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Animated molecular dynamics simulations of hydrated cesium-smectite interlayers

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Computer animation of center of mass coordinates obtained from 800 ps molecular dynamics simulations of Cs-smectite hydrates (1/3 and 2/3 water monolayers) provided information concerning the structure and dynamics of the interlayer region that could not be obtained through traditional analytical methods. Cs^+ could be seen to jump from one attracting location near a layer charge site to the next, and water molecules were observed to migrate from the hydration shell of one ion to that of another. Neighboring ions maintained a partial hydration shell by sharing water molecules, such that a single water molecule hydrated two ions simultaneously for hundreds of picoseconds. The extent of this sharing interaction in the interlayer was determined by the smectite charge distribution, but increased with increasing water content. Water molecules also could be seen to interact directly with the mineral surface, entering its ditrigonal cavities to approach attracting charge sites. The frequency and duration of cavity habitation increased with increasing water content and tetrahedral charge, and was inhibited the more perpendicular was the structural hydroxyl orientation relative to the mineral surface. Competition between Cs^+ and water molecules for surface sites was evident. These important cooperative and competitive features of interlayer molecular behavior were uniquely revealed by animation of an otherwise highly complex simulation output.

Introduction

The high bioavailability and long halflives of radioactive isotopes of Cs make them a significant environmental hazard[1-3]. To isolate this hazard, nuclear waste containment facilities are separated from host bedrock by compacted bentonite liners[2], shown in laboratory experiments to slow the diffusion of Cs^+ [1,2,4-7]. The smectite minerals making up these liners are 2:1 layer type clay minerals[8]. Each layer consists of an alumina (dioctahedral) or magnesia (trioctahedral) sheet sandwiched between two silica tetrahedral sheets. Isomorphic substitution of Mg for Al, or Li for Mg, results in negative octahedral charge sites, while substitution of Al for Si creates negative tetrahedral charge sites. These charge sites are balanced by cations in the interlayer which attract waters of hydration to this region, causing the clay mineral to swell. Although Cs-smectite hydrates have been studied for many years[9], little detailed information about the mechanisms involved in Cs^+ adsorption, hydration, and diffusion has been adduced from experimental findings. Molecular simulation thus has proven to be a useful adjunct to experimental work concerning the smectite interlayer[10-15].

A number of XRD studies show that the layer spacing of Cs-smectites remains in the range 11.9-12.5 Å after exposure to water vapor at any relative humidity[9,16-20], or even after immersion in an aqueous solution[9]. Water vapor adsorption isotherms[16-20] indicate increasing hydration of Cs-smectite with increasing relative humidity, but Calvet[17] and Prost[18] argued that most of the water adsorbed resides in micropores, not in the interlayer region. Indeed, measurements of the micropore volume in homoionic montmorillonites[21] have established the extensive microporosity of Cs-smectites. Calvet[17] and Prost[22] suggested that the 12.4 Å layer spacing in Cs-smectite was achieved and stabilized after the adsorption of only about 1.2-1.4 H_2O per unit cell of the clay mineral, well below the nominal monolayer water content of 4 H_2O per unit cell observed for smectites containing the strongly hydrating Li^+ cation[17,19]. Our recent Monte Carlo (MC) simulations of model Cs-smectite hydrates at low water contents[15] confirmed this speculation, showing that the 12.4 Å hydrate of Cs-smectite likely contains no more than 2.7 H_2O per unit cell (about 2/3 monolayer).

The Cs-smectites we investigated were (Table 1): Cs-hectorite with 1.3 and 2.7 H_2O per unit cell (1/3 and 2/3 water monolay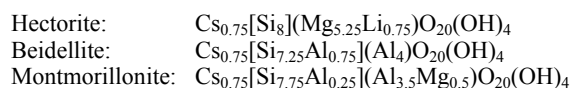er), Cs-beidellite with 1/3 water monolayer, and Cs-montmorillonite with 1/3 and 2/3 water monolayer. Cesium-smectites with 1.0, 1.31, 0.844, and 0.75 monolayers of water also were modeled for up to 10 million MC steps, but did not meet our MC equilibration criteria of achieving both a minimum average potential energy and a stable layer spacing.

