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Structure, Energetics and Dynamics of Cs⁺ and H₂O in Hectorite: Molecular Dynamics Simulations with an Unconstrained Substrate Surface

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Abstract

Classical molecular dynamics (MD) simulations were performed for the smectite clay, hectorite, with charge balancing Cs^+ cations using a newly developed structural model with a disordered distribution of Li/Mg substitutions in the octahedral sheet and the fully flexible CLAYFF force field. Calculations for systems with interlayer galleries containing 0 to 19 $\text{H}_2\text{O}/\text{Cs}^+$ suggest that the mono-layer hydrate is the only stable state at all relative humidities at ambient pressure and temperature, in agreement with experimental results and previous molecular calculations. The basal spacing of this structure is also in good agreement with experimental values. In contrast to previous molecular modeling results, however, the new simulations show that interlayer Cs^+ occurs on 2 different inner sphere (IS) adsorption sites: above the center of ditrigonal cavities and above Si tetrahedra. Unlike previous simulations, which employed a rigid clay model and fixed orientations of the structural $-\text{OH}$ groups, the present results are obtained for an unconstrained clay substrate structure, where the structural $-\text{OH}$ groups are able to assume various orientations, including being nearly parallel to the clay layers. This flexibility allows the Cs^+ ions to approach the surface more closely above the centers of the hexagonal rings. In this structural arrangement, Cs^+ ions are not hydrated by the H_2O molecules which share the same interlayer plane, but rather by the H_2O molecules coordinated to the opposite surface. In contrast, on the external basal surface, a significant fraction of H_2O molecules are adsorbed above the centers of ditrigonal cavities adjacent to adsorbed Cs^+ ions. For these H_2O molecules, both $\text{H}_{\text{H}_2\text{O}}$ atoms coordinate and H-bond to O_b surface oxygen atoms. The mean residence times for the $\text{Cs}^+ - \text{H}_2\text{O}$, $\text{Cs}^+ - \text{O}_b$ and $\text{H}_2\text{O} - \text{O}_b$ coordination pairs show that Cs^+ ions are more strongly coordinated with O_b atoms than H_2O molecules. This result is the opposite of the behavior in Ca-hectorite, due to the much smaller hydration energy of Cs^+ compared to Ca^{2+} .

Introduction

Processes in clay mineral interlayer galleries and at mineral-water interfaces play a pivotal role in a wide variety of environmental and geochemical systems¹⁻⁵. The adsorption of hydrated metal ions at mineral surfaces often controls their distribution in both natural and technological settings⁶⁻¹⁰. In particular, the very low permeability of natural clay-containing formations makes them potential host rocks for long-term geological disposal of toxic and radioactive waste,¹¹⁻¹⁵ CO₂ sequestration,¹⁶⁻¹⁸ and control of reactive transport in the environment.¹⁹⁻²¹ The sorption and transport properties of clays are strongly influenced by the following parameters: (i) the structure and composition of the clay mineral substrate,^{22, 23} (ii) the composition and structure of the near-surface solution and its dynamics, which are different than in the bulk liquid phase,²³⁻²⁶ and (iii) the structure of the nano-porous space connecting clay interlayers with inter-particle pores, including the pore size distribution. The transport properties and binding of mobile, hydrated species are different in the interlayer galleries and on external basal surfaces and edge sites than in bulk solution.^{27,28} Molecular scale understanding of these differences is a prerequisite for developing quantitatively accurate transport models. Consequently, computational and experimental studies of the structure and mobility of H₂O and dissolved species at the surfaces and in the interlayers of clay minerals have increased greatly in recent years.²⁹⁻⁵¹

Smectite clays are of particular importance because of their ability to intercalate cations and H₂O molecules in their interlayers and exchange these species with exterior pore solution. This exchange can cause interlayer expansion and bulk swelling that affects the macroscopic transport properties of fluids in clays.^{36-38,44,47,50,52-58} The swelling energetics is strongly controlled by the clay composition, layer charge and cation hydration energy. For instance, the

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3 swelling of the smectite mineral hectorite and its interactions with metal ions and H₂O molecules
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5 have been probed in detail using X-ray diffraction (XRD),⁵⁹⁻⁶¹ thermo-gravimetric analysis
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7 (TGA),^{59,62,63} neutron scattering,⁶⁴⁻⁶⁷ and NMR spectroscopy.^{10,38,59,62,68-70} Interlayer structure and
8
9 dynamics have been investigated by NMR^{10,59,62,68-70} and neutron scattering studies.⁶⁴⁻⁶⁷ Hectorite
10
11 is widely used in NMR studies of smectites,^{10,59,62,68,71} because its low Fe content minimizes
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13 paramagnetic effects on the probe nuclei. The results show that metal cations with higher
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15 hydration energies and smaller ionic radii are more prone to be hydrated and less often
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17 coordinated to the basal surface in inner sphere coordination than those with lower hydration
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19 energies and large ionic radii. The results clearly show that, irrespective of the metal cation,
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21 proximity-restricted H₂O molecules have structural and dynamical behavior different from that
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23 of the bulk solution. It is difficult, however, to experimentally distinguish H₂O molecules and
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25 cations in the interlayer galleries from those on external surfaces and to separately characterize
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27 their structural and dynamical behavior.
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35 Computational molecular modeling studies are providing invaluable atomistic
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37 information about the underlying physico-chemical properties of smectite-water-cation systems
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39 and deeper, molecular scale interpretation of the experimental data. For instance, the
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41 intercalation of organic compounds and inorganic metal cations into hydroxy/fluoro-hectorites
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43 has been examined in detail using molecular simulations.^{57,65,70,72-76} For hydroxyl-hectorite,
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45 Morrow et al.⁷³ showed that Na⁺ ions are adsorbed as outer sphere surface complexes, except at
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47 low H₂O contents. Recent modeling of Na⁺ and H₂O sorption on the surfaces of inter-particle
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49 hectorite nano-pores by Greathouse et al.⁷⁴ has shown that the structure of the siloxane surface of
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51 the clay affects the H₂O adsorption.
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Adsorption and transport of Cs^+ in clay materials is of particular interest, because Cs^+ is a principal component of many radioactive wastes, has high aqueous solubility, and is not subject to solubility-limiting precipitation.^{10,62,77} Recent studies have focused on the adsorption of Cs^+ in clay minerals following the substantial discharge of ^{137}Cs in the aftermath of the Fukushima incident.^{78,79} After accidental release, the retention of Cs^+ near and just below the earth's surface is controlled primarily by its sorption in soils, in which clay minerals are important constituents. The sorption characteristics of Cs^+ varies greatly between different mineral surfaces. Experimental studies have reported that it adsorbs in inner sphere coordination at the relatively highly charged muscovite surface,³² whereas EXAFS studies using the lower charge montmorillonite suggest outer sphere complexation.⁸⁰⁻⁸² In addition, Cs^+ also has the smallest charge/ionic radius ratio and the smallest hydration energy of all of the group I and II elements, making it an important end member case for understanding the behavior of smectites with a wide range of other exchangeable cations. Simulations by Sutton and Sposito^{75,76} suggested that Cs^+ is adsorbed in inner sphere coordination in the interlayers of hydroxyl-hectorite and other smectites at all hydration states. Recent experiments and associated simulations by Porion et al.⁷⁰ indicate that at 97% relative humidity (RH), the interlayer water content of synthetic Cs-fluorohectorites with a basal spacing of 12.2 Å, corresponding to a mono-layer hydrate, is 4.2 H_2O molecules per Cs^+ . Although these results provide new insight into the behavior of Cs^+ and water molecules in hydrated interlayer galleries, the specific structural environments of these species and the differences in the structural arrangements, H_2O orientation, and the dynamics of Cs^+ and H_2O molecules in the interlayer galleries and on the external basal surfaces remain incompletely understood.

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3 The main objectives of the current study are to fill this gap by developing larger and more
4 realistic hectorite models with disordered distributions of Li^+ for Mg^{2+} substitution in the
5 octahedral sheet and to use these models to more deeply examine the structure, dynamics and
6 swelling energetics of Cs-hectorite. We observe significant differences in the adsorption sites for
7 Cs^+ and the orientation of H_2O molecules when compared to earlier studies.^{75,76} These
8 differences suggest that the adsorption structure and dynamics is strongly correlated with the
9 reorientation of OH^- groups in the octahedral layer of the clay. Potentially stable hydration states
10 are determined based on calculated thermodynamic parameters related to swelling, and the
11 molecular-scale structure and dynamics of the potentially stable hydration states are evaluated.
12 The relationships between the structures of the surface adsorption sites, the orientation of the
13 interfacial water molecules, their participation in the hydrogen bonding network, and the
14 $\text{Cs}^+/\text{H}_2\text{O}$ ratios for both clay interlayer and external hectorite surface are characterized in detail.
15 The simulation results are in good agreement with available experimental NMR and XRD
16 measurements.^{10, 62, 70, 83, 84}

37 Simulation Details

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40 Hectorite is a 2:1 trioctahedral smectitic clay mineral that develops permanent, negative
41 structural charge by Li^+ for Mg^{2+} substitution in the octahedral layer. Our model has the
42 structural formula of $\text{M}^+(\text{Mg}_5\text{Li})\text{Si}_8\text{O}_{20}(\text{OH})_4$. The structure is composed of two sheets of SiO_4
43 tetrahedra sandwiching a sheet of $\text{Mg,Li}(\text{OH})_2$ octahedra. The net negative structural charge is
44 compensated by interlayer cations. The model hectorite structure used in our simulations is based
45 on that of Breu et al.⁸⁵ The $\text{Li}^+/\text{Mg}^{2+}$ ratio of 1/5 is similar to the composition of natural San
46 Bernardino hectorite used in our experimental studies,^{10,38,59,62,68,71} although the natural sample
47 contains both OH^- and F^- . The hydration of fluoro-hectorite has been previously

