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Structural Implications of Interfacial Hydrogen Bonding in Hydrated Wyoming-Montmorillonite Clay

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ABSTRACT

Montmorillonite (MMT) clay – a layered porous nanomaterial used as seals in engineered waste containment barriers for spent nuclear fuel – adopts discrete hydration/swelling states depending upon surrounding water and ion activities and confining pressure. The structure of nanoconfined water and charge-balancing counterions in the clay mineral interlayers dictate the swelling and mechanical behavior of MMT, so a molecular model for this clay with high structural fidelity is required to accurately predict the reliability of long-term nuclear waste storage. Here we present a molecular model for MMT that is based on high resolution transmission electron microscopy of Wyoming-MMT single crystals. Imaging data unambiguously show a cis-vacant arrangement of structural hydroxyl groups in the octahedral sheet, whereas existing molecular models assume a centrosymmetric trans-vacant configuration for MMT. Using atomistic simulations, we find that the cis-vacant arrangement of structural hydroxyl groups significantly affects the structure of adsorbed water yielding a larger population of hydrogen bonds with bridging oxygens on the mineral sheet and weak hydrogen bonding between the hydroxyl groups in the octahedral sheet and water in the clay mineral interlayers. As a result, water adsorbed in the interlayer is more ‘ice-like’, with stronger ordering and lower density, although the diffusivity of the interlayer species is not significantly diminished. Our improved structural model for MMT provides insight into the energetics of water adsorption, which ultimately dictates its pore- to macro-scale swelling, transport, and fracture properties.

1. INTRODUCTION

Clay-rich geological formations are abundant and possess low permeability, high surface area and cation exchange capacity (CEC), and physiochemical properties that make clay minerals suitable materials in engineered barriers for subsurface storage repositories of nuclear waste, CO₂, and other fuels and fuel byproducts. Swelling clays such as montmorillonite (MMT) are widely used in clay barriers because their expansive behavior provides mechanical support to repositories and closes pores that can provide pathways for preferential flow or diffusion. The intrinsic negative structural charge in clay mineral layers from isomorphic substitutions is especially valuable in nuclear waste repositories because of the presence of radionuclides with a general tendency to form oxyanions ^{1,2}, and anion transport is inhibited by Debye screening.

Depending on the location of hydroxyl sites in the octahedral sheet relative to the vacancy site, clays can occur in cis-vacant (cv) and trans-vacant (tv) configurations. A tv configuration occurs when the hydroxyls are located across the vacancy site, and a cv configuration indicates that the hydroxyls are adjacent to one side of the vacancy site (Fig. 1). Montmorillonite clays, particularly those used in engineered barriers, are usually cis-vacant ³⁻⁵ and this structure favors a local charge compensation. In the Mg-OH-Mg arrangement within a tv sheet, two adjacent hydroxyls are bonded to two Mg²⁺ resulting in an undersaturated hydroxyl oxygen atom. A cv octahedral sheet, on the other hand, produces hydroxyls that are bonded to three octahedral metal ions resulting in a more effective local charge balance. Drits and Zviagina ⁵ argue that this is likely the reason for most Mg-rich MMT being cis-vacant. Consequently, tv MMT cannot have random Mg substitution in the octahedral sheet so as to minimize the occurrence of Mg-OH-Mg arrangements. It has also been reported that an increase in Al-for-Si substitution in the tetrahedral layers leads to the occurrence of tv MMT. Although the energy differences between the cv and tv isomers are lower

than the energy changes produced by the distribution of isomorphic substitutions in the octahedral sheet ⁶, *ab initio* studies ⁷ of the two configurations of MMT found that the tv configuration has a higher surface basal charge than the cv configuration (supported by the localization of isomorphic substitutions in the tetrahedral sheet). A study pertaining to the transformation of cv to tv configuration through dehydroxylation and rehydroxylation also suggested that the CEC for cv clays is slightly lower ^{8,9}. Thus, the difference in hydroxyl arrangement and the subsequent non-centrosymmetric clay structure is predicted to influence the edge structure, water and ion adsorption in the interlayers, and swelling of MMT.

Figure 1. Octahedral sheet with cis-vacant and trans-vacant configurations. Two out of three adjacent octahedral positions are occupied by Al atoms in dioctahedral smectites and one position is vacant; M corresponds to a vacancy in the octahedral sheet. In the tv structure, the hydroxyls in the octahedral sheet occupy positions at the opposite ends of the vacancy, whereas in cv clay, the hydroxyls occupy adjacent positions [image from ¹⁰]

Molecular simulations have proven to be a powerful tool to obtain insight into forces that control the structure^{11–14}, diffusion^{15,16}, and energetics of clay minerals under a variety of ambient conditions. Studies involving molecular dynamics (MD) and Monte Carlo methods confirm that detailed consideration of the clay structure and charge distribution significantly impact the ion adsorption¹⁷ and mass transport properties in the interlayer¹⁸. To date, all prior simulation studies involving diffusion¹⁹, exchange kinetics²⁰, and swelling^{21,22} have investigated clays with a trans-vacant structure. Furthermore, these simulation studies also employ a trans smectite structure in which cation substitutions are restricted to the octahedral layer (typical for smectites). However, naturally occurring trans MMT are uncommon and contain a higher proportion of cation substitutions in the tetrahedral sheet resulting in a higher surface potential for a constant layer charge. Given the influence of hydrogen bonding on the organization of molecules in swelling states^{23,24} as well as the differences in CEC and hydrophilic nature between the trans and cis configurations, it is important to develop an accurate structural model for swelling clay. A clear understanding of the connections between composition, structure, and ion transport in the interlayers is also critical to developing pore-scale swelling predictions²⁵. Thus, the goal of this study, and the starting point for future phase change models of clay swelling, is to develop a molecular model for cis-vacant clay that is consistent with the structure of Wyoming Montmorillonite (Wy-MMT). First, we develop a more accurate structural description of MMT based on recently acquired imaging data²⁶, and second, we investigate the implications of this model on the structure and diffusion of interlayer and adsorbed water and cations.