The MC simulations were followed by molecular dynamics (MD) simulations[15]. These latter results were analyzed for average properties, such as interlayer water self-diffusion coefficients, as well as for individual molecular properties, such as plots of xyz coordinates sampled by specific Cs^+ ions or by water molecules. These traditional simulation outputs were not able to characterize the full complexity of interactions among cations, water molecules, and mineral surface sites. To continue analysis of the MD results, we constructed animations of molecular motions in the five Cs-smectite hydrate systems to examine the effects of charge site and hydration state on the behavior of interlayer species. Stereo viewing and animated motion have been shown to increase comprehension of three dimensional structures[23]. Because humans understand and navigate through a dynamic, three dimensional world, depiction of MD animations as a collection of spheres in three dimensional space that change position over time is a familiar metaphor that is intuitive to most viewers[23]. Other more traditional forms of presentation, such as a display of the entire path of a molecule over time, can result in a "tangled mess" that is not easy to interpret[23]. Animations thus can be helpful in understanding the complex three dimensional relationships between interacting molecules over time.

Methods

Model Cs-Smectite Hydrates

The simulation cell used consists of two opposing halves of a 2:1 clay layer surrounding an interlayer region filled with rigid water molecules and Cs^+ ions (Figure 1). The crystallographic unit cell formulae of the three Cs-smectites we simulated are:

Hectorite: $Cs_{0.75}[Si_8](Mg_{5.25}Li_{0.75})O_{20}(OH)_4$
Beidellite: $Cs_{0.75}[Si_{7.25}Al_{0.75}](Al_4)O_{20}(OH)_4$
Montmorillonite: $Cs_{0.75}[Si_{7.75}Al_{0.25}](Al_{3.5}Mg_{0.5})O_{20}(OH)_4$

Hectorite is a trioctahedral 2:1 clay mineral, whereas montmorillonite and beidellite are dioctahedral[12]. Moreover, hectorite shows charge substitution exclusively in the octahedral sheet, whereas beidellite contains only tetrahedral charge substitution. Montmorillonite has both types of charge substitution, with twice as much octahedral as tetrahedral layer charge. Our simulation cell contains eight unit cells, and has lateral (ab) dimensions 21.12×18.28 Å^2. The layer spacing is determined for each simulation system individually during MC equilibration.

Interactions between the interlayer species, and between them and atoms in the clay layers, are represented parametrically by a MCY-type potential function[11]:

$$U = \sum_{i=1}^{N} \sum_{j>i}^{N} \left[\frac{q_i q_j}{r_{ij}} - A_{ij} e^{-B_{ij} r_{ij}} + C_{ij} e^{-D_{ij} r_{ij}} \right] \quad (1)$$

where U is the potential energy of the system, i and j are sites on atoms within the simulation cell, r_{ij} is the distance between sites i and j, q represents atom charge, and A, B, C, and D are van der Waals interaction parameters. We used this form of potential function because it has led to accurate modeling of experimentally accessible quantities such as layer spacing and interlayer species configuration and mobility[10-15]. In addition, the MCY potential function for the water-water interaction is optimized on dimer structures[25] and, therefore, does not enforce the tetrahedral configuration of bulk water as strongly as do other, more empirically-based water-water potential functions. This fact may explain its enhanced ability to model water molecules in the especially constrained geometry of the clay interlayer region[10,11,13]. Van der Waals parameters for the Cs-O interaction were obtained through conversion of Lennard-Jones (LJ) (6-12) potential function parameters taken from Smith and Dang[26], described previously[15]. The MCY Cs-O interaction parameters were: A = 51.0 kJ mol^{-1}, B = 1.0850 Å^{-1}, C = 3.72×10^6 kJ mol^{-1}, D = 4.2758 Å^{-1}. Van der Waals interactions for Cs-H, Cs-Al, and Cs-Si atom pairs were assumed to be negligible.
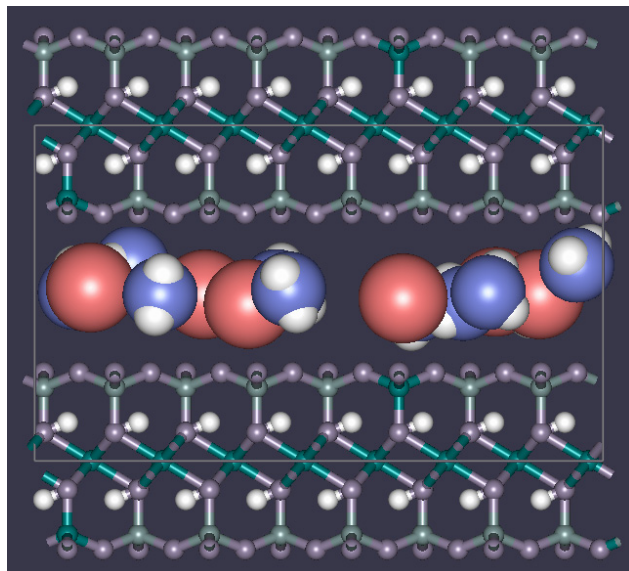
Fig. 1 A view of the simulation cell, outlined in grey, for Cs-montmorillonite, 1/3 water monolayer. Interlayer Cs$^+$ are represented by orange spheres, while interlayer water oxygens are represented by blue spheres and water hydrogens by white spheres. The surrounding mineral layers are displayed in ball and stick style, with the greyish purple balls representing the mineral oxygen atoms, white balls representing H, grey balls representing Si, and green balls representing Al.