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3 investigated.^{65,67,86} The natural sample also has a very small fraction (0.25%) of tetrahedral
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5 Al³⁺/Si⁴⁺ substitution that is not incorporated into the simulations.
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9 For studies of the interlayer galleries, the simulation supercell contains 2 interlayers and
10 consists of 40 unit cells of hectorite (5×4×2) with lateral dimensions of approximately $L_x \approx 26 \text{ \AA}$
11 and $L_y \approx 36 \text{ \AA}$. This size allows for a disordered distribution of the substitution sites and
12 corresponding structural charge (Figure 1a). This distribution was developed by replicating the
13 unit cell of hectorite in all crystallographic directions to fill the simulation supercell before
14 isomorphic substitutions were assigned. This procedure yields a simulation supercell in which
15 each TOT layer has a different arrangement of Li⁺ in the octahedral sheet. Substitutions were
16 performed ensuring that there is no aggregation of structural charge around a substituted
17 octahedral site, thereby eliminating charge gradients in the system. All interlayer Na⁺ in the
18 constructed model were replaced by Cs⁺, which were initially placed at the mid-plane of the
19 interlayers. In order to understand the effects of interlayer hydration, the models were prepared
20 using 25 different hydration levels with the water contents ranging from 0 to 20 H₂O molecules
21 per Cs⁺ ion. The initial *c* dimensions of the models were slightly larger than the expected final
22 value to allow for better equilibration. Since the clay layer charge in our system is $-1.0|e|$ per
23 crystallographic unit cell, the quantitative measure of water content expressed as H₂O/Cs⁺ or
24 H₂O/(unit cell) in our case is numerically the same.
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48 The external hectorite surface was constructed by cleaving the structure along the (001)
49 plane at the middle of the interlayer space. After cleavage, one-half of the interlayer Na⁺ ions
50 were retained at their initial positions on the basal (001) surface and replaced by Cs⁺. As for the
51 interlayer simulations, the simulation cell consists of 3 hectorite layers with a thickness of
52 ~29 Å. In the final simulation supercell, these surfaces were separated by ~144 Å along the *z*
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3 direction to simulate a nano-pore. Both lateral dimensions were ~ 72 Å. The large nano-pore
4 thickness perpendicular to the surface eliminates any direct interaction of one surface with the
5 other when the periodic boundary conditions are applied. As for the interlayer simulations, all the
6 octahedral $\text{Li}^+/\text{Mg}^{2+}$ substitutions were distributed in a disordered manner. All the Cs^+ were
7 initially placed 15 Å from the hectorite surface to allow them to choose their preferred
8 adsorption sites during the course of the simulation. The interlayers contained no H_2O to save
9 computation time. Initially, two separate H_2O slabs each with a thickness of 50 Å were placed
10 on the two hectorite (001) surfaces with ~ 15 Å vapor phase at the middle of the nano-pore. This
11 water film is sufficiently thick to characterize both the interfacial features of the structure and the
12 bulk-water behavior in the nano-pores, as demonstrated in previous simulation studies.^{39,42,58}
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28 Molecular Dynamics (MD) simulations using the statistical *NPT* (constant *N* number of
29 atoms, constant pressure *P* and constant Temperature *T*) and *NVT* (constant *N* number of atoms,
30 constant volume *V* and constant Temperature *T*) ensembles were performed using the LAMMPS
31 simulation code.⁸⁷ A Nosé-Hoover thermostat and barostat were used to control the temperature
32 and the pressure independently in all 3 dimensions.^{88,89} Three-dimensional periodic boundary
33 conditions were employed, and the interatomic interactions for all species were calculated using
34 the CLAYFF⁹⁰ force field that is well tested in molecular simulations of clays and related
35 materials.^{73,74,91,92} The flexible SPC water model was used to describe the interactions of H_2O
36 molecules with the clay structure and hydrated ions.⁹³ *NPT* simulations were first carried out for
37 each hydration level at ambient conditions ($P = 1$ bar and $T = 300$ K). A cutoff distance of 10 Å
38 was applied for the short range non-electrostatic interactions, and Ewald summation technique
39 was used to calculate long range electrostatic interactions. A time step of 1 fs was employed to
40 integrate the equations of atomic motion, and each system was equilibrated for 2 ns before a data
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3 production run of another 2 ns was started. The MD trajectory was recorded every 10 fs over the
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5 last 2 ns of the *NPT* production run. In these simulations the cell dimensions were allowed to
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7 vary independently and change with water content. The cell dimensions and thermodynamic
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9 quantities (e.g., basal spacing, hydration and immersion energies, and isosteric heats of
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11 adsorption) were calculated for every hydration state. These quantities were computed using 10
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13 equal, statistically independent time blocks, yielding small standard errors for the reported
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15 averages. Potentially stable hydration states were determined by analyzing the data from the *NPT*
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17 simulations. *NVT* simulations for these stable hydration states were performed for another 4 ns,
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19 which includes 2 ns of additional equilibration followed by 2 ns of data production. The initial
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21 configurations for the *NVT* simulations were the average atomic positions during the last 2 ns of
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23 the *NPT* production run. The *NVT* simulations of the external basal surface were performed in a
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25 similar manner after initial equilibration under ambient conditions for 6 ns. The data from the
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27 last 2 ns trajectory of the *NVT* simulation runs were recorded every 10 fs were used to determine
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29 the structure and dynamics of the water molecules and exchangeable cations for both the
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31 interlayer and external surface simulations.
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40 The swelling energetics were evaluated using the hydration and immersion energies and
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42 the isosteric heats of adsorption. The hydration energy is the energy change that occurs when
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44 water is added to the dry clay and is given by
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$$\Delta U = \frac{\langle U(N) \rangle - \langle U(0) \rangle}{N} \quad (1)$$

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47 where N is the number of interlayer water molecules adsorbed on the clay, and $\langle U(N) \rangle$ and
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49 $\langle U(0) \rangle$ are the average potential energies of the equilibrated hydrated and dry clays,
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51 respectively.^{23,94} The immersion energy, Q is the energy released or gained when the clay
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53 hydration is increased from one level to another by adding water to the system and is given by
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$$Q = \langle U(N) \rangle - \langle U(N_{\text{ref}}) \rangle - (N - N_{\text{ref}})U_{\text{bulk}} \quad (2)$$

where N_{ref} and $\langle U(N_{\text{ref}}) \rangle$ are the number of interlayer water molecules and the average potential energy of a reference hydration state. Here we use the system with the highest water content as the reference hydration level, because its value is closer to that of bulk water than any of the other simulations. The isosteric heat of adsorption is the enthalpy change of a system per mole of water when an infinitesimal amount of water is added to an existing water content^{50,54,94} and is given by

$$q_{st} = RT - \frac{\langle U(N) \rangle - \langle U(N') \rangle}{(N' - N)} \quad (3)$$

where N and N' are number of water molecules in two consecutive hydration levels, R is the ideal gas constant, T indicates temperature, and the term RT is used to convert energy and enthalpy for the vaporization process. Stable hydration states are represented by the water contents at which the computed relationship crosses the bulk vaporization enthalpy of SPC water (-44 kJ/mol) with negative slope. Although all three of these quantities are based on the same computed thermodynamic information, they are related to different experimental techniques. The immersion energies yield a clear representation of the hydration states and can be directly compared with calorimetric measurements.

The structural properties of the hydrated interlayers and external surfaces were quantified by calculating the atomic density distributions of all species both perpendicular and parallel to the hectorite surface. The widths and positions of each peak of the atomic density profiles perpendicular to the surface were used to define the limits for the analysis of the atomic densities for structurally different types of atoms within planar volumes parallel to the surface. The orientations of H₂O molecules with respect to the hectorite surface were evaluated using the angles that the molecular dipoles and H-H vectors make with respect to the surface normal.

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Though other H-bond definitions are possible,^{95,96} the H-bonding networks reported here both within the interlayer galleries and at the external basal surface were analyzed by applying a commonly used geometric criteria of an H-bond. In this definition, a hydrogen bond is assumed to exist if and only if the intermolecular O...H distance is less than 2.45 Å and the angle between the O...O and O-H vectors is less than 30°. ^{23,39,42} For the purpose of H-bonding calculations, the oxygen atoms of the basal clay surface (O_b) were treated in the same way as O_{H2O} (i.e., as potential H-bond acceptors). The origin for analysis of the atomic density profiles was the mean position of the surface O_b atoms. In the structures of the mono-, bi- and tri-layer hydrates these profiles were calculated by averaging over two statistically independent interlayer regions, each with the same number of water molecules. H₂O diffusion coefficients were calculated from all simulations using mean-square displacements,^{39,42,50,73} but diffusion along *z* direction is limited in the interlayer. Diffusion coefficients of the cations are correlated with the distribution and orientation of H₂O molecules near the hectorite surface.

The dynamical behavior of the H₂O molecules were quantified through the characteristic time they spend in coordination with the O_b atoms, in the first hydration shell of Cs⁺, and in coordination with other H₂O molecules. The average residence times of H₂O molecules in different coordinations were determined using time autocorrelation functions in a way similar to those employed in the description of hydrogen bond lifetimes.^{97,98} Two different mean residence times are reported here based on the population analysis and are termed the intermittent $c(t)$ and continuous $C(t)$ time correlation functions. For the intermittent correlation function, $c(t) = 1$ when an H₂O molecule is present in the first coordination shell of a metal ion or an O_b at time $t=0$ and at a later time t . Otherwise $c(t) = 0$. For this function, an individual H₂O molecule can leave the coordination shell and still be considered coordinated ($c(t)=1$) if it re-enters the same

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3 coordination shell during the time period considered. For the continuous correlation function,
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5 $C(t) = 1$ when an H₂O molecule is present in the first coordination shell of a metal ion or O_b at
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7 time $t=0$ and remains in the same coordination continuously thereafter until the end of the
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9 simulation. Otherwise $C(t) = 0$. Re-entries do not cause $C(t)$ to become 1 again. A time interval
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11 of 2 ps was used for computing these averages. This period is comparable to the residence times
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13 of H₂O molecules in cation hydration shells, as determined in earlier studies.⁹⁹⁻¹⁰¹ The methods
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15 of analysis used here have been previously described in detail.^{39,42,50,73}
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20 **Results and Discussion**