2. METHODS

2.1. High Resolution Transmission Electron Microscopy (HRTEM)

Direct images of cv MMT structure were obtained using low-dose HRTEM (Fig. 2). In-plane lattice parameters of cis-vacant MMT were determined to be $a = 5.20 \pm 0.04 \text{ \AA}$, $b = 9.00 \pm 0.06 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$ from the single-crystalline pattern in the Fourier transformation (Fig. 2b) of the HRTEM image in Fig. 2a. Note that β could not be determined imaging orthogonal to the basal plane. Distances were calibrated using bulk powder X-ray Diffraction (XRD) (Fig. 2c) and are consistent with previously reported lattice constants for cv MMT²⁷ within the measurement error. Uncertainty in the lattice constants measured from HRTEM images arises in part from bending of the crystal, which results in contrast variation across the field of view and radial streaking of the Bragg spots (SI Fig. 3). Nonetheless, high magnification regions aligned normal to the optic axis (Fig. 2d) are very well reproduced by simulations replicating the experimental imaging conditions of an individual cis-vacant MMT layer (Fig. 2e). Over focused imaging ($\Delta f = 145 \text{ nm}$) produced dark-atom contrast in which the ditrigonal cavities appear bright (Fig. 2f), revealing the full symmetry of the crystal with $1.25 \text{ \AA}$ resolution.

Classically forbidden, low symmetry lattice spots in the FFT unequivocally confirm the cis-vacant structure. In particular, a bright pair of spots in between the (260) and (170) planes corresponds to the $1.3 \text{ \AA}$ distance between a hydroxyl within a ditrigonal cavity and an adjacent oxygen projected onto the x - y plane (Fig. 2b). The axis on which these oxygens lie is rotated -26.8° with respect to the b -axis (Fig. 2b), in good agreement with simulated structures (SI Fig. 4). Another spot at $1.6 \text{ \AA}$ oriented -10.2° from the b -axis corresponds to an Si-O tetrahedral bond length. Note that these classically forbidden spots are only observable in extremely thin samples,

as the reciprocal lattice rods must be sufficiently elongated to yield appreciable contrast at lattice sites where the Bragg condition is not strictly satisfied. Simulated images of trans-vacant structures are not consistent with these observations (SI Fig. S5). To our knowledge, this is the first time HRTEM was successfully implemented to distinguish between cis-vacant and trans-vacant structures in MMT.

Figure 2. Structure of cis-vacant MMT. (a) HRTEM image of single MMT layer. Variation in contrast across field of view is due to bending. Scale bar: 10 nm; (b) Fourier transform of (a), showing 1.25 Å resolution of MMT lattice. Scale bar: 2 nm⁻¹; (c) XRD of the bulk cv MMT powder used to calibrate HRTEM image scale. Prominent lattice planes of cv MMT are indicated, and

quartz peaks (Q) were used as an internal standard; (d) Enlarged region indicated in (a) where layer is oriented perpendicular to optic axis. Scale bar represents 5 Å and is the same in (d)-(g); (e) HRTEM contrast simulation of single cv MMT layer in orientation determined by Fourier transform (b), in good agreement with (d); (f) cv MMT structural model used to generate simulated HRTEM overlaid on image (c), indicating that the light contrast arises from ditrigonal cavities and dark contrast from the atoms comprising the layer itself; (g) Model structure with unit cell of cis-vacant MMT shown in black. Blue=Si, teal=Al, red=O, white=H.

2.2. Molecular Modeling

We developed the molecular structure for cis-vacant MMT with lattice parameters from HRTEM as a monoclinic unit cell belonging to C 121 space group; the lattice parameters $c = 10.07$ Å, and $\beta = 99.5^\circ$ were adopted from Douillard et al.²⁷. Replication of this unit cell in the a - b plane followed by isomorphic substitution of Mg^{2+} for Al^{3+} in the octahedral sheet yields an MMT layer, where structural hydroxyl groups occupy positions that are consistent with experimental data for Wy-MMT with a structural charge of $-0.57e$ per unit cell ($\text{O}_{20}(\text{OH})_4$). Monovalent counterions (Na^+/K^+) were introduced to neutralize the net structural charge of the MMT layer. The key outcome is the first atomistic model for 2:1 cis-vacant clay that is directly comparable to HRTEM data, and we use this MMT layer model henceforth in all our simulations.