Monte Carlo and Molecular Dynamics Simulations

Allen and Tildesley[24] have outlined the general principles of MC and MD simulations of liquids. Chang et al.[10,11] and Greathouse and Sposito[12] have developed simulation methodologies customized for exploration of the interlayer region of 2:1 clay mineral hydrates. Detailed description of MC calculations performed to establish the equilibrated Cs-smectite hydrate structures has been provided previously[15]. The program MONTE[27] was used to run MC ($N\sigma T$ ensemble) simulations on a variety of Cs-smectite hydrates at 300 K and 100 kPa normal stress (σ). Monte Carlo calculations began with a simulation cell that had a 14 Å layer spacing and contained 6 Cs$^+$ in the midplane of the interlayer along with several randomly placed water molecules. Three-dimensional periodic boundary conditions were applied[24]. Simulation started with an optimization developed by Chang et al.[10,11], consisting of 20,000 MC steps in which only water molecules were allowed to move, followed by another 20,000 steps in which water molecules could move and interlayer spacing could vary. After this optimization, all molecules were allowed to move in any direction, provided that the clay layer only moved about once for every five interlayer molecule movements. Information about total potential energy and layer spacing was collected every 500 steps. Systems were considered MC-equilibrated when convergence profiles of total potential energy and layer spacing provided minimum average values. The standard deviation of the average layer spacing was further required to be consistent with the precision of available experimental data on layer spacing[15].

The program MOLDY[28] was used to perform MD (NVE ensemble) simulations of the Cs-smectite hydrates which had converged under MC simulation. Monte Carlo-equilibrated configurations in which the layer spacing was held constant were used as initial coordinates for the MD simulations. With the clay layers fixed in position, initial velocities were assigned randomly to interlayer molecules following a Maxwell-Boltzmann distribution. In order to stabilize the temperature at 300 K, the simulations began with 20 ps of temperature scaling[28] using a 0.5 fs time step. Temperature scaling was performed for each molecular species individually, with rotational and translational kinetic energies scaled separately. After initial scaling, the MD simulations proceeded for 800 ps.

Molecular center-of-mass coordinates collected at 0.1 ps intervals during the simulations were used as the input data for our animations. We used a custom animation tool to create a series of JPEG images, one for each set of coordinates, based on the center-of-mass information. The custom animation tool, created by the Lawrence Berkeley National Laboratory/National Energy Research Scientific Computing Center (LBNL/NERSC) Visualization Group[29] in collaboration with the authors, runs on Windows or Unix/Linux platforms, and is based on OpenRM Scene Graph, an Open Source, cross-platform scene graph library[30]. These images were then converted to Quicktime™ format using the MediaConvert tool. We used the Quicktime™ RLE encoding option in order to reduce the size of the final movie files. The conversion was performed using the MediaConvert tool and executed on a visualization server located in the Visualization Laboratory at LBNL.

Results and Discussion

Molecular dynamics simulation and subsequent animation revealed complex and fascinating interactions between Cs$^+$ ions, water molecules, and the charged clay surface. Short animations of around fifty picoseconds (~10 MB) illustrating features relevant to the discussion below may be obtained from the links provided. Full-length (800 ps) versions of the five animated molecular dynamics simulations are supplied in the Appendix (~80-120 MB, coordinates used from every other time step).