21 **Thermodynamic quantities**

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27 The interlayer spacing of Cs-hectorite increases continuously with increasing water
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29 content, with a somewhat smaller slope between 1 and 4 H₂O/Cs⁺ as water molecules fill the
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31 spaces between Cs⁺ ions (Figure 2a). The computed interlayer spacing of the completely
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33 dehydrated hectorite is 10.75 Å, in good agreement with the experimental value of 10.65 ± 0.2 Å
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35 obtained using X-ray diffraction techniques (Table 1).^{83,102} It is also consistent with the values
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37 for other dry Cs-smectites such as Cs-montmorillonite.^{50,94,103} It is significantly greater than the
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39 computed value for dry Na-hectorite⁷³ due to the larger ionic radius of Cs⁺ (~1.7 Å vs ~1.0 Å).
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41 With increasing hydration, a stable monolayer hydrate is represented by the plateau at ~12.4 Å.
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43 This value is also in good agreement with the values of 12.2-12.5 Å obtained in previous
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45 molecular simulations and experimental studies of Cs-hectorite.^{70,75,76,83,84,104} This stable
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47 monolayer hydrate has 4 H₂O/Cs⁺, also consistent with previous simulation and experimental
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49 studies,⁷⁰ although some of the experimental values are for synthetic fluoro-hectorites.⁷⁰ The
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51 similarity between the experimental and computed values suggests that the basal spacings are not
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53 greatly affected by OH⁻/F⁻ substitution, assuming the same interlayer water content. Further
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3 increase in hydration results in a linear increase in the computed interlayer spacing of Cs-
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5 hectorite.
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9 Previous experimental and simulation studies have shown that smectite minerals can have
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11 stable structures with up to 4 water layers depending on the nature of the charge-balancing cation
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13 and structure and composition of the clay.^{50,55,94,103} For Cs-hectorite, however, the available
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15 experimental data show only the mono-layer hydrate at all externally imposed water activities at
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17 ambient temperature and pressure.^{70,84} The computed hydration energies^{50,73} for Cs-hectorite
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19 (Figure 2b) show a well-defined energy minimum (-50 kJ/mol) at $H_2O/Cs^+ = 4$. The location and
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21 depth of this minimum are consistent with our basal spacing calculations and previous simulation
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23 results^{70,75,76} for the mono-layer hydrate. The quantitative energy differences (~4 kJ/mol)
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25 between the computed hydration energies here and in previous studies of Cs-hectorite are
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27 probably due to the different interaction models (SPC vs MCY) employed in the simulations.^{75,76}
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29 The hydration energies also shows two shallower minima at $H_2O/Cs^+ = 9$ and 14.5 with values of
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31 -44.5 and -43 kJ/mol, respectively, but there are no corresponding plateaus in the computed basal
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33 spacings (Figure 2a). These two states represent bi- and tri-layer hydrate structures. The values
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35 of the minima are only a few kJ/mol less than value of the internal energy of bulk SPC water (-
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37 41.2 kJ/mol), suggesting that mono-layer structure is stable and the others are not. This
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39 conclusion is in good agreement with the experimental studies, and the bi- and tri-layer hydrates
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41 should be considered as hypothetical. As the water content increases, the hydration energy
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43 approaches the value for bulk SPC water.
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52 The calculated immersion energies (Eq. 2; Figure 2c) help better define the positions of
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54 the bi- and tri-layer hydrates and corroborate the H_2O/Cs^+ ratios of the hydration states at 4, 9
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56 and 14.5. Even though stable hydration states with more than one water layer are not observed
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3 experimentally under ambient conditions, analysis of the higher hydrates yields useful structural,
4 dynamical and energetic information about such experimentally inaccessible hypothetical
5 structures, thus helping to understand the underlying molecular origins of the observed behavior
6 of the modeled material and other comparable phases,^{50,91} including hectorite with other
7 exchangeable cations. The computed isosteric heats of adsorption (Figure 2d) also clearly show
8 the three hydration states. The overall conclusions for Cs-hectorite are comparable to those for
9 Cs-montmorillonite, for which only the mono-layer structure is observed experimentally,^{84,104,105}
10 but for which hypothetical higher hydration states were also simulated.^{50,54,55,94,103} The H₂O/Cs⁺
11 ratios in hectorite are always less than for Cs-montmorillonite for all 3 hydration states. This
12 could be due to the inherent structural differences (trioctahedral vs dioctahedral T-O-T layers)
13 between hectorite and montmorillonite or due to the presence of both tetrahedral (Al³⁺ for Si⁴⁺)
14 and octahedral (Mg²⁺ for Al³⁺) substitution in the modeled montmorillonites (see, e.g., refs. 50,
15 54). Nevertheless, the H₂O/Cs⁺ ratios for different hydration states in our study are consistent
16 with the range reported for Cs-montmorillonite simulated using only octahedral substitutions.¹⁰³
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36 Atomic density profiles

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41 The atomic density profiles (ADPs) of Cs⁺ ions and H₂O molecules as a function of
42 distance from the hectorite surface for external surfaces and for interlayer galleries with 1, 2 and
43 3 water layers, as defined by the minima in the hydration energies, show similar patterns with
44 Cs⁺ occupying predominantly two types of inner sphere sites (Figure 3).
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51 For the monolayer hydrate (Figure 3a), the Cs⁺ ions located at distances of approximately
52 2.1 Å and 3.9 Å from the reference basal surface ($z = 0$ Å) are on the same types of adsorption
53 sites but are coordinated to the left (~ 0 Å) and right (~ 6 Å) hectorite surfaces, respectively. The
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3 Cs⁺ peak at 3.0 Å is at the center of the interlayer. Based solely on the ionic radii of Cs⁺ (1.9Å)
4 and O_b (1.5Å) it is clear that the Cs⁺ ions at 2.1 Å and 3.9 Å are in inner sphere coordination with
5 respect to one of the basal surfaces and that the one at 3.0 Å is inner sphere coordination with
6 respect to both surfaces. The O_{H2O} ADP of the monolayer hydrate consists of 2 peaks of equal
7 intensity located at 2.6Å and 3.4Å. These two peaks represent layers of H₂O molecules that are
8 not far enough apart along the *z* direction to be separated by Cs⁺ ions. The corresponding H_{H2O}
9 peaks are centered at 1.6, 3.0 and 4.4 Å. Since the integral intensities of O_{H2O} at 2.6 and 3.4 Å
10 and the H_{H2O} peaks at 1.6 and 4.4 Å are similar and the distance between them is approximately
11 1.0 Å (i.e., comparable with the length of the intramolecular O-H bond of H₂O molecules), we
12 can conclude that these water molecules are oriented in a manner that, at least in principal,
13 allows them to donate one H-bond to the O_b. Evaluation of H-bond donation to other water
14 molecules by the H-atoms in the mid-plane peak at 3 Å requires additional information and is
15 discussed below.
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35 The O_{H2O} distribution with two maxima for the monolayer hydrate of Cs-hectorite
36 contrasts with that of the monolayer hydrate of Na-hectorite, which has one maximum at the
37 mid-plane of the interlayer.⁷³ This is due to the fact that all the Na⁺ ions lie in the middle of the
38 interlayers, and to hydrate them the H₂O molecules are arranged in the same plane. In contrast, in
39 our simulations of Cs-hectorite, the Cs⁺ ions are equally distributed between the two basal
40 surfaces leading to two H₂O sub-layers for this hydration state.
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50 Although the computed interlayer spacings for our monolayer Cs-hectorite and those
51 from the previous work^{75,76} are similar, the Cs⁺ ADPs are significantly different. The previous
52 simulations suggest that at this hydration state Cs⁺ occurs on one type of site, is located at the
53 mid-plane of the interlayer gallery at the same level as the O_{H2O}, and has a coordination number
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3 of 6.0 with respect to both basal surfaces. In contrast, our results suggest that Cs^+ occurs on two
4 types of sites at different distances from the basal surfaces, consistent with ^{133}Cs NMR
5 results.^{10,62} These NMR spectra for samples equilibrated at 100% RH and mixed with water to
6 form a paste show the presence of two Cs sites. We assign the NMR peak at -29 ppm to the Cs^+
7 ions closest to the basal surfaces and one with less negative or more positive chemical shifts to
8 the Cs^+ ion further from the surface.^{10,62}
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19 The differences between our results and those from previous simulations are most
20 probably due to the differences in the force fields used in the simulations. Compared to our
21 model, Sutton and Sposito^{75,76} used a hecorite unit cell with a slightly lower total structural
22 charge ($-0.8|e|$ vs $-1.0|e|$) and the Skipper-Smith force field parameterization^{94,106} that assigns full
23 formal charges to the atoms in the octahedral layer ($q_{\text{Mg}} = +2.0|e|$; $q_{\text{Li}} = +1.0|e|$). In contrast, the
24 CLAYFF parameterisation used here⁹⁰ assigns partial charges ($q_{\text{Mg}} = +1.36|e|$; $q_{\text{Li}} = +0.525|e|$). In
25 addition, in the Skipper-Smith model the charges on the hydroxyl O atoms are much more
26 negative than in CLAYFF ($-1.42|e|$ vs $-0.95|e|$), while the apical O atoms ($-1.31|e|$ around Li and -
27 $1.28|e|$ around Mg) in CLAYFF have slightly higher negative charge than in the Skipper-Smith
28 model which uses $-1.0|e|$ for all O atoms around Mg or Li octahedra. Thus, on balance, the
29 electrostatic repulsion between the octahedral cations and the surface Cs^+ ions is expected to be
30 higher in their simulations than in our's. Another important difference is that the Skipper-Smith
31 model^{94,106} used by Sutton and Sposito^{75,76} assumes a rigid structure for the T-O-T clay layers in
32 which the structural $-\text{OH}$ groups are all constrained to be oriented perpendicular to the layers. In
33 contrast, our simulations allowed all atoms of the hecorite structure to move according to the
34 interaction parameters described by the CLAYFF force field,⁹⁰ resulting in fully flexible T-O-T
35 clay layers. The most important outcome of this is that in our simulations the structural $-\text{OH}$
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3 groups are reoriented to angles up to 90° with respect to the normal to the hectorite layers, rather
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5 than always staying perpendicular to them. Together, these differences allow Cs^+ ion in our
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7 simulations to find adsorption sites closer to the surface. In our structures, the $-\text{OH}$ groups that
8
9 are part of Li-substituted octahedral sites can be oriented both parallel and perpendicular to the
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11 surface, whereas almost all of them that are part of non-substituted Mg-octahedra are usually at
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13 high angles between 60° and 90° to the surface normal.
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18 The ADPs for the hypothetical bi- and tri- layer hectorite hydrates are similar to that of
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20 the monolayer structure in the near surface region (Figures 3b and 3c). These similarities are in
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22 agreement with the general notion that Cs^+ prefers coordination by O_b atoms to being hydrated
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24 by water molecules. The Cs^+ density distributions in the bi- and tri-layer hydrates both have 2
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26 peaks at 2.1 and 3.0 Å, comparable to the two peaks observed for the monolayer hydrate. There
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28 is also a small, broad distribution of Cs^+ atomic density in the central part of the interlayer at
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30 distances greater than 4.0 Å from the surface. The latter represents Cs^+ ions that move between
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32 the basal surfaces and form outer sphere surface complexes, as they do in other smectites.^{50,76}
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34 The ADPs of $\text{O}_{\text{H}_2\text{O}}$ and $\text{H}_{\text{H}_2\text{O}}$ are also similar for the different hydrates. $\text{O}_{\text{H}_2\text{O}}$ has maxima at 2.6
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36 and 3.6 Å, positions similar to the two maxima in the monolayer hydrate. $\text{H}_{\text{H}_2\text{O}}$ has maxima at
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38 1.6 and 3.0 Å, again similar to the positions for the monolayer hydrate. The structural
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40 interpretation for these peaks is the same for all hydration states. The mid-plane regions of the
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42 bi- and tri-layer hydrates are quite different, with broad peaks for $\text{O}_{\text{H}_2\text{O}}$ and $\text{H}_{\text{H}_2\text{O}}$ for the 3 layer
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44 hydrate due to the need to fill the interlayer space.
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52 The interlayer ADP's for Cs^+ ions and H_2O molecules for all hydration states are in
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54 reasonable agreement with modeling studies of Cs-montmorillonite⁵⁰ using the CLAYFF⁹⁰ force
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56 field, but differ from the previous simulation studies of Cs-montmorillonite^{75,76,94,103,107} for
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3 monolayer hydrate using the Skipper-Smith force field^{94,106} (see the discussion above). However,
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5 as the hydration state increases, Cs⁺ ions in those previous simulations^{103,107} are shown to
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7 predominantly adsorb closer to the substrate surface. This result is qualitatively consistent with
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9 present study. In contrast, the first H₂O molecular layer is adsorbed at similar distances with
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11 H_{H₂O} atoms lying closer to the substrate surface in accordance with our results.^{94,103,107}
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16 The ADPs of Cs⁺ and H₂O in the near-surface (~4 Å) region of the external surfaces are
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18 essentially identical to their distributions in interlayers of the bi- and tri-layer hydrates, except
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20 for a shoulder for O_{H₂O} at approximately 2.2 Å, which we discuss below (Figure 3d). Further
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22 from the surface, Cs⁺ atomic density exhibits a peak at 5.3 Å, and O_{H₂O} and H_{H₂O} show several
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24 broad features up to 10 Å. Beyond this distance both O_{H₂O} and H_{H₂O} distributions show bulk-like
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26 water behavior. These results are in reasonable agreement with previous simulation studies of
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28 external surfaces of Cs-montmorillonite, which show Cs⁺ in both inner and outer sphere
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30 coordination.^{108,109} However, these studies^{108,109} suggest that inner sphere Cs⁺ adsorption occurs
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32 dominantly above Si tetrahedra, in contrast to our results, which indicate Cs⁺ adsorption (~65%)
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34 above the center of ditrigonal cavities is dominant. In addition, the proximity-restricted H₂O
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36 molecules in previous studies coordinate and form H-bonds with the surface only through one of
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38 their H_{H₂O} atoms, whereas in our simulations, ~25% of the surface ditrigonal cavities have H₂O
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40 molecules coordinating through two H-bonds, as we discuss below in detail.
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48 **Angular distributions: the orientation of the water molecules**