Interatomic interaction terms that represent the van der Waals and electrostatic forces are obtained from ClayFF²⁸, which is a robust classical force field for a range of mineral interface simulations. Interaction parameters for the water molecule are obtained from the SPC/E model²⁹. Periodic boundary conditions were imposed to the simulation volume along all three dimensions. The pairwise Lennard Jones energy was calculated using $E_{\text{pair}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$, where r is the

distance between two particles, and ϵ and σ are the maximum depth of the potential energy well and the distance of zero potential, respectively. Lennard-Jones interaction terms between dissimilar atom types are calculated via Lorentz-Berthelot mixing rules. We employ a cutoff distance of 15 Å for short-range interactions, and Ewald's summation method with an accuracy of 99.99% for long range electrostatics. A grand canonical Monte Carlo (GCMC) approach³⁰ with a target chemical potential (μ) in combination with MD simulation in the canonical ensemble (μ VT) was employed to determine the amount of water adsorbed in the interlayers for a given basal spacing. The temperature and pressure of the reservoir were fixed at 300 K and 1 atm, respectively, with a bulk density of 0.998 g/cm³. We obtained the target chemical potential from a GCMC simulation of pure water at 300 K in a box of size (40 × 40 × 40) Å³ resulting in $\approx$ 2100 molecules. Using this target chemical potential of -49.0 kJ/mol³¹, insertions and deletions of water molecules occur in the 2:1 interlayer in combination with Monte Carlo moves such as translation and rotation of molecules to yield the hydrate of MMT in pure water. The system was subsequently equilibrated in the NVT (T = 300 K) ensemble for 1 ns and subsequently, in the NPT (P = 1 atm, T = 300 K) for 5 ns to allow for the diffusion of water and ions.

3. RESULTS AND DISCUSSION

3.1. Interlayer Structure

The resulting hydrate contained 5.0 water molecules per unit cell per layer for Na-MMT and 4.95 water molecules per unit cell per layer for K-MMT, which is close to the average of 5.1 water molecules per unit cell for the water layer bound to tv clay reported by Bourg and Sposito¹⁶. For the layer charge modeled (-0.57 e/unit cell), we obtain around 18.7 H₂O molecules and 8.9 H₂O molecules per monovalent exchangeable cation in the two-layer (2W) and one-layer (1W) hydrate states, respectively. Atomic density profiles for equilibrium 1W and 2W hydrates for cis-vacant

Na-MMT and K-MMT are presented in Fig. 3. In addition to smaller atomic radius, the more negative hydration enthalpy of sodium resulted in a 1W Na-MMT hydrate with slightly higher water content than its K-MMT equivalent. For the 2W states with a basal spacing of $\approx 15.5 \text{ \AA}$, the difference in water content is insignificant.

While the arrangement of interlayer water perpendicular to c was notably similar in the sodium and potassium cases, the preferential residence of the cations was different. In the 1W and 2W cases for Na-MMT (Figs. 3(a), (c)), the sodium cations tend to reside in the interlayer midplane. Studies have confirmed that sodium ions prefer tightly bound hydration shells and therefore, are likely to be in the middle surrounded by interlayer water^{22,32}. The equilibrium structure for K-MMT, on the other hand, reveals that potassium ions prefer residing in the interlayer midplane in the 1W case (Fig. 3(b)), while in the 2W case, they reside close to the basal surfaces (Fig. 3(d)). Existing reports for simulated potassium hydrates of tv MMT present conflicting conclusions, particularly for the 1W configuration. Liu & Lu³³ performed MD simulations on an Arizona-MMT model wherein the potassium ions form inner sphere complexes with the ditrigonal cavities of the clay mineral layer. Similarly, Tambach et al.²³ inferred through molecular simulations that potassium ions, with their relatively small hydration energy, favored less hydration and screened the negatively charged clay platelets more effectively than sodium and therefore, would likely exist on the clay surface. It should be noted that both these molecular models had different layer charges representative of their samples of interest and, unlike real tv clay, the layer charge was entirely localized in the octahedral sheet. This localization of layer charge plays a critical role in the formation of cation inner sphere complexes.

Evidence from spectroscopy and direct imaging of cv MMT, however, is well aligned with the counterion distribution profiles shown in Figs. 3 (b), (d). Vao-soongnern et al.³⁴ presented X-ray

adsorption spectroscopy data that indicate the residence of potassium above the ditrigonal cavities on the a - b plane but in the midplane for the 1W structure, and bound to the basal surfaces in the 2W structure along c . The results of our study agree with this observation and are also confirmed by TEM data ²⁶ for the 2W case. The favorable local charge compensation mechanism in cv MMT alluded to in the introduction section leads to a reduction in the surface basal charge of the clay mineral layer. This could explain the weaker adsorption of potassium ions in the 1W structure. Its large atomic radius combined with a poor tendency to hydrate could cause it to migrate to towards the basal surfaces as the water activity increases when more water is squeezed into the interlayers. The rearrangement of K ions in the interlayer during transitions among the 1W and 2W hydration states has tremendous implications for the swelling behavior observed in MMT because it implies a restructuring of the clay mineral interlayer in addition to a phase change.

Figure 3. Atomic density profiles for different swelling states in Na-MMT and K-MMT based on the newly developed cis-vacant structure. (a) 1W Na-MMT with d-spacing of 12.6 Å; (b) 1W K-MMT with d-spacing of 13.7 Å; (c) 2W Na-MMT with d-spacing of 15.5 Å; (d) 2W K-MMT with d-spacing of 15.8 Å. Density profiles of Na-MMT indicate the presence of Na⁺ counterions in the midplane of the interlayer, whereas in K-MMT, K⁺ counterions reside in the midplane in 1W state and closer to the basal surfaces in the 2W state.