Animations of the five systems share some basic similarities of molecular behavior. For example, Cs^+ tend not to roam, but instead to hover near the charge sites recessed within the clay layer. When the ions do move, they display jump diffusional behavior, in which the ions vibrate in one place for some time, then jump to new locations (Animation 1, Cs-hectorite with 1/3 water monolayer). These motions tend to be confined to different locations around the charge sites attracting the cations. In contrast, the water molecules display continuous diffusion on the timescale of these animations. Both ions and water molecules move more frequently in the 2/3 monolayer systems, a trend indicated for water molecules by an increased self-diffusion coefficient (Table 1). However, both Cs^+ and water molecule movements in the interlayer are substantially slower than in bulk ionic solution, where these species have self-diffusion coefficients of 2 x 10^{-9} m^2s^{-1} [32,34].

Cshect11.mov

Animation 1 A 50 ps portion of the Cs-hectorite, 1/3 water monolayer MD simulation animation (75-125 ps). Interlayer Cs^+ are represented by orange spheres, while interlayer water molecules are represented by blue spheres. The greyish purple spheres symbolize the surface oxygen atoms of the lower clay layer surrounding this interlayer region. The rest of the atoms making up this lower clay layer, as well as all the atoms making up the upper clay layer, have been removed to improve the visibility of the interlayer region. Due to the periodic nature of the simulations, interlayer species which exit from one side of the simulation cell will reappear on the opposite side. If the animation does not play smoothly when accessed directly from the web, we recommend downloading it first and then playing it. The highlighted Cs^+ (red) can be seen to display jump diffusion, while the highlighted water molecule (lighter blue) in the center of the simulation cell is characterized by continuous diffusional behavior as it moves from one Cs^+ partial hydration shell to another. Another highlighted water molecule to the left can be seen visiting a ditrigonal cavity site for a short time.

Animations allow us to see changes in the structure of hydrating water molecules around interlayer Cs^+ over time. Water molecules move from one Cs^+ to another, but are rarely far from an interlayer ion (Animation 1). This behavior leaves small regions of the smectite surface empty in the 1/3 monolayer simulations. Despite the weak coulomb field of Cs^+ and its large size, these ions are able to organize water molecules into partial hydration shells (water molecules within a radial distance of <5 Å

from the cation, as shown by our MC RDF calculations[15]). The number of water molecules within each shell varies substantially with time for each cation. The hydrophilic nature of some portions of the smectite surface, a result of the charge sites as well as of the inherent polarity of the structural hydroxyls, does not seem to influence substantially the organization of interlayer water molecules. The exchange behavior seen among Cs^+ waters of hydration contrasts with the results of MD calculations of similarly low water content Li-smectites[12], in which waters of hydration remained near the same ion for as long as 200 ps. The difference may be attributed to the smaller radius of the Li^+ ions, which results in stronger electrostatic attraction for water molecules, as well as to the shorter timespan of the Li-smectite simulations[12], which may not have been long enough to capture water exchange processes.

The animations bring to light the phenomenon of water molecule sharing between two Cs^+ ions, an effect seen in all five simulations to varying degrees (Figure 2). A shared water molecule may be defined as one which lies within the 5 Å hydration shells of two Cs^+ simultaneously for a period of hundreds of picoseconds or more. Shared water molecules remain in a fairly fixed position relative to the two Cs^+ they hydrate during this period of sharing. The animations appear to be the first evidence for such an interaction, which likely requires the conditions of confined geometry, presence of surface charge, and close proximity of ions that are found in clay interlayers. Cs-hectorite with 1/3 water monolayer (Animation 1) exhibits the least water sharing, with two Cs^+ pairs (the top left and bottom right Cs^+ are one pair, and the middle two Cs^+ on either side of the simulation cell are another), each sharing one water molecule for hundreds of picoseconds. Cs-montmorillonite with 1/3 water monolayer (Animation 2) contains two pairs of Cs^+ that share two water molecules per pair over the entire simulation (two Cs^+ at the bottom of the simulation cell form one pair, while the other is made up of the middle two Cs^+ on either side of the simulation cell). The molecules making up the two Cs^+ - two water complex near the bottom of the Cs-montmorillonite, 1/3 water monolayer animation are so strongly bound that, near the beginning of the simulation, they can be seen to rotate as a unit (Animation 2). In addition, other Cs^+ pairs in this system share one or two water molecules, but only for a few hundred picoseconds or less. Such entrapment of the water molecules could underlie the nonlinear

Table 1 Layer Spacing and Molar Potential Energy of Water (MC Simulation)[15] and Self-Diffusion Coefficients for Interlayer Water (MD Simulation) in Cs-Smectite Hydrates