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51 The orientation of H₂O molecules in the interlayer galleries of smectite minerals plays an
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53 important role in determining the basal spacings and is critical to the formation of stable H-
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55 bonding networks. We characterize the H₂O orientations using the angles between the calculated
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3 dipole and HH vectors and the normal to the clay surface for both the interlayer and external
4 basal surface. The probability density distribution of the angle between the surface normal and
5 the H₂O dipole vector as a function of distance from the basal surface (Figure 4a) clearly shows
6 that for the experimentally stable monolayer hydrate, the near surface adsorbed H₂O molecules (z
7 $\sim 2\text{-}3 \text{ \AA}$ and $3\text{-}4 \text{ \AA}$) have their dipole vectors oriented towards the left ($100^\circ\text{-}140^\circ$) and right (35°-
8 80°) hectorite surfaces in Figure 3, respectively. The average angle between the H₂O dipole and
9 the surface normal is 60.75° . However, the dipole vectors of a small fraction ($\sim 2\%$) of H₂O
10 molecules at distances $z < 2 \text{ \AA}$ or $z > 4 \text{ \AA}$ are oriented perpendicular to the corresponding
11 hectorite surfaces (Figure 4a). Nevertheless, the absence of HH vectors parallel to the hectorite
12 surface for H₂O molecules at these distances (Figure 4b) show that orientations with the dipole
13 vector perpendicular to the hectorite surface are statistically unlikely. This conclusion is
14 consistent with the ADPs of the monolayer hydrate, which indicate that the H₂O molecules are
15 principally arranged with only one H_{H2O} pointing towards the surface. This result is quite
16 different than in previous studies of Cs-hectorite.^{75,76} For instance, these earlier studies proposed
17 that irrespective of the water content, the dipole vectors exhibit two orientations, parallel and
18 perpendicular to the basal surface, with the perpendicular orientation dominating at high water
19 content. In our simulations, H₂O molecules at distances $z < 3 \text{ \AA}$ have their dipoles pointed
20 towards the hectorite surface at all hydration states. As for the differences in the ADPs discussed
21 above, these differences are probably caused by a combination of the differences in the clay
22 structural charge, interaction potentials,^{94,106} and the flexibility of the clay structure. Earlier
23 simulation studies of Cs-montmorillonite with only octahedral substitutions have clearly
24 indicated that the near surface adsorbed H₂O molecules have their dipoles oriented towards the
25 smectite surface, consistent with current study.^{103,107}

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3 The orientations of the H₂O molecules in the near surface region ($z < 10.0 \text{ \AA}$) of the
4 external Cs-hectorite basal surface in our simulations are very similar to those in the interlayer
5 galleries except at distances $z < 2.0 \text{ \AA}$ (Figures 4c and 4d). The dipole vectors of H₂O molecules
6 at these distances are parallel to the surface normal and the HH vectors are perpendicular to it.
7 This result is in disagreement with the calculations of Sutton and Sposito,^{75,76} which locate the
8 O_{H2O} atoms closer to the surface than the H-atoms. Again, we believe that this is the result of the
9 different structural charge, different interaction potentials,¹⁰⁶ and substrate flexibility, which
10 allows the structural –OH groups in our simulations to reorient. In the Sutton and Sposito
11 simulations,^{75,76} the near surface electrostatic attraction between the H_{OH} and the O_{H2O} is greater
12 than when the H_{OH} can relax to their expected non-perpendicular configurations, as in our
13 calculations. With increasing distance from the surface, the H₂O molecules in our simulations are
14 arranged with their dipoles oriented towards and away from the hectorite surface, consistent with
15 previous studies of the surface of Cs-muscovite mica and Cs-montmorillonite.^{32,39,108} The H-
16 bond structure in our simulations is consistent with these interpretations and is discussed in detail
17 in the Supplementary Materials.

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43 The radial distribution functions (RDFs) and running coordination number (RCNs) for
44 Cs⁺ - O_{H2O} and Cs⁺ - O_b pairs in the interlayer region for mono-, bi- and tri-layer hydrate and on
45 the external basal surface (Figures 5a and 5b) show that irrespective of the hydration level the
46 mean interatomic distances between Cs⁺ - O_{H2O} and Cs⁺ - O_b pairs are centered at 3.1 Å and
47 3.3 Å, respectively. These values are very similar to the Cs⁺-H₂O distances in bulk solution^{111,112}
48 and in previous simulations studies of smectite surfaces.^{103,108} The hydration structure reported
49 for montmorillonite using experimental EXAFS methods indicates average Cs - O distances of
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3 3.0 – 3.2 Å and 3.6 - 4.2 Å for 1st and 2nd coordination shell respectively.^{80,81} However, Bostick
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5 et al.⁸⁰ and Fan et al.⁸¹ claim that the Cs⁺ ions with the shorter Cs - O distances, which have
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7 RCNs of 3-5, are present in outer sphere surface complexes, completely hydrated and hence
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9 separated from surface through H₂O molecules. They also propose that the Cs⁺ ions with larger
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11 Cs – O distances are in partially dehydrated inner sphere complexes. However, our simulations
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13 results indicate that the Cs⁺-O_b distances are slightly greater than the Cs⁺-O_{H2O} distances, and do
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15 not support these conclusions. Instead, our results clearly indicate that the majority of the Cs⁺
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17 ions are adsorbed on inner sphere sites coordinated to 4-6 surface O_b atoms. The Cs⁺-O_b RCN
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19 decreases with increasing hydration state, but Cs⁺ still prefers to be in inner sphere coordination,
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21 as also observed in previous simulation studies using montmorillonite.¹⁰³ It is worth noting that
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23 EXAFS measurements cannot distinguish between O_b and O_{H2O} atoms around Cs,⁸² and this can
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25 probably explain the above disagreements in interpretation of the surface structure.
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33 The RCNs in our simulations of the monolayer hydrate are, however, quite different from
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35 those of the other hydration states and the external surface. For the monolayer hydrate, the
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37 nearest neighbor coordination of Cs⁺ is 6.4 O_b and 4.2 O_{H2O} for total of 10.5. As the interlayer
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39 hydration level increases, Cs⁺ is coordinated by progressively fewer O_b and more O_{H2O}, but the
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41 total average coordination remains in the range of 10.2-10.5. These results are in reasonable
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43 agreement with previous simulation studies for the interlayers of Cs-hectorite and other Cs-
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45 smectites.^{50,54,75,76} The RDF and RCN of both pairs on the external surfaces are similar to the
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47 distributions for the bi- and tri-layer hydrates, although the RCN of O_b coordination is even less.
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49 The total coordination of the surface Cs⁺ ions is 10.1 with 3.3 O_b and 6.8 O_{H2O}. These values are
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51 in good agreement with previous simulations at higher hydration levels^{75,76} in the interlayer
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53 region. Again, the differences in the RCNs in our simulations and in earlier simulations are
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3 probably due to differences in the substrate surface charge, the clay structure, the interaction
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5 potentials used, and the substrate flexibility used in our models.^{50,103,107-109}
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8 9 **Planar atomic density distributions**