3.2. Water Adsorption

We performed a series of paired simulations using cv and tv clay with the same layer charge to directly assess the influence of structural hydroxyl hydrogen bonding on surface adsorbed water and interlayer water. Our surface adsorbed water results are benchmarked against previous water adsorption simulations reported by Bourg & Sposito¹⁵ using the exact simulation set up in a mixed electrolyte (NaCl/CaCl₂) nanopore of ≈ 6.5 nm width. Figure 4 illustrates the water profile relative to the tv and cv clay basal surface, respectively, for an electrolyte concentration of 0.67 mol/dm³ in the nanopore. Although the location of the water density peaks relative to the basal surface coincides with the results of tv MMT¹⁶, the magnitudes are significantly different. We observe that cv clay results in a higher density of the first adsorbed water layer compared to the tv clay. The adsorbed water layer is found at a distance of ≈ 1.5 Å from the basal surface and consists of water molecules where both hydrogen atoms form hydrogen bonds with the clay oxygen. Furthermore, the main water density peak at ≈ 2.7 Å from the basal surface corresponds to water molecules that are hydrogen bonded to one clay oxygen. While the magnitude of the main water peak in tv clay is significantly higher than its cv equivalent, the peak corresponding to water directly adsorbed on to the clay surface is higher in the cv clay. This implies that there is a stronger tendency for each adsorbed water molecule to be doubly hydrogen bonded to clay oxygen, allowing the adsorbed water to be more structured in cv clay. We found that this effect is more pronounced in the cv clay owing to the presence of adjacent hydroxyls in the octahedral sheet. However, the overall density of water in the first monolayer (within 3 Å of clay surface) of the tv clay is higher than in the cv case. The main takeaway from this comparison is that the water structure and density close to the clay surface are strongly dependent of the location of the hydroxyl group in the octahedral sheet, which warrants an investigation of the structure of interlayer water.

Figure 4. Density profile of water in a clay nanopore containing mixed NaCl/CaCl₂ electrolyte adjacent to cis-vacant and trans-vacant ¹⁶ MMT surfaces. The density profile was constructed by averaging density values within *z* slices of 0.1 Å every 100 ps over 50 ns of NVE equilibration. The location of the main water peak remains consistent, but the magnitude is significantly lower in cv clay. The water density profile within 3 Å of the clay surface indicates a higher proportion of surface adsorbed water in cv MMT and an overall higher density of water in the first monolayer in tv MMT.

Simulations to compare the structure of interlayer water between tv and cv clay were performed on 2W hydrates of MMT. Figure 5 presents the density map of interlayer water in a 2W hydrate, acquired from snapshots every 100 ps over the duration of 10 ns equilibration. The water density maps in Figs. 5(a) (b), parallel to the *a-b* plane of the clay, correlate strongly with the positions of the hydroxyl groups in both tv and cv clay (SI Fig. S1). Dark contrast spots in the map revealing high water density occur along the orientation of the -OH bond, further confirming that hydrogen bonding is critical to the clay-water interface. As a result, the distribution of water in the interlayer of cv clay is more localized near the adjacent hydroxyl groups, inducing more structure to the

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3 water in cv clay. Figures 5(c), (d) illustrate the density distribution of interlayer water
4 perpendicular to the clay surface and provide further evidence to the presence of localized, tightly
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6 bound water in the cv MMT interlayer. The existence of symmetry in interlayer water structure
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8 about the crystallographic axes of the cv clay could impact the distribution of counterions.
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10 However, in the present study we do not make inferences on whether such structural order persists
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12 among interlayer counterions. It must be noted that the interlayer water in cv clay, despite being
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14 more structured via stronger hydrogen bonding, is less dense compared to tv clay. The combination
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16 of higher structural order and lower density of interlayer water arising from the nature of hydrogen
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18 bonding with cv clay makes it more ‘ice-like’ than its tv equivalent ³⁵.
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Figure 5. Density map of interlayer water on the x-y plane (a) tv clay surface; (b) cv clay surface; on the y-z plane (c) tv clay surface; (d) cv clay surface. The map was constructed by averaging densities obtained within x, y, and z slices of $0.5\text{\AA}$, every 100 ps over 5 ns of NPT equilibration of 2W hydrate.

To quantify the structural order in interlayer water, we calculate a tetrahedrity index that captures the network of hydrogen bonds and the likelihood of water molecules forming an ideal tetrahedral network whose index would be zero^{36,37} (see Supporting Information). Reports suggest that ‘ice-like’ liquid water possesses a tetrahedrity index much closer to zero than bulk water at the same temperature. Results of this analysis on 2W tv and cv hydrates clearly point to interlayer water on cv MMT exhibiting more ‘ice-like’ behavior than on tv clay, with a larger proportion of water molecules in the first monolayer tightly bound to the mineral surface.

Considering the tetrahedrality parameter (SI Fig.S2) and the hydrogen bond distances at the mineral-water interface, two types of hydrogen bonding are possible: (i) the bridging oxygens in the siloxane linkages serve as hydrogen bond acceptors from water molecules; (ii) octahedral Mg-OH sites serve as weak hydrogen bond acceptors. Based on Fig. 4 and Fig. S3 (see SI), we infer that water on the cv MMT surface is more likely to be doubly hydrogen bonded to the surface, as indicated by the higher intensity of the water-H peak adjacent to the cv MMT surface. On the other hand, the second water-H peak on the tv MMT surface has a higher intensity suggesting the presence of stronger hydrogen bonding within the interlayer/bulk water (SI Fig. S3). These findings reveal that the cis-vacant MMT surface is more hydrophilic³⁸ when the layer charge and charge distribution are kept consistent among the tv and cv configurations.