Hydrate	MC Steps[a]	Layer Spacing (Å)	Potential Energy of Water (kJ mol^{-1})[b]	Self-Diffusion Coefficient (D_w) (10^{-9} m^2s^{-1})[c]
		1/3 water monolayer		
Cs-hectorite	10^6	12.37 ± 0.08	-47.43 ± 3.53	0.229 ± 0.001
Cs-beidellite[d]	4×10^6	12.31 ± 0.10	-42.98 ± 4.58	0.342 ± 0.002
Cs-montmorillonite	10^6	12.46 ± 0.09	-32.33 ± 4.04	Nonlinear[e]
		2/3 water monolayer		
Cs-hectorite	3.0×10^6	12.41 ± 0.07	-46.56 ± 2.00	0.685 ± 0.006
Cs-montmorillonite	3.5×10^6	12.68 ± 0.10	-36.66 ± 2.12	1.168 ± 0.006
Bulk liquid water[f]			-35.4 ± 0.2[31]	2.3[32]

[a]Monte Carlo steps required for convergence.
[b](Total potential energy of hydrate – total potential energy of clay mineral) ÷ moles of water per simulation cell[13].
[c]Value calculated from linear regression of MSD on elapsed time with P=0.05 confidence interval[15].
[d]This hydrate exhibited MC convergence only at the lower water content[15].
[e]This hydrate did not produce a linear relationship between MSD and elapsed time[15].
[f]MCY water[33] yields D_w = 2 x 10^{-9} m^2s^{-1}.

relationship between their MSD and elapsed time noted for this system[15], which signaled the absence of self-diffusion in the interlayer water (Table 1). Cs-beidellite with 1/3 water monolayer (Animation 3) features three pairs of cations which participate in water sharing of one or two water molecules for substantial portions of the 800 ps simulation (cations to the left and right of the animation are one pair, cations to the top and bottom of the animation are another, and the third consists of the top cation and its neighbor to the lower left). Cs-beidellite with 1/3 water monolayer may be considered to have an intermediate level of water sharing, as compared to the hectorite and montmorillonite systems, as it features more water sharing cation pairs than hectorite, but reduced number of shared water molecules and duration of water sharing per pair as compared to montmorillonite.
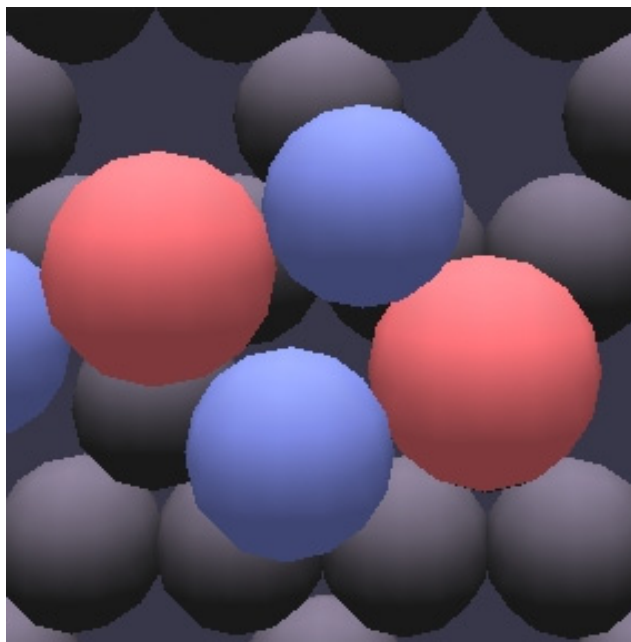
Fig. 2 A view in the xy plane of the two Cs$^+$ - two water complex seen in the Cs-montmorillonite, 1/3 water monolayer animation (Animation 2).

The degree of water sharing in each system may be influenced by the distribution of tetrahedral and octahedral charge, with the presence of both favoring sharing, while the presence of only octahedral charge provides less encouragement. Our previous research[15] noted a larger range of movement among the interlayer Cs$^+$ on montmorillonite, possibly as a result of the disorder produced by the presence of both octahedral and tetrahedral charge (Figure 3). Perhaps this greater flexibility in position along the z axis allows sharing interactions to develop and perpetuate over the timescale of our MD simulations. Cs$^+$ within beidellite show another type of spatial variation, in that they are segregated into two layers along the z axis, one containing ions attracted to charge sites in the upper mineral layer, the other containing ions attracted to charge sites in the lower mineral layer[15]. This vertical separation of cations may enhance the potential for sharing water molecules. In contrast, the charge of hectorite is located solely in the octahedral sheet, which compels the Cs$^+$ ions to remain in stable, mid-plane positions,

possibly inhibiting the formation of sharing configurations.