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12 Planar atomic density distributions (PADDs; also known as atomic density maps) provide
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14 more detailed information about the structural environments of the water molecules and
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16 exchangeable cations in the interlayers and external surfaces. For Cs-hectorite they show that in
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18 the interlayers and on the external surfaces Cs⁺ ions are adsorbed on two types of sites with
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20 different coordinations to the O_b, as expected from the ADP's (Figures 6a-6d). The Cs⁺ ions
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22 located closest to the surface (atomic density maximum at ~2.1 Å) are adsorbed at the centers of
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24 ditrigoal cavities and are highly localized (Figure 6a). In contrast, those located ~3.0 Å from the
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26 surface are adsorbed above the Si tetrahedra and are much more mobile (Figure 6a). In the
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28 monolayer hydrate, the Cs⁺ ions located above the center of the ditrigoal cavities are
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30 coordinated by 6.0 O_b, while the coordinating water molecules are themselves adsorbed on the
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32 opposite interlayer surface (Figure 6b). Thus, the PADDs of O_{H2O} coordinating Cs⁺ shown in
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34 Figure 6a are not located in the same plane as the Cs⁺ ($z \leq 2.5$ Å) but at $z > 3$ Å with their H_{H2O}
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36 pointing towards and away from the hectorite surface at $z = 6$ Å (see Figures S2 and S3 in the
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38 Supporting Information). The dense O_{H2O} contours clearly reveal that the H₂O molecules
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40 hydrating the hectorite surface are responsible for the hydration of Cs⁺ ions that are adsorbed at
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42 the opposite surface. To our knowledge, no previous simulation studies have reported similar
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44 interlayer structures. In contrast, the Cs⁺ ions at $z = 3$ Å are partially hydrated by both H₂O
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46 molecular layers and are dispersed over the interlayer surface.
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3 The Cs⁺ ions at $z < 2.5 \text{ \AA}$ (center of ditrigonal cavities) in the monolayer hydrate are not
4 adsorbed uniformly within the plane of the interlayer, but are concentrated in regions with lateral
5 dimensions of approximately $20 \text{ \AA} \times 17 \text{ \AA}$. The other regions are occupied by H₂O molecules,
6 which share approximately the same plane. The long range ordering of the Cs⁺ ions and H₂O
7 molecules is similar to their arrangements in previous simulations using mica.¹¹⁰ Such
8 arrangements occur because they allow H₂O molecules to form more and stronger H-bonds
9 among themselves than they would otherwise have. Two important points support the computed
10 structural arrangement. (i) The absence of significant charge inhomogeneities in the modeled
11 hectorite structures rules out their impact on the interlayer structure, since the charge is
12 homogeneously distributed over entire surface, but without any repetitive Li⁺/Mg²⁺ pattern. (ii) In
13 additional simulations with high initial temperatures (700 K) that were gradually reduced to
14 300 K the final arrangement of Cs⁺ ion and H₂O molecules was essentially identical to that in the
15 original simulations. The initial high temperature provides greater atomic mobility and reduces
16 the possibility of artifacts in the final computed models. However, the Cs⁺ ions located $\sim 3 \text{ \AA}$
17 from the surface (center of interlayer) are dispersed over the entire hectorite surface which
18 suggests that they oscillate between lower and upper hectorite surfaces of the interlayer and are
19 mobile when compared to Cs⁺ ions located at the center of ditrigonal cavities.
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44 The computed model of the bilayer hydrate also shows significant long range ordering of
45 Cs⁺, the PADDs show that the H₂O molecules contributing to the O_{H₂O} ADP peak at 2.6 \AA
46 (sharing same plane as Cs⁺) are responsible for the hydration of both a hectorite surface and
47 metal ions belonging to that surface (See Figure 6c). Figure S4 (see Supporting Information)
48 indicates a strong ordering of H_{H₂O} contours pointing towards the O_b atoms, and the H_{H₂O}
49 contours in Figure S5 (Supporting Information) show a dispersed structure. This structure
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3 indicates that the H₂O molecules are arranged with one hydrogen pointed towards a surface, with
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5 the other is responsible for H-bond interactions with other H₂O molecules at the same plane or at
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7 larger distances from the surface.
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11 In the discussion above, we claim that the H₂O molecules on the external (basal) surface
12 show characteristics similar to the hypothetical bi- and tri-layer hydrates, except at distances $z <$
13 2 \AA . These H₂O molecules are in the shoulder region in the ADP (Figure 3d). The PADD in
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15 Figure 6d confirms that they are adsorbed at the centers of ditrigonal cavities with their H_{H₂O}
16 pointing towards the surface and that they exhibit symmetric, rotationally averaged contours.
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18 This structure is consistent with the results from the H₂O orientation and H-bond distribution
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20 calculations. This is also in reasonable agreement with previous simulations with higher charge
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22 mica substrates.^{23,39,110} Because of the relatively small structural charge of hectorite, only a
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24 fraction of the ditrigonal cavities are occupied by H₂O molecules. This is in contrast to the
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26 muscovite surface, where ~50% of the cavities are occupied due to the high structural charge due
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28 to isomorphic substitution in the tetrahedral layer. The PADD of the water molecules
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30 contributing to the peak at 2.7 \AA of the O_{H₂O} ADP (Figure S6 of Supporting Information) shows
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32 a distribution similar to the ones for interlayer H₂O molecules in the bi- and tri-layer hydrates.
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34 Previous simulation studies of Cs-montmorillonite have suggested a similar adsorption structure
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36 for the first adsorbed H₂O molecular layer.^{107,108} However, in contrast to our studies, in which the
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38 O_{H₂O} distributions overlap the distribution of H_{H₂O} atoms pointing towards the surface O_b atoms,
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40 the earlier studies showed O_{H₂O} atoms offset from the H_{H₂O} atoms and located slightly towards
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42 the ditrigonal cavities. As for the other differences between the earlier results and ours, this
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44 difference is probably due to a combination of the different clay structural charges, clay
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46 structures, interaction potentials¹⁰⁶ and flexibility of the clay substrate. Overall, it is evident in
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our results that at all water contents, the maxima of the H_{H_2O} distributions (but not those of O_{H_2O}) are closer to the hectorite surface, than it was concluded from the previous studies.^{75,76} These results clearly indicate how the simulation methods and interatomic potentials can affect the water arrangement in the interlayer galleries and on external surfaces.

Water diffusion

Many computational MD studies have reported that the H_2O diffusion coefficients in interlayer galleries are significantly lower than in bulk solution or on the external surfaces and that they increase with increasing the interlayer water content.^{43,50,54,73,75,76,103,113,114} The diffusion coefficients from our simulations (Table 2) are in generally good agreement with previous simulations.^{43,50,54,73,75,76} However, the diffusion coefficient reported here for the monolayer hydrate is a factor of four smaller than in previous simulations of hectorite.^{75,76} This difference is probably due to the interlayer H_2O molecules being split into two sublayers hydrating the hectorite surfaces separately, in contrast to previous results that show the H_2O molecules located in the mid-plane of the interlayer.^{75,76} Nevertheless, the values are in the same range ($0.15 - 0.70 \times 10^{-9} m^2/s$ – monolayer : $1.2 - 1.5 \times 10^{-9} m^2/s$ - bilayer) as reported for the smectite mineral, montmorillonite, using molecular simulation and neutron scattering techniques.^{107,113,115} The reported diffusion coefficient of H_2O molecules in bilayer hydrate is slightly higher than previous simulations studies using montmorillonite.^{107,113} This difference is probably due to the combination of different substrate structure and associated charge, interaction potentials and substrate flexibility. In addition, the interlayers in previous studies contained only Na^+ ions¹¹³ or 99% Na^+ ions and 1% Cs^+ ,¹⁰⁷ in contrast to our homoionic Cs^+ hectorite. Despite having interlayer spacings similar to Na- and Ca-hectorites,^{73,116} the Cs-hectorite here has larger H_2O diffusion coefficients at all hydration states (Table 2). This difference is probably due to the

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3 smaller hydration energy of Cs^+ compared to Na^+ and Ca^{2+} . In contrast, the H_2O diffusion
4 coefficients on the external surfaces do not depend significantly on the counterion, and are all
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6 $\sim 3.0 \times 10^{-9} \text{ m}^2/\text{s}$.^{42,43} This value is in excellent agreement with self-diffusion coefficients
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8 calculated for bulk SPC water.^{42,43,70} However, it should be noted that the diffusion of the H_2O
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10 molecules close to the hectorite surface ($\sim < 10\text{-}15\text{\AA}$) is more restricted because of the presence of
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12 charged hectorite surface, as reported by earlier simulation studies on montmorillonite
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14 surfaces.^{108,109,113,114,117} Since we are focusing on the effect of the opposing surface on the
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16 dynamics of H_2O molecules, the lateral diffusion coefficients as a function of distance from
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18 hectorite surface are not reported here.
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25 **Site residence times**

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29 The intermittent and continuous residence times for three different pairs ($\text{Cs}^+ - \text{H}_2\text{O}$, $\text{Cs}^+ -$
30 O_b and $\text{H}_2\text{O} - \text{O}_b$) in Cs-hectorite interlayers (Table 3) are consistent with the results above
31
32 showing that Cs^+ , with its large ionic radius and low hydration energy, prefers to be adsorbed in
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34 inner sphere coordination close to the hectorite surface. Both types of mean residence times for
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36 all pairs decrease with increasing interlayer hydration, and as expected the intermittent residence
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38 times are longer than the continuous residence times. The $\text{Cs}^+ - \text{O}_b$ residence times are longer
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40 than the $\text{Cs}^+ - \text{H}_2\text{O}$ ones, which are longer than the $\text{H}_2\text{O} - \text{O}_b$ ones. This order clearly shows the
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42 effects of the low hydration energy of Cs^+ and the relative weakness of H-bonding to the O_b
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44 atoms. This result is in direct contrast to the results for Ca-hectorite, which show that the $\text{Ca}^{2+} -$
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46 H_2O residence times are more than a factor of 2 greater than the $\text{Ca}^{2+} - \text{O}_b$ ones due to the higher
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48 hydration energy of Ca^{2+} .¹¹⁶
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Conclusions

Classical MD simulations of the structure, energetics and dynamics of Cs^+ and H_2O in the interlayers of Cs-hectorite clay and on the Cs-hectorite surface using a new hectorite model with a disordered distribution of isomorphic $\text{Li}^+/\text{Mg}^{2+}$ substitution in the octahedral sheet suggest that only the mono-layer hydrate is stable at ambient pressures and temperatures, in agreement with experimental results. The calculated basal spacings and the $\text{H}_2\text{O}/\text{Cs}^+$ ratios are in good agreement with previous experimental and simulation studies. In the interlayer and on the basal surface, Cs^+ ions occur on two different types of inner sphere adsorption sites: (i) at center of the ditrigonal cavities (~ 2.1 Å from the surface) and (ii) above the Si tetrahedra (~ 3 Å from the surface). In the monolayer hydrate, Cs^+ ions are hydrated by the H_2O molecules that are coordinated to the opposite surface confining the interlayer, but not by those that share the same plane. For all hydration states, the near surface adsorbed H_2O molecules are oriented in a manner in which they donate ~ 1 H-bond to the hectorite surface, with the second $\text{H}_{\text{H}_2\text{O}}$ being donated to other H_2O molecules. The H_2O structural arrangements at the external basal surface are very similar except for a shoulder at $z < 2.0$ Å, which represents H_2O molecules adsorbed at the center of ditrigonal cavities with both $\text{H}_{\text{H}_2\text{O}}$ coordinating the surface. The angular distributions of the H_2O molecules contributing to the peak at 2.6 Å in the atomic density profiles have their dipoles oriented towards the surface, in contrast to the results of previous simulations.^{75,76} We attribute the differences between our study and previous simulations to a combination of different structural charges on the clay, different interatomic potentials and our use of the CLAYFF force field, which allows the atoms in the clay substrate to move. Most importantly, this flexibility allows the H-atoms of the structural $-\text{OH}$ groups of the clay to reorient to be more parallel to the clay layers rather remaining perpendicular to the surface as in previous simulations with a rigid

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3 substrate model. This change reduces the $\text{-OH}\cdots\text{O}_{\text{H}_2\text{O}}$ attraction and allows Cs^+ ions to be
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5 coordinated in the centers of hexagonal rings. The calculated interlayer H_2O diffusion
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7 coefficients are generally similar to previous studies and are smaller than on external surfaces.
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9 The residence time correlation functions for the pairs $\text{Cs}^+ - \text{H}_2\text{O}$, $\text{Cs}^+ - \text{O}_b$ and $\text{H}_2\text{O} - \text{O}_b$ show
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11 that the $\text{Cs}^+ - \text{O}_b$ residence times are longer than the $\text{Cs}^+ - \text{H}_2\text{O}$ ones, which are longer than the
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13 $\text{H}_2\text{O} - \text{O}_b$ ones. This order reflects the low hydration energy of Cs^+ and the relative weakness of
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15 H-bonding to the O_b atoms. It is in direct contrast to the results for Ca-hectorite, which show that
16
17 the $\text{Ca}^{2+} - \text{H}_2\text{O}$ residence times are more than a factor of 2 greater than the $\text{Ca}^{2+} - \text{O}_b$ ones due to
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19 the higher hydration energy of Ca^{2+} .
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42 Nantes, funded by ANDRA, Areva, and EDF.
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48 ASSOCIATED CONTENT

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51 **Supporting Information.** Details of H-Bonding Structure and planar atomic density
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53 distributions (PADDs) of near surface adsorbed $\text{H}_{\text{H}_2\text{O}}$ for mono and bilayer hydrate, 1st $\text{O}_{\text{H}_2\text{O}}$
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55 peak for the external basal surface.
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3 **Notes**
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6 The authors declare no competing financial interest.
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FIGURE CAPTIONS

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Figure 1. Snapshots of the simulated Cs-hectorite system illustrating the disordered distribution of $\text{Li}^+/\text{Mg}^{2+}$ substitution in the octahedral sheet. a) View perpendicular to the clay layers. b) External basal surface viewed parallel to the clay layers along the xy direction. Purple balls – octahedral Li^+ , green balls – octahedral Mg^{2+} , yellow – Si tetrahedra, blue balls – interlayer Cs^+ ions, red sticks – $\text{O}_{\text{H}_2\text{O}}$, white sticks – $\text{H}_{\text{H}_2\text{O}}$. For the sake of clarity the structural OH^- groups are not shown.