Szczerba et al.³⁹ confirm the presence of a high-frequency, sharp OH band ($\approx 3630\text{ cm}^{-1}$) in the infrared spectra of smectite-water interface that is linked to an interaction between the OH in the water molecules and the smectite surface. The sharp band emerges when at least one of the O-H bonds of the water molecules is directed towards the siloxane surface and the other towards the bulk interlayer resulting in ‘dangling’ OH groups. The study also concludes that theoretical calculations allow for one or two water-OH groups directed towards the siloxane surface. This is consistent with our finding of a stronger hydrogen bonding network in cv MMT where a larger proportion of OH groups are directed towards the siloxane surface.

Figures 5 (a), (b) also highlight the difference between the tv and cv isomers due to hydrogen bonding from scenario (ii). What we observe is that the in-plane structure of interlayer water correlates very well with the structural hydroxyl positions in both the cv and tv isomers. A combination of (i) and (ii) hydrogen bonding scenarios provides the ‘ice-like’ structure to water on the cv MMT surface.

3.3. Diffusion of Interlayer Species

Water and ion diffusion coefficients near mineral-water interfaces are critical parameters that influence solute fluxes in clays and the rates of transport-limited interfacial reactions. Self-diffusion coefficients were calculated from the slope of the mean-square displacement $\langle l^2 \rangle$ vs. time plot using the well-known Einstein relation in Eq (1). Since our focus was only in the interlayer region extending up to time intervals of 1000 ps, the diffusion perpendicular to the clay was assumed to be negligible compared to diffusion parallel to the clay surface $\langle l^2 \rangle \approx \langle l_{xy}^2 \rangle$. Therefore, our two-dimensional diffusion equation considered $n = 4$. The diffusion coefficient of bulk water at 298 K (D_0) was found to be $2.4 \times 10^{-9} \text{ m}^2/\text{s}$ from experimental data and SPC/E water model prediction^{40,41}.

$$D = \frac{1}{2n} \lim_{\tau \rightarrow \infty} \frac{d\langle l^2 \rangle}{d\tau} \quad (n = \text{degree of freedom}) \quad (1)$$

Bourg and Sposito⁴² reported that accurate values for the diffusion coefficient parallel to the clay especially near the mineral surface is attainable only for $\tau > 100 \text{ ps}$. Therefore, our calculations were performed only after a preliminary equilibration under the micro-canonical ensemble (NVE) for 200 ps. We then used time intervals of 1000 ps and 500 ps for the 1W and 2W states, respectively, and calculated the average diffusion coefficient values over a 5 ns equilibration run. Table 1 presents the diffusion coefficients of water and cations (Na^+ , K^+) in the interlayer region of 1W and 2W MMT hydrates. It must be noted that we only used water molecules that remained in the interlayer over the entire time interval to perform this calculation. However, in the 2W case, we did not consider the diffusion of water molecules from one monolayer to another (two-dimensional assumption). The diffusion coefficients of water in the interlayer were not significantly affected by the cation type for a given layer state, so an average value is calculated for each layer state from both Na-MMT and K-MMT. Surprisingly, the

diffusion of water appeared to be unaffected by the arrangement of ions in the interlayer, particularly in the 2W state.

Table 1. Two-dimensional diffusion coefficients of interlayer species in homoionic cis-vacant MMT interlayers at 298 K

		$D_{interlayer} (\times 10^{-9} \text{ m}^2/\text{s})$	Average $\frac{D_{interlayer}}{D_0}$
H ₂ O	1W	0.196 ± 0.027	0.065
	2W	1.029 ± 0.009	0.286
Na	1W	0.052 ± 0.012	0.021
	2W	0.353 ± 0.005	0.147
K	1W	0.016 ± 0.008	0.007
	2W	0.133 ± 0.003	0.055

Molecular scale diffusion data probed from quasi-elastic neutron scattering (QENS) spectroscopy for SWy- MMT have yielded conflicting results ^{43–47}, owing to the fact that the diffusion of water in the interlayer is tightly coupled with the diffusion of cations. For example, Marry et al. ⁴⁶ showed that the diffusion of sodium ions can reach levels of up to $10^{-9} \text{ m}^2/\text{s}$ in saturated clay where the ions are strongly hydrated. Additional factors that make it challenging to compare our simulation results to available QENS data are the choice of appropriate time scales to measure diffusion and the difficulty to obtain a single uniform swelling state in experimental samples. Considering only experimental $D_{interlayer}$ values obtained from a uniform state hydrate (pure 1W Na-MMT and pure 2W Na-MMT), our results for water and sodium diffusion coefficients agree well ⁴⁶. Experimental data for diffusion in saturated K-MMT is scarce; however, studies have concluded that the diffusivity of potassium ions is comparable to that of sodium and lithium ions in the interlayer, while cesium ions exhibit lower diffusion coefficients ^{48–51}. Our results, on the other hand, indicate that the diffusivity of potassium ions is lower than that of sodium ions by an order of magnitude. Our two-dimensional assumption may have underpredicted

the diffusion coefficient of potassium, particularly in the 2W state since ion diffusion between the monolayers (perpendicular to clay plane) was neglected.

Literature is abundant on diffusion mechanisms in saturated homoionic MMT probed via MD simulations^{15,16,42,51,52}. To our knowledge, all the molecular diffusion investigations were performed on tv clay. Our results on cv clay falls within the range of values reported for diffusion coefficients but often, closer to the lower end. This was found to be true particularly for coefficients for 1W interlayers, ranging from $0.15 - 0.43 \times 10^{-9} \text{ m}^2/\text{s}$ for water⁴², $0.06 - 0.1 \times 10^{-9} \text{ m}^2/\text{s}$ for sodium ions⁵¹, and $0.03 - 0.12 \times 10^{-9}$ for potassium ions^{49,51}. While the ‘ice-like’ structure of adsorbed water in the interlayers of cv clay indicates a reduction in diffusivity, our diffusion coefficients are statistically comparable to that of tv clay. In future, a more thorough analysis is required to confirm if the difference in diffusivity of cv MMT interlayer species is statistically significant and can be attributed to the altered hydrogen bonding network.