Extensive water sharing occurs in the Cs-montmorillonite with 2/3 water monolayer system (Animation 4). In the lower right of the animation we see a complex consisting of four Cs$^+$ and five shared water molecules. This complex is stable over the 800 ps timespan of the simulation. The ions are located directly over one tetrahedral charge site and under one octahedral charge site, but also are close to other tetrahedral and octahedral charge sites. In addition, we see the two Cs$^+$ not involved in the shared configuration roam over the clay surface in a typical diffusional manner, unlike the hovering motions seen in the other systems. That is, jump diffusion for these two ions occurs on the time scale of this simulation, while jump diffusion for the other four ions must occur on a much longer time scale. Plots of MSD vs. elapsed time for the two more mobile Cs$^+$ are nonlinear[15], which may indicate some form of entrapment. These Cs$^+$ can be seen to engage in ion exchange, as first one and then the other is attracted to an octahedral charge site submerged within the clay structure, located in the upper left corner of the simulation cell (Animation 4).

Cs$^+$ are not the only interlayer species attracted to specific sites within the clay mineral surface. Water molecules in the Cs-hectorite system with 1/3 water monolayer (Animation 1) frequently dip into the ditrigonal cavities in the mineral surface, but rarely remain for more than a hundred picoseconds. Dipolar water molecules find these cavities attractive because a similarly dipolar hydroxyl group, with its positive charge residing along a normal to the clay surface, rests at the bottom of each cavity in hectorite. The negatively charged, oxygen end of water will seek out this positive charge within the clay layer, creating a population of water molecules with their dipole moments pointing away from the mineral surface. Such a water orientation was also found in MC simulations of Cs-hectorite[15]. However, because the charges are small, the attractive force is similarly small and, therefore, the interaction is not very strong. As a result, water molecules visit the cavities for tens of picoseconds or less.

Ditrigonal cavities receive more attention in Cs-beidellite (Animation 3) because the negative charge sites just below the mineral surface can attract the positive end of a dipolar water molecule just as they attract Cs$^+$. Water molecules so attracted arrange themselves with a hydrogen ion directed toward the clay surface, as seen in distributions of water dipolar orientation from MC simulation[15]. Because the magnitude of the negative layer charge is greater than the magnitude of the positive structural hydroxyl charge, and because the hydroxyl groups are oriented at about 23° relative to the plane of the clay surface[35], some water molecules in the Cs-beidellite simulation can remain in the surface cavities for hundreds of picoseconds. Calculations based on an electrostatic model of a hydrated trioctahedral K-vermiculite interlayer[36] showed that, if the charge on the water hydrogen was at least 0.6e, water molecules competed with K$^+$ very well for tetrahedral charge sites. A direct comparison with the Cs-beidellite system is not straightforward, because the vermiculite modeled contained almost three times as much tetrahedral charge as beidellite, thus creating a more attractive surface for both ions and water, and because it featured structural hydroxyls oriented nearly perpendicularly (70.5^o) to the mineral surface. Nonetheless, the electrostatic charge on the MCY water hydrogen is 0.717e, large enough to produce water molecules capable of challenging cations for positions near tetrahedral charge sites in the electrostatic vermiculite model mineral[36].

Csmont11.mov

Animation 2 A 50 ps portion of the Cs-montmorillonite, 1/3 water monolayer MD simulation animation (50-100 ps). Interlayer species are represented as described in Animation 1. The two highlighted Cs$^+$ (red) share the two highlighted water molecules (lighter blue). The molecules making up this two Cs$^+$ - two water complex are so strongly bound that they are observed to rotate as a unit during this animation. Interlayer water molecules do not enter ditrigonal cavities in this portion of the simulation.

Csbeid11.mov

Animation 3 A 50 ps portion of the Cs-beidellite, 1/3 water monolayer MD simulation animation (350-400 ps). Interlayer species are represented as described in Animation 1. The three highlighted water molecules (lighter blue) reside within ditrigonal cavities of the lower clay surface for extended time periods. One of these water molecules, located near the top of the small view at the top left of the animation, and nearly hidden by a 2 Cs$^+$ - 2 water molecule complex, stays within the ditrigonal cavity for the 50 ps length of this animation.