Figure 2. Thermodynamic properties of Cs-hectorite as a function of interlayer water content. a) Interlayer spacing. b) Hydration energy. c) Immersion energy. d) Isostatic heats of adsorption. The dashed lines indicate the bulk internal energy of SPC water in b) and the bulk vaporization enthalpy for SPC water in d). The errors bars are at the 90% confidence level.

Figure 3. Atomic density profiles of Cs^+ (gold), $\text{O}_{\text{H}_2\text{O}}$ (red), and $\text{H}_{\text{H}_2\text{O}}$ for Cs-hectorite as functions of distance from the basal surface for the indicated hydration levels and the external surface. a) Monolayer hydrate. b) Bi-layer hydrate. c) Tri-layer hydrate; d) Basal Surface. The 0 of distance is the mean position of the basal O-atoms of the left surface clay surface.

Figure 4. Orientation distributions of H_2O molecules at the Cs-hectorite interlayers and on the external basal surface. a) Dipole vector of H_2O molecules in the mono-layer hydrate b) HH vector of H_2O molecules in the mono-layer hydrate c) Dipole vector of near surface adsorbed H_2O molecules at the external surface. b) HH vector of near surface adsorbed H_2O molecules at the external surface.

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3 **Figure 5.** Radial distribution functions (RDFs, solid lines) and corresponding running
4 coordination numbers (RCNs, dashed lines) for a) Cs^+ - H_2O pairs and b) Cs^+ - O_b
5 pairs in the interlayers and on external surfaces of Cs-hectorite. Color code: monolayer
6 hydrate – black, bilayer hydrate – red, trilayer hydrate – green, external basal surface –
7 blue.
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16 **Figure 6.** Planar atomic density distributions (PADDs) of Cs^+ ions and $\text{O}_{\text{H}_2\text{O}}$ in the interlayers
17 and on external surfaces of Cs-hectorite. a) Cs^+ ions and $\text{O}_{\text{H}_2\text{O}}$ atoms at distances
18 $z < 3 \text{ \AA}$ in the monolayer hydrate. b) schematic representation of the structural
19 arrangement of H_2O (oxygen – red, hydrogen - cyan) molecules and Cs^+ ions (blue) in
20 the monolayer hydrate. c) Cs^+ ions at distances $z < 2.8 \text{ \AA}$ and $\text{O}_{\text{H}_2\text{O}}$ atoms at $z < 3.1 \text{ \AA}$
21 in the bilayer hydrate. d) Cs^+ ions at $z < 2.8 \text{ \AA}$ and $\text{O}_{\text{H}_2\text{O}}$ atoms at $z < 2.4 \text{ \AA}$ on external
22 basal surfaces. Color code: O_b – gray, Si – yellow, Cs^+ ions at the center of ditrigonal
23 cavities – blue, Cs^+ ions above Si tetrahedron – green, $\text{O}_{\text{H}_2\text{O}}$ – red, $\text{H}_{\text{H}_2\text{O}}$ – cyan.
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FIGURES

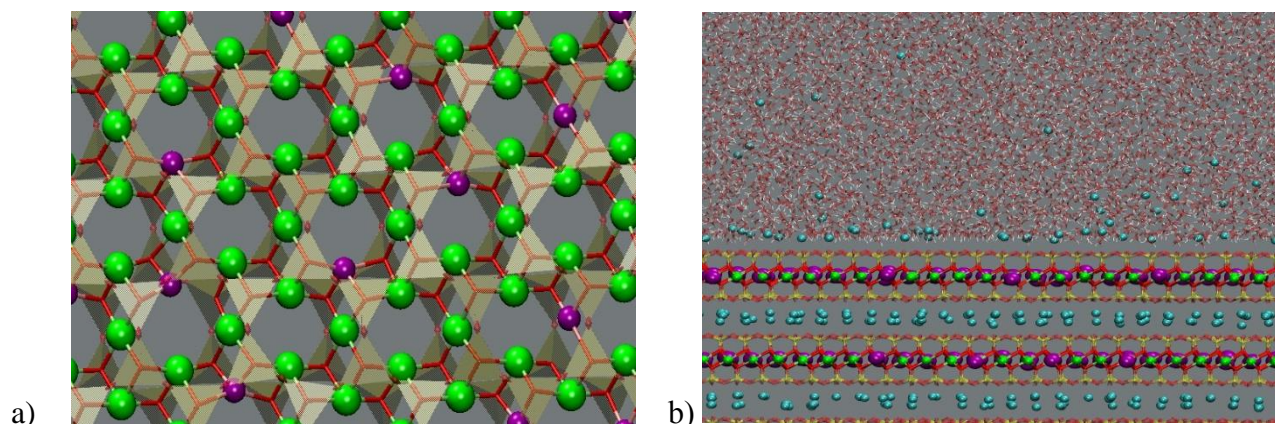


Figure 1. Snapshots of the simulated Cs-hectorite system illustrating the disordered distribution of $\text{Li}^+/\text{Mg}^{2+}$ substitution in the octahedral sheet. a) View perpendicular to the clay layers. b) External basal surface viewed parallel to the clay layers along the xy direction. Purple balls – octahedral Li^+ , green balls – octahedral Mg^{2+} , yellow – Si tetrahedra, blue balls – interlayer Cs^+ ions, red sticks – $\text{O}_{\text{H}_2\text{O}}$, white sticks – $\text{H}_{\text{H}_2\text{O}}$. For the sake of clarity the structural OH^- groups are not shown.

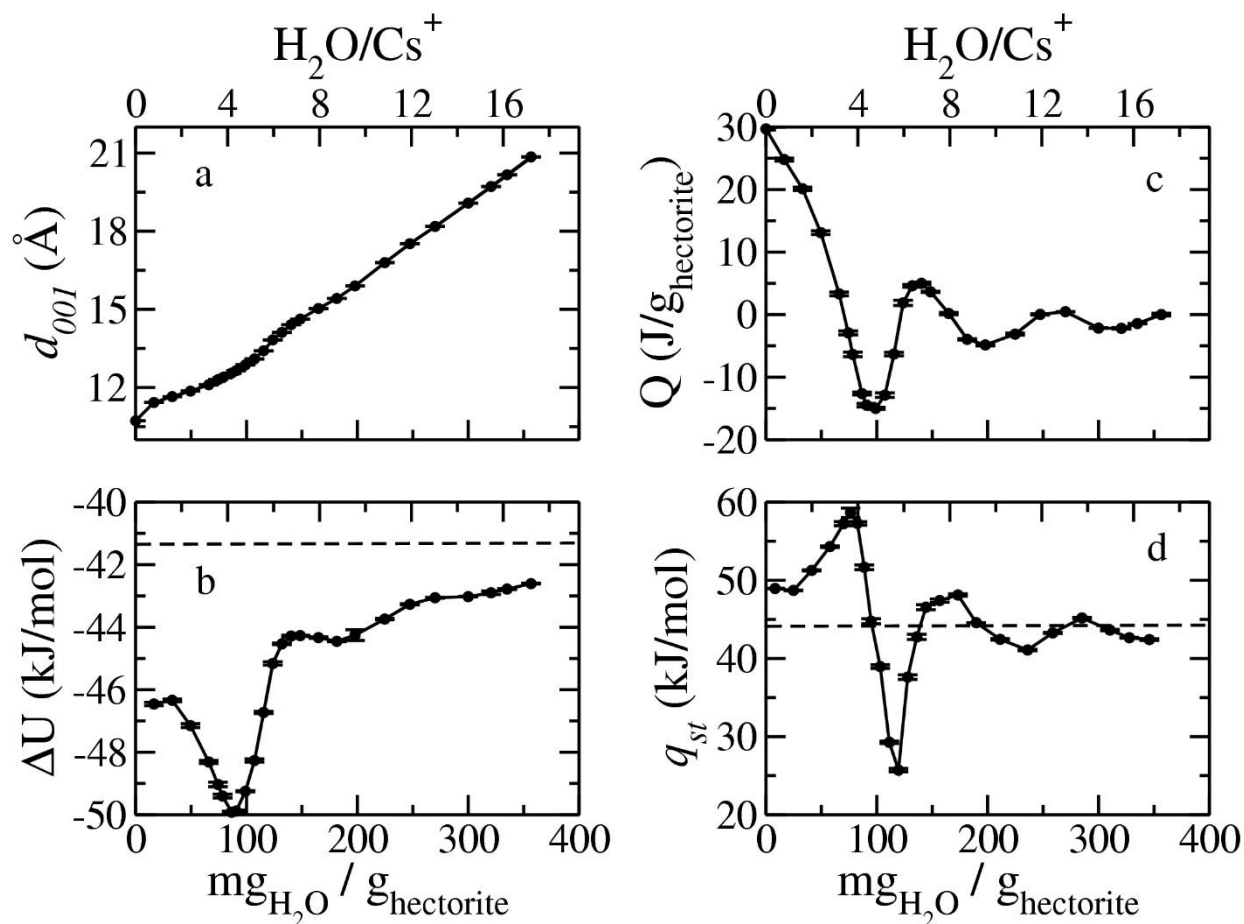


Figure 2. Thermodynamic properties of Cs-hectorite as a function of interlayer water content. a) Interlayer spacing. b) Hydration energy. c) Immersion energy. d) Isosteric heats of adsorption. The dashed lines indicate the bulk internal energy of SPC water in b) and the bulk vaporization enthalpy for SPC water in d). The errors bars are at the 90% confidence level.