4. CONCLUSIONS

Existing molecular models for MMT restrict the isomorphous substitutions to the octahedral layer while considering a trans-vacant distribution of octahedral cations. However, reported data show that the occurrence of tv MMT is rare and its structure contains a larger proportion of isomorphous substitutions in the tetrahedral sheet (e.g. more illitic than cv MMT). We address a critical gap by developing a new structural model for commonly found MMT in its cis-vacant isomer form consistent with acquired HRTEM data for Wy-MMT. We performed molecular dynamic simulations with the cis-vacant MMT model to determine the structure of the interlayer with Na^+ and K^+ as the counterions. The Na^+ and K^+ counterions in the two-water hydrates occupy different preferential positions and the diffusivity of the K^+ counterions were determined to be an order of magnitude lower than that of the Na^+ ions. While it is difficult to conclude if the positions of the

counterions perpendicular to the clay mineral layer are dictated by cv isomer, we found that a change in hydroxyl group arrangement and the relative shift induced between tetrahedral layers in the cis-vacant structure produce a stronger hydrogen bonding network with adsorbed water molecules in the interlayer. Water in the cis-vacant MMT interlayers has more structure and its diffusivity is not significantly affected by the cation type. This insight into the structured nature of interlayer water has tremendous implications for the stability of swelling states in clay-rich engineered barriers. The cv clay model and the equilibrium interlayer structure serve as a reliable starting point to investigate structure-property relationships in swelling/collapse reactions influenced by the chemical composition and mobility of interlayer species.

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SUPPORTING INFORMATION DESCRIPTION

Simulation methods, tetrahedrality calculation, and experimental methods (PDF)

Structure file for cis-vacant MMT (CisVacant_MMT.xyz)

REFERENCES

- (1) Toulhoat, P. Confinement and Migration of Radionuclides in a Nuclear Waste Deep Repository. *Comptes Rendus Phys.* **2002**, 3 (7–8), 975–986.
- (2) Schindler, M.; Legrand, C. A.; Hochella, M. F. Alteration, Adsorption and Nucleation Processes on Clay–Water Interfaces: Mechanisms for the Retention of Uranium by Altered Clay Surfaces on the Nanometer Scale. *Geochim. Cosmochim. Acta* **2015**, 153, 15–36.
- (3) Gard, J. A. *The Electron-Optical Investigation of Clays*; Mineralogical Society. Monograph; Mineralogical Society (Clay Minerals Group): London, 1971.
- (4) Drits, V. A.; McCarty, D. K.; Zviagina, B. B. Crystal-Chemical Factors Responsible for the Distribution of Octahedral Cations over trans- and cis-sites in Dioctahedral 2:1 Layer Silicates. *Clays Clay Miner.* **2006**, 54 (2), 131–152.
- (5) Drits, V. A.; Zviagina, B. B. Trans-Vacant and Cis-Vacant 2: 1 Layer Silicates: Structural Features, Identification, and Occurrence. *Clays Clay Miner.* **2009**, 57 (4), 405–415.
- (6) Sainz-Díaz, C. I.; Escamilla-Roa, E.; Hernández-Laguna, A. Quantum Mechanical Calculations of Trans-Vacant and Cis-Vacant Polymorphism in Dioctahedral 2: 1 Phyllosilicates. *Am. Mineral.* **2005**, 90 (11–12), 1827–1834.
- (7) Minisini, B.; Tsobnang, F. Ab Initio Comparative Study of Montmorillonite Structural Models. *Appl. Surf. Sci.* **2005**, 242 (1–2), 21–28.
- (8) Emmerich, K.; Plötze, M.; Kahr, G. Reversible Collapse and Mg²⁺ Release of De- and Rehydroxylated Homoionic Cis-Vacant Montmorillonites. *Appl. Clay Sci.* **2001**, 19 (1–6), 143–154.
- (9) Emmerich, K.; Kahr, G. The Cis- and Trans-Vacant Variety of a Montmorillonite: An Attempt to Create a Model Smectite. *Appl. Clay Sci.* **2001**, 20 (3), 119–127.
- (10) Christidis, G. E. Industrial Clays. In *Advances in the characterization of industrial minerals*; Ferraris, G., Christidis, G. E., Eds.; European Mineralogical Union, 2010; pp 341–414.
- (11) Greathouse, J. A.; Hart, D. B.; Bowers, G. M.; Kirkpatrick, R. J.; Cygan, R. T. Molecular Simulation of Structure and Diffusion at Smectite–Water Interfaces: Using Expanded Clay Interlayers as Model Nanopores. *J. Phys. Chem. C* **2015**, 119 (30), 17126–17136.
- (12) Gadikota, G.; Dazas, B.; Rother, G.; Cheshire, M. C.; Bourg, I. C. Hydrophobic Solvation of Gases (CO₂, CH₄, H₂, Noble Gases) in Clay Interlayer Nanopores. *J. Phys. Chem. C* **2017**, 121 (47), 26539–26550.
- (13) Sainz-Díaz, C.; Hernández-Laguna, A.; Dove, M. Theoretical Modelling of Cis-Vacant and Trans-Vacant Configurations in the Octahedral Sheet of Illites and Smectites. *Phys. Chem. Miner.* **2001**, 28 (5), 322–331.
- (14) Rotenberg, B.; Morel, J.-P.; Marry, V.; Turq, P.; Morel-Desrosiers, N. On the Driving Force of Cation Exchange in Clays: Insights from Combined Microcalorimetry Experiments and Molecular Simulation. *Geochim. Cosmochim. Acta* **2009**, 73 (14), 4034–4044.
- (15) Holmboe, M.; Bourg, I. C. Molecular Dynamics Simulations of Water and Sodium Diffusion in Smectite Interlayer Nanopores as a Function of Pore Size and Temperature. *J. Phys. Chem. C* **2013**, 118 (2), 1001–1013.
- (16) Bourg, I. C.; Sposito, G. Molecular Dynamics Simulations of the Electrical Double Layer on Smectite Surfaces Contacting Concentrated Mixed Electrolyte (NaCl–CaCl₂) Solutions. *J. Colloid Interface Sci.* **2011**, 360 (2), 701–715.