Cs-hectorite

Cs-beidellite

Cs-montmorillonite
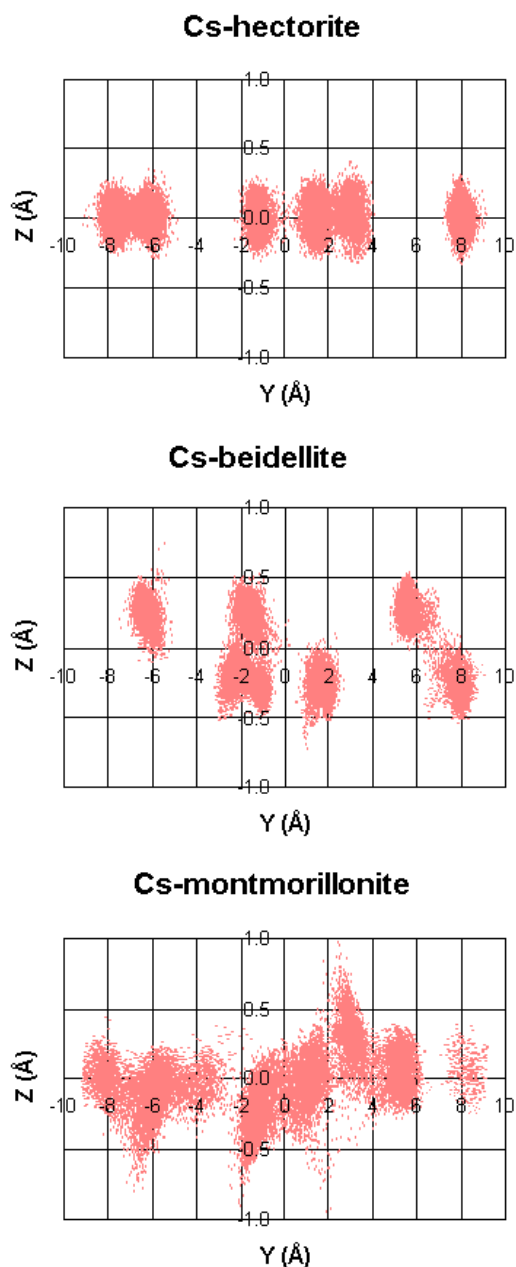
Fig. 3 Cumulative z-y coordinates of Cs^+ (first 400 ps) for Cs-smectites with 1/3 water monolayer. The surrounding clay layers are located out of the figure at ± 1.52, ± 1.44 Å, and ± 1.54 Å along the z-axis for Cs-hectorite, Cs-beidellite, and Cs-montmorillonite, respectively.

In the Cs-montmorillonite, 1/3 water monolayer simulation, we see relatively little water entry into surface cavities. Montmorillonite contains 1/3 as much tetrahedral charge as beidellite, and its hydroxyl groups are oriented at a low angle with respect to the clay surface. It is possible that the few positive tetrahedral charge sites and the negative charge from hydroxyl groups tend to balance each other, making the clay surface less attractive to water molecules. However, our MC results[15] indicated that a portion of the water molecules within montmorillonite have a similar orientation to the fraction of water molecules in beidellite that are attracted to the mineral surface. Our previous research[15] also indicates that the Cs^+ within the montmorillonite interlayer exhibit much more movement than the cations within the other two clays (Figure 3), possibly as a result of disorder induced by the presence of both tetrahedral and octahedral charge sites, which creates an environment where cations can occupy both near-surface and midplane interlayer

positions. Perhaps cations tend to block the entry of water into the ditrigonal cavities in Cs-montmorillonite.

The amount of interlayer water modifies the surface sampling behavior of water molecules. Animations of both Cs-montmorillonite and hectorite with 2/3 water monolayer (Animations 4 and 5) show a crowded interlayer featuring more extensive and lengthier sampling of the surface cavities by water molecules. As noted above, water movement in these systems is faster and more diffusional, and many ions exhibit more rapid jump diffusion. Why do the 2/3 water monolayer systems, though more tightly packed than the 1/3 water monolayer systems, exhibit more movement among their interlayer species? Competition between ions and water molecules for surface charge sites may be the answer. An example of such competitive action takes place in the animation of the Cs-hectorite system (Animation 5). A Cs^+ displaces a water molecule from a surface cavity above and in which it has hovered for tens of picoseconds. After only a few picoseconds, this cation is displaced in turn by another water molecule, as might be predicted from the results of the vermiculite study by Jenkins and Hartman[36]. Similar and more subtle interactions across the clay surface would lead to greater movement of both water and Cs^+. The electrostatic attraction between Cs^+ and the polar water molecules, responsible for the organization of the partial hydration shell, further encourages these competitive interactions by maintaining the two species in close proximity to each other as well as to the surface sites to which they are attracted.