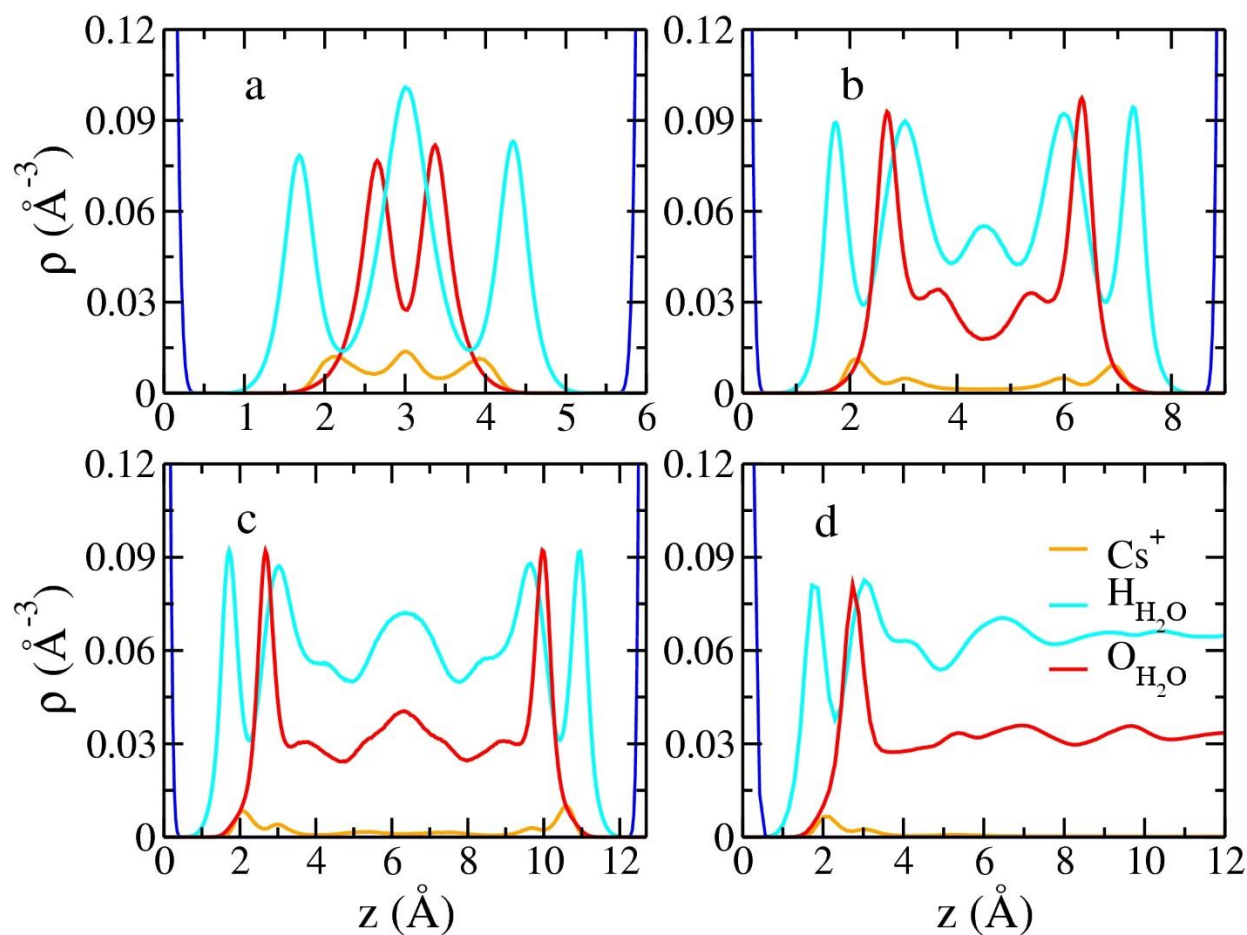


Figure 3. Atomic density profiles of Cs^+ (gold), $\text{O}_{\text{H}_2\text{O}}$ (red), and $\text{H}_{\text{H}_2\text{O}}$ for Cs-hectorite as functions of distance from the basal surface for the indicated hydration levels and the external surface. a) Monolayer hydrate. b) Bi-layer hydrate. c) Tri-layer hydrate; d) Basal Surface. The 0 of distance is the mean position of the basal O-atoms of the left surface clay surface.

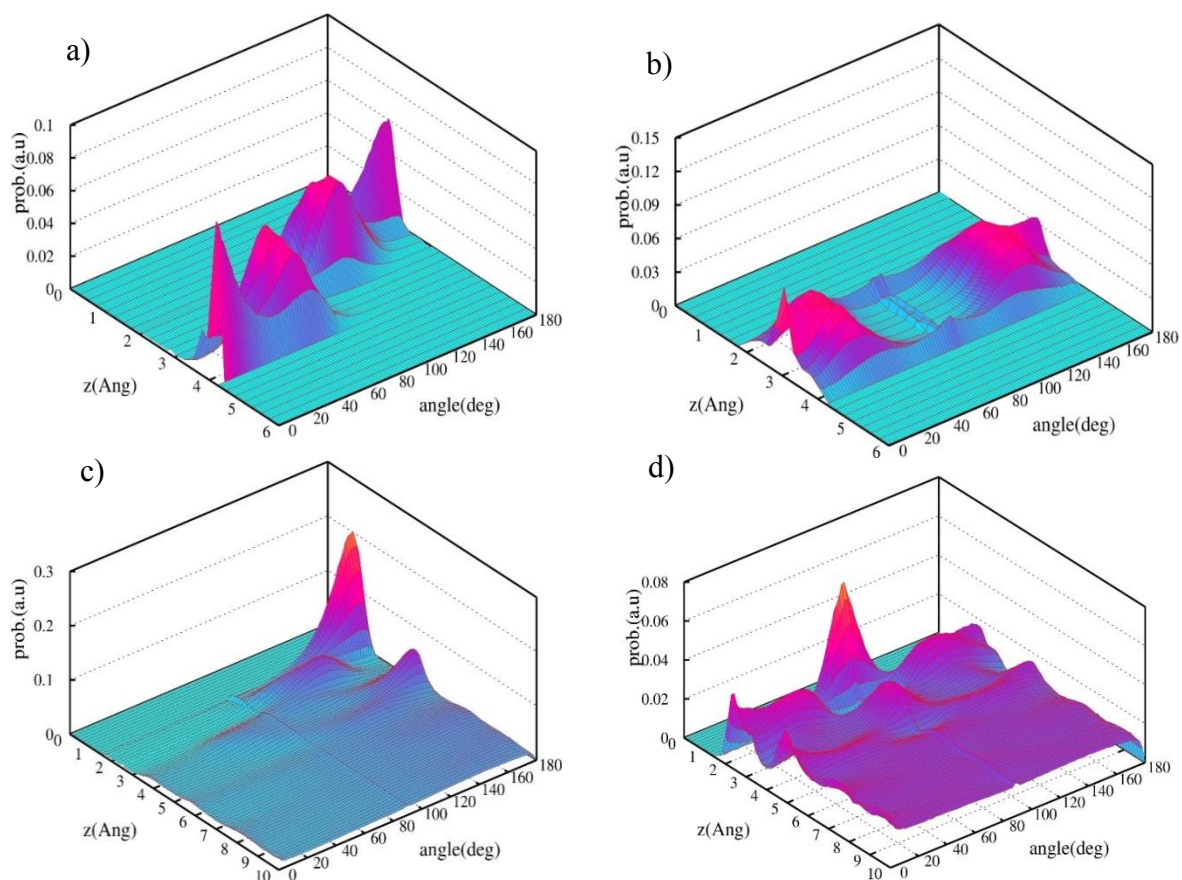


Figure 4. Orientation distributions of H₂O molecules at the Cs-hectorite interlayers and on the external basal surface. a) Dipole vector of H₂O molecules in the mono-layer hydrate b) HH vector of H₂O molecules in the mono-layer hydrate c) Dipole vector of near surface adsorbed H₂O molecules at the external surface. b) HH vector of near surface adsorbed H₂O molecules at the external surface.