- (17) Lammers, L. N.; Bourg, I. C.; Okumura, M.; Kolluri, K.; Sposito, G.; Machida, M. Molecular Dynamics Simulations of Cesium Adsorption on Illite Nanoparticles. *J. Colloid Interface Sci.* **2017**, *490* (Journal Article), 608–620.
- (18) Tournassat, C.; Davis, J. A.; Chiaberge, C.; Grangeon, S.; Bourg, I. C. Modeling the Acid–Base Properties of Montmorillonite Edge Surfaces. *Environ. Sci. Technol.* **2016**, *50* (24), 13436–13445.
- (19) Greathouse, J. A.; Cygan, R. T.; Fredrich, J. T.; Jerauld, G. R. Molecular Dynamics Simulation of Diffusion and Electrical Conductivity in Montmorillonite Interlayers. *J. Phys. Chem. C* **2016**, *120* (3), 1640–1649.
- (20) Tournassat, C.; Bourg, I. C.; Holmboe, M.; Sposito, G.; Steefel, C. I. Molecular Dynamics Simulations of Anion Exclusion in Clay Interlayer Nanopores. *Clays Clay Miner.* **2016**, *64* (4), 374–388.
- (21) Hsiao, Y.-W.; Hedström, M. Swelling Pressure in Systems with Na-Montmorillonite and Neutral Surfaces: A Molecular Dynamics Study. *J. Phys. Chem. C* **2017**, *121* (47), 26414–26423.
- (22) Teich-McGoldrick, S. L.; Greathouse, J. A.; Jove-Colon, C. F.; Cygan, R. T. Swelling Properties of Montmorillonite and Beidellite Clay Minerals from Molecular Simulation: Comparison of Temperature, Interlayer Cation, and Charge Location Effects. *J. Phys. Chem. C* **2015**, *119* (36), 20880–20891.
- (23) Tambach, T. J.; Bolhuis, P. G.; Smit, B. A Molecular Mechanism of Hysteresis in Clay Swelling. *Angew. Chem. Int. Ed.* **2004**, *43* (20), 2650–2652.
- (24) Ho, T. A.; Criscenti, L. J.; Greathouse, J. A. Revealing Transition States during the Hydration of Clay Minerals. *J. Phys. Chem. Lett.* **2019**, *10* (13), 3704–3709.
- (25) Norrish, K. Crystalline Swelling of Montmorillonite: Manner of Swelling of Montmorillonite. *Nature* **1954**, *173* (4397), 256.
- (26) Whittaker, M. L.; Lammers, L. N.; Carrero, S.; Gilbert, B.; Banfield, J. F. Ion Exchange Selectivity in Clay Is Controlled by Nanoscale Chemical–Mechanical Coupling. *Proc. Natl. Acad. Sci.* **2019**, *116* (44), 22052–22057.
- (27) Douillard, J. M.; Lantenois, S.; Prelot, B.; Zajac, J.; Henry, M. Study of the Influence of Location of Substitutions on the Surface Energy of Dioctahedral Smectites. *J. Colloid Interface Sci.* **2008**, *325* (1), 275–281.
- (28) Cygan, R. T.; Liang, J.-J.; Kalinichev, A. G. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J. Phys. Chem. B* **2004**, *108* (4), 1255–1266.
- (29) Mark, P.; Nilsson, L. Structure and Dynamics of the TIP3P, SPC, and SPC/E Water Models at 298 K. *J. Phys. Chem. A* **2001**, *105* (43), 9954–9960.
- (30) Frenkel, D.; Smit, B. Understanding Molecular Simulations: From Algorithms to Applications. *Acad. San Diego* **1996**, No. Journal Article.
- (31) Boğan, A.; Rotenberg, B.; Marry, V.; Turq, P.; Noetinger, B. Hydrodynamics in Clay Nanopores. *J. Phys. Chem. C* **2011**, *115* (32), 16109–16115.
- (32) Honorio, T.; Brochard, L.; Vandamme, M. Hydration Phase Diagram of Clay Particles from Molecular Simulations. *Langmuir* **2017**, *33* (44), 12766–12776.
- (33) Liu, X.-D.; Lu, X.-C. A Thermodynamic Understanding of Clay-Swelling Inhibition by Potassium Ions. *Angew. Chem. Int. Ed.* **2006**, *45* (38), 6300–6303.