Csmont21.mov

Animation 4 A 50 ps portion of the Cs-montmorillonite, 2/3 water monolayer MD simulation animation (750-800 ps, includes data from every other time step). Interlayer species are represented as described in Animation 1. The four Cs^+ toward the right of the animation are bound together by extended water sharing arrangements into a structure that is stable over the timespan of the simulation. The two Cs^+ toward the left of the simulation (red and brown) display continuous diffusional motion and participate in an exchange reaction, with first one and then the other taking up a position near an octahedral charge site in the clay layer. During the time that each cation is associated with this exchange site, a pale color is assigned to the relevant sphere.

Cshect21.mov

Animation 5 A 35 ps portion of the Cs-hectorite, 2/3 water monolayer MD simulation animation (610-645 ps). Interlayer species are represented as described in Animation 1. The highlighted Cs^+ (red) can be seen to compete with surrounding water molecules for favorable positions over ditrigonal cavities towards the end of this animation, when it moves forward to occupy surface sites closer to the viewer.

Conclusions

Animations of 800 ps MD simulations have provided new information concerning the structure and dynamics of the hydrated Cs-smectite interlayer region. A comparison of the five animations presented here reveals the behavior of interlayer species as modified by water content and charge site location. Cs-smectite systems feature ions hovering near charge sites and occasionally using jump diffusional movements to relocate. Higher water contents encourage more rapid movement in the interlayer for both Cs^+ and the water molecules which solvate them. Different mineral charge patterns create interlayer dynamics with different propensities for water molecule sharing between two Cs^+. A mix of tetrahedral and octahedral charge, as in montmorillonite, provokes a higher degree of disorder in the interlayer structure relative to smectites with only one type of charge site. This may allow ions a greater flexibility in placement, and therefore increased ability to enter into water-sharing arrangements. Tetrahedrally charged clays like beidellite provide a different form of flexibility in ion position, due to the

segregation of ions into two layers along the c axis. This segregation may encourage formation of water sharing arrangements as well. Octahedrally charged clays like hectorite contain fewer water sharing complexes because the Cs^+ in the interlayer are held in stable, mid-plane locations in the interlayer. The water sharing phenomenon predicted by our animations reaches an extreme state in the Cs-montmorillonite, 2/3 water monolayer hydrate, in which four Cs^+ are held together throughout the 800 ps simulation period in an extended complex of ions and shared water molecules. All animations also document the attraction between water molecules and the clay mineral surface. This attraction increases in the presence of higher water contents, tetrahedral charge sites, and structural hydroxyl groups oriented at shallow angles with respect to the mineral surface. Animation even reveals competition between water molecules and Cs^+ for sites on the mineral surface.

Thus, animation of MD data has provided substantial information not available from traditional simulation methods. Use of this visualization technique will enhance greatly the predictive capabilities of MD simulations.

Acknowledgments

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Appendix

Csh1full.mov

Animation 6 Animation of an 800 ps MD simulation of Cs-hectorite, 1/3 water monolayer (includes data from every other coordinate-collection time step). Interlayer species are represented as described in Animation 1.

Csm1full.mov

Animation 7 Animation of an 800 ps MD simulation of Cs-montmorillonite, 1/3 water monolayer (includes data from every other time step). Interlayer species are represented as described in Animation 1.

Csb1full.mov

Animation 8 Animation of an 800 ps MD simulation of Cs-beidellite, 1/3 water monolayer (includes data from every other coordinate-collection time step). Interlayer species are represented as described in Animation 1.

Csm2full.mov

Animation 9 Animation of an 800 ps MD simulation of Cs-montmorillonite, 2/3 water monolayer (includes data from every other coordinate-collection time step). Interlayer species are represented as described in Animation 1.

Csh2full.mov

Animation 10 Animation of an 800 ps MD simulation of Cs-hectorite, 2/3 water monolayer (includes data from every other coordinate-collection time step). Interlayer species are represented as described in Animation 1.