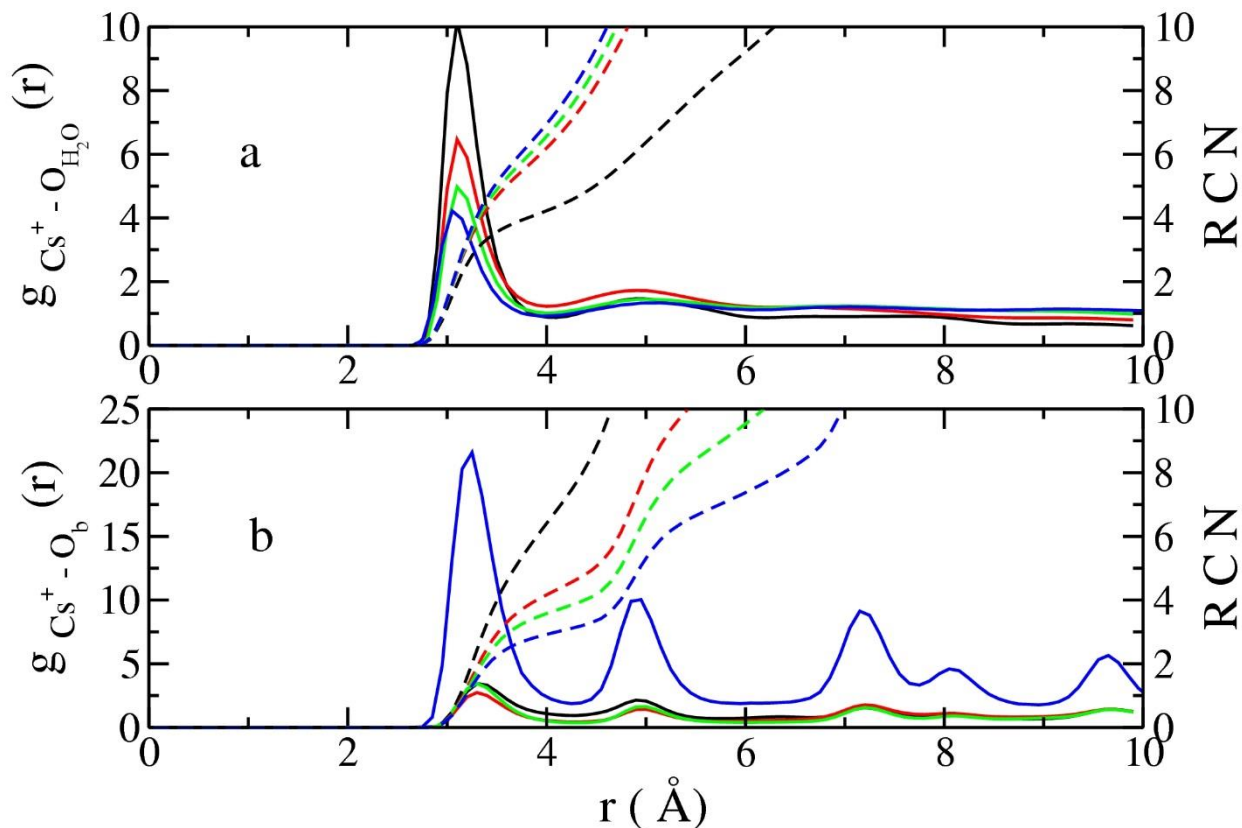
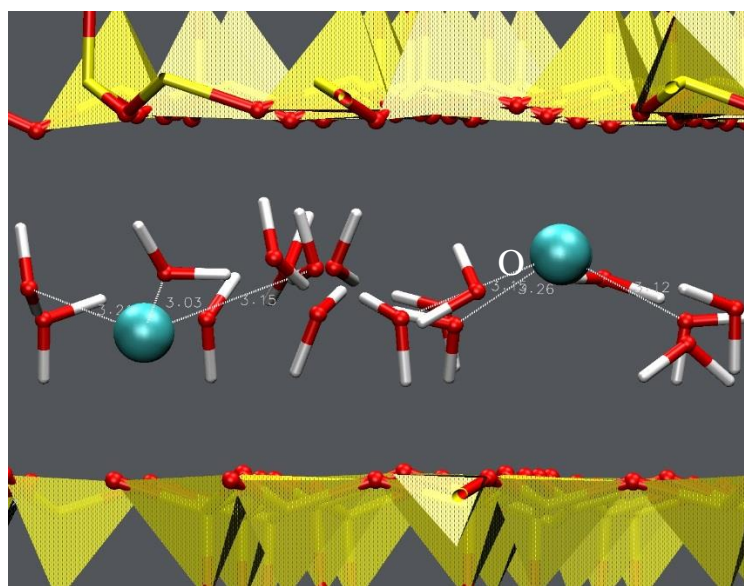
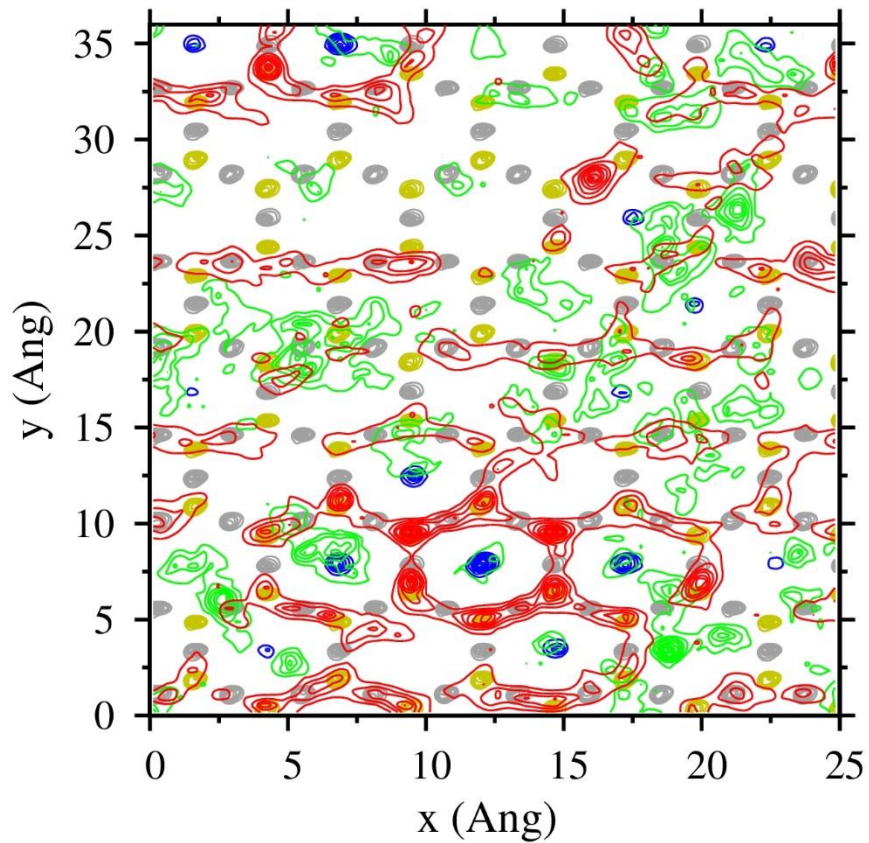
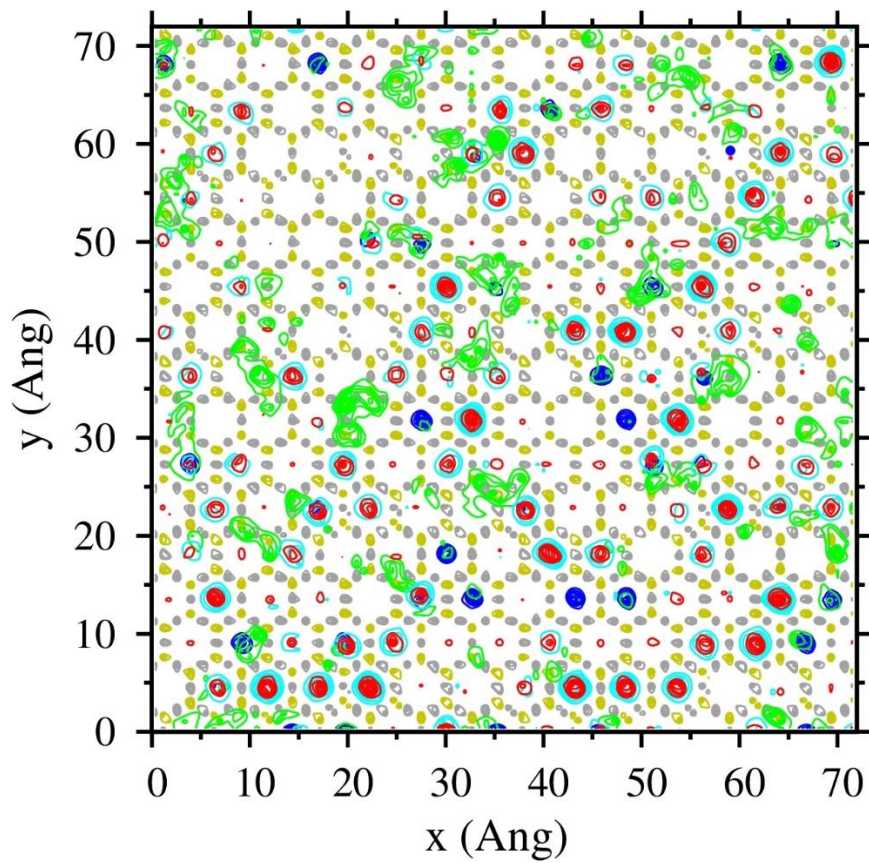
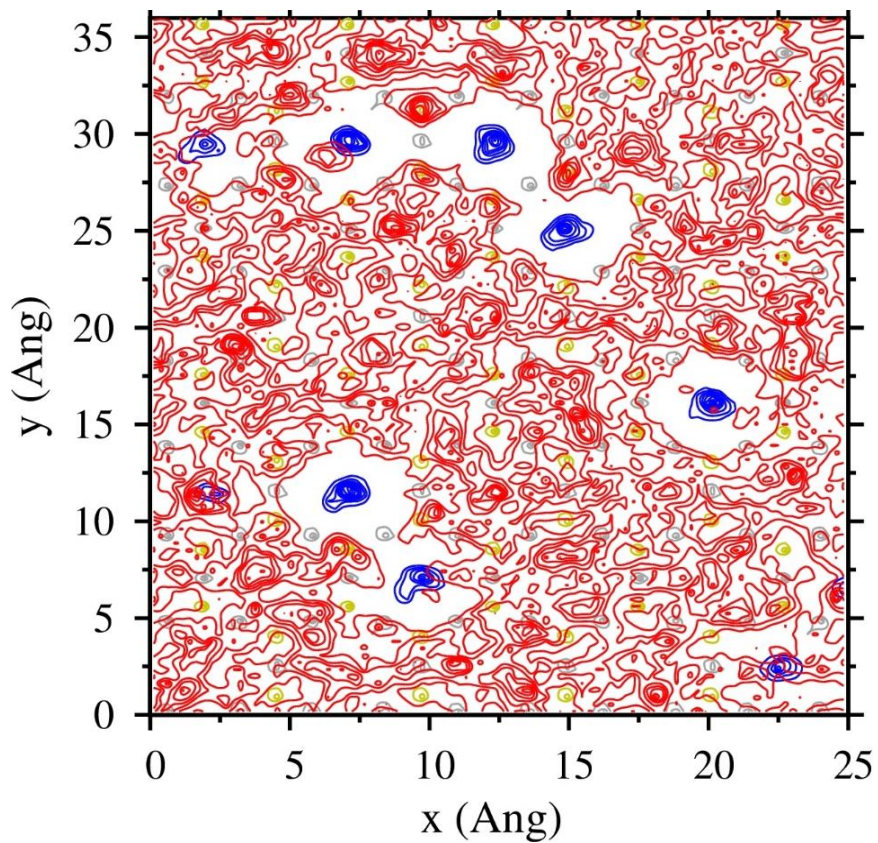


Figure 5. Radial distribution functions (RDFs, solid lines) and corresponding running coordination numbers (RCNs, dashed lines) for a) Cs^+ - H_2O pairs and b) Cs^+ - O_b pairs in the interlayers and on external surfaces of Cs-hectorite. Color code: monolayer hydrate – black, bilayer hydrate – red, trilayer hydrate – green, external basal surface – blue.





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2
3 **Figure 6.** Planar atomic density distributions (PADDs) of Cs⁺ ions and O_{H2O} in the interlayers
4 and on external surfaces of Cs-hectorite. a) Cs⁺ ions and O_{H2O} atoms at distances
5 and on external surfaces of Cs-hectorite. a) Cs⁺ ions and O_{H2O} atoms at distances
6 $z < 3 \text{ \AA}$ in the monolayer hydrate. b) schematic representation of the structural
7 arrangement of H₂O (oxygen – red, hydrogen - cyan) molecules and Cs⁺ ions (blue) in
8 the monolayer hydrate. c) Cs⁺ ions at distances $z < 2.8 \text{ \AA}$ and O_{H2O} atoms at $z < 3.1 \text{ \AA}$
9 in the bilayer hydrate. d) Cs⁺ ions at $z < 2.8 \text{ \AA}$ and O_{H2O} atoms at $z < 2.4 \text{ \AA}$ on external
10 basal surfaces. Color code: O_b – gray, Si – yellow, Cs⁺ ions at the center of ditrigonal
11 cavities – blue, Cs⁺ ions above Si tetrahedron – green, O_{H2O} – red, H_{H2O} – cyan.
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TABLES.

<i>Hydration</i>	<i>d (00l) Å</i>
Exp-dry ⁹⁶	10.665
Exp-dry ⁸⁰	11.700
Sim-dry (This work)	10.758
Exp-wet ⁸⁰ (43%)	12.100
Exp-wet ⁸¹ (43%)	12.300
Sim-H ₂ O (This work)	12.426
Sim-H ₂ O ^{75,76}	12.410
Sim-H ₂ O ⁷⁰	12.420

Table 1. Interlayer spacings of dry and hydrated Cs-hectorites compared with previous experiments and simulation studies.

<i>Hydration level</i>	<i>H₂O diffusion (10⁻⁹m²/s)</i>
Mono-layer	0.179 ± 0.03
Bi-layer	1.152 ± 0.01
3 – layer	1.675 ± 0.05
External Surface	3.024 ± 0.02

Table 2. Diffusion coefficients of H₂O molecules in the interlayer galleries of the mono-, bi-, tri-layer hydrates and at the external basal surface of Cs-hectorite.

<i>Hydration state</i>	<i>Cs⁺ - O_{H2O} (ps)</i>	<i>Cs⁺ - O_b (ps)</i>	<i>O_{H2O} - O_b (ps)</i>
<u>Intermittent (τ_{res}^I)</u>			
Mono-layer	507	1038	326
Bi-layer	250	508	150
3 - layer	198	356	101
<u>Continuous (τ_{res}^C)</u>			
Mono-layer	28.5	62.5	6.5
Bi-layer	9.2	52.4	2.0
3 - layer	6.0	49.2	1.9

Table 3. Intermittent and continuous residence times for the indicated pairs in the interlayers of Cs-hectorite. Values are in ps.

TOC Graphics