- (34) Vao-soongnern, V.; Pipatpanukul, C.; Horpibulsuk, S. A Combined X-Ray Absorption Spectroscopy and Molecular Dynamic Simulation to Study the Local Structure Potassium Ion in Hydrated Montmorillonite. *J. Mater. Sci.* **2015**, *50* (21), 7126–7136.
- (35) Tambach, T. J.; Bolhuis, P. G.; Hensen, E. J. M.; Smit, B. Hysteresis in Clay Swelling Induced by Hydrogen Bonding: Accurate Prediction of Swelling States. *Langmuir* **2006**, *22* (3), 1223–1234.
- (36) Brovchenko, I.; Oleinikova, A. Four Phases of Amorphous Water: Simulations versus Experiment. *J. Chem. Phys.* **2006**, *124* (16), 164505.
- (37) Smolin, N.; Daggett, V. Formation of Ice-like Water Structure on the Surface of an Antifreeze Protein †. *J. Phys. Chem. B* **2008**, *112* (19), 6193–6202.
- (38) Wang, J.; Kalinichev, A. G.; Kirkpatrick, R. J. Asymmetric Hydrogen Bonding and Orientational Ordering of Water at Hydrophobic and Hydrophilic Surfaces: A Comparison of Water/Vapor, Water/Talc, and Water/Mica Interfaces. *J. Phys. Chem. C* **2009**, *113* (25), 11077–11085.
- (39) Kuligiewicz, A.; Derkowski, A.; Szczerba, M.; Gionis, V.; Chrysikos, G. D. Revisiting the Infrared Spectrum of the Water–Smectite Interface. *Clays Clay Miner.* **2015**, *63* (1), 15–29.
- (40) Molinero, V.; Moore, E. B. Water Modeled As an Intermediate Element between Carbon and Silicon †. *J. Phys. Chem. B* **2009**, *113* (13), 4008–4016.
- (41) Becker, C. R.; Schad, L. R.; Lorenz, W. J. Measurement of Diffusion Coefficients Using a Quick Echo Split NMR Imaging Technique. *Magn. Reson. Imaging* **1994**, *12* (8), 1167–1174.
- (42) Bourg, I. C.; Sposito, G. Connecting the Molecular Scale to the Continuum Scale for Diffusion Processes in Smectite-Rich Porous Media. *Environ. Sci. Technol.* **2010**, *44* (6), 2085–2091.
- (43) Michot, L. J.; Ferrage, E.; Jiménez-Ruiz, M.; Boehm, M.; Delville, A. Anisotropic Features of Water and Ion Dynamics in Synthetic Na- and Ca-Smectites with Tetrahedral Layer Charge. A Combined Quasi-Elastic Neutron-Scattering and Molecular Dynamics Simulations Study. *J. Phys. Chem. C* **2012**, *116* (31), 16619–16633.
- (44) Gates, W. P.; Aldridge, L. P.; Carnero-Guzman, G.; Mole, R. A.; Yu, D.; Iles, G. N.; Klapproth, A.; Bordallo, H. N. Water Desorption and Absorption Isotherms of Sodium Montmorillonite: A QENS Study. *Appl. Clay Sci.* **2017**, *147* (Journal Article), 97–104.
- (45) Tazi, S.; Boğan, A.; Salanne, M.; Marry, V.; Turq, P.; Rotenberg, B. Diffusion Coefficient and Shear Viscosity of Rigid Water Models. *J. Phys. Condens. Matter* **2012**, *24* (28), 284117.
- (46) Marry, V.; Dubois, E.; Malikova, N.; Breu, J.; Haussler, W. Anisotropy of Water Dynamics in Clays: Insights from Molecular Simulations for Experimental QENS Analysis. *J. Phys. Chem. C* **2013**, *117* (29), 15106–15115.
- (47) Salles, F.; Douillard, J.-M.; Bildstein, O.; El Ghazi, S.; Prélôt, B.; Zajac, J.; Van Damme, H. Diffusion of Interlayer Cations in Swelling Clays as a Function of Water Content: Case of Montmorillonites Saturated with Alkali Cations. *J. Phys. Chem. C* **2015**, *119* (19), 10370–10378.
- (48) Chang, F.-R. C.; Skipper, N. T.; Sposito, G. Monte Carlo and Molecular Dynamics Simulations of Interfacial Structure in Lithium-Montmorillonite Hydrates. *Langmuir* **1997**, *13* (7), 2074–2082.

(49) Chang, F.-R. C.; Skipper, N. T.; Sposito, G. Monte Carlo and Molecular Dynamics Simulations of Electrical Double-Layer Structure in Potassium–Montmorillonite Hydrates. *Langmuir* **1998**, *14* (5), 1201–1207.

(50) Chang, F.-R. C.; Skipper, N. T.; Sposito, G. Computer Simulation of Interlayer Molecular Structure in Sodium Montmorillonite Hydrates. *Langmuir* **1995**, *11* (7), 2734–2741.

(51) Zheng, Y.; Zaoui, A. How Water and Counterions Diffuse into the Hydrated Montmorillonite. *Solid State Ion.* **2011**, *203* (1), 80–85.

(52) González Sánchez, F.; Van Loon, L. R.; Gimmi, T.; Jakob, A.; Glaus, M. A.; Diamond, L. W. Self-Diffusion of Water and Its Dependence on Temperature and Ionic Strength in Highly Compacted Montmorillonite, Illite and Kaolinite. *Appl. Geochem.* **2008**, *23* (12), 3840–3851.

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