26] Experimental adsorption isotherms in which not only water content but layer spacing are measured as a function of water vapor pressure

provide, in principle, an excellent method for simulation model validation. Comparison with these experiments requires grand canonical ensemble simulations in order to match experimental water vapor pressures. With such simulations, both layer spacings and the vapor pressures for layer-spacing transitions can be compared directly. In addition, ion exchange calculations facilitated by the grand canonical method may be compared with numerous experimental measurements, thus validating the model with an experimental quantity that bears direct relevance to transport of radionuclides in the environment. Finally, these and similar comparisons with experiment will facilitate the development of a reliable, empirical simulation model for tetrahedral substitution sites in the clays.

2. Swelling. Swelling free energies will be calculated for a set of clays with variable layer-charge magnitude, layer-charge location (once a reliable model for tetrahedral sites is developed), and interlayer ion identity. These results may be used to develop a comprehensive theoretical model of crystalline swelling in clay minerals that includes discrete swelling transitions and the possibility of hysteresis.

3. Ion Exchange. Ion exchange simulations will be conducted for several clays in order to elucidate the dependence of exchange upon clay composition, the extent of exchange, and the swelling state of the clay. Correlation of ion exchange and the degree of swelling will be related to exchange hysteresis observed in experimental measurements. Theoretical models of ion exchange may then be developed using a combination of simulation and experimental data.

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