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# Competitive Adsorption of H<sub>2</sub>O and CO<sub>2</sub> in 2-Dimensional Nano-confinement: GCMD Simulations of Cs- and Ca-Hectorite

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**Abstract**

The intercalation of H<sub>2</sub>O, CO<sub>2</sub>, and other fluid species in expandable clay minerals (smectites) may play a significant role in controlling the behavior of these species in geological carbon sequestration and enhanced petroleum production and has been the subject of intensive study in recent years. This paper reports the results of a computational study of the effects of the properties of the charge balancing, exchangeable cations on H<sub>2</sub>O and CO<sub>2</sub> intercalation in the smectite mineral, hectorite, in equilibrium with an H<sub>2</sub>O-saturated supercritical CO<sub>2</sub> fluid under reservoir conditions using Grand Canonical Molecular Dynamics (GCMD) methods. The results show that the intercalation behavior is greatly different for the cations with relatively low hydration energies and high affinities for CO<sub>2</sub> (here Cs<sup>+</sup>) than for cations with higher hydration energies (here Ca<sup>2+</sup>). With Cs<sup>+</sup>, CO<sub>2</sub> intercalation occurs in a 1-layer structure and does not require H<sub>2</sub>O intercalation, whereas with Ca<sup>2+</sup> the presence of a sub-monolayer of H<sub>2</sub>O is required for CO<sub>2</sub> intercalation. The computational results provide detailed structural, dynamical and energetic insight into the differences in intercalation behavior and are in excellent agreement with *in situ* experimental XRD, IR, quartz crystal microbalance, and NMR results for smectite materials obtained under reservoir conditions.

## Introduction

Clay minerals are important components of the deep sedimentary formations that are potential reservoirs for geological CO<sub>2</sub> sequestration and shale/tight gas production.<sup>1-16</sup> The competitive interaction of CO<sub>2</sub> and H<sub>2</sub>O with clays is, thus, central to understanding fluid behavior in these situations. The common smectite and mixed-layer illite-smectite clay minerals contain expandable interlayer galleries that contain intercalated charge balancing cations and variable numbers of fluid molecules. The partitioning of CO<sub>2</sub> and H<sub>2</sub>O between the intergranular pore fluid and the interlayer galleries may be significant in controlling the overall transport and physical properties of the host rock and has been a topic of substantial recent experimental and computational study.<sup>16-42</sup> Due to the presence of two basal surfaces separated by less than one to a few nm, the structure and dynamics of fluids nano-confined in the interlayer galleries are substantially different than on external clay surfaces (interparticle pores) or in the bulk fluid phase. Recent experimental and computational modeling studies have clearly shown that the clay swelling behavior depends strongly on the nature of the charge balancing cation (characterized by the CO<sub>2</sub> and H<sub>2</sub>O solvation energies) and on the composition and location of the permanent structural charge of the clay.<sup>43-57</sup>

Experimental and computational modeling studies have shown that at reservoir conditions the amount of intercalated CO<sub>2</sub> and its structural, dynamical, and energetic properties depend on the basal spacing and the solvation energies of the charge-balancing cation with H<sub>2</sub>O and CO<sub>2</sub> in smectite interlayers under supercritical conditions (scCO<sub>2</sub>,  $T_c \sim 31^\circ\text{C}$ ,  $P_c \sim 73$  bar).<sup>17-42</sup> X-ray diffraction (XRD) studies at pressurized CO<sub>2</sub> conditions by Giesting et al.<sup>18,19</sup> showed that increase (expansion) of the basal spacing of the common smectite, montmorillonite, depends on the initial interlayer H<sub>2</sub>O content. Similar studies by Schaefer et al.<sup>26,28</sup> at 323 K and 90 bar fluid pressure have confirmed that the intercalation of CO<sub>2</sub> in Na-, Ca- and Mg-montmorillonite is possible only when there is at least a sub-

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3 monolayer amount of H<sub>2</sub>O that props open the interlayer. For these cations, solvation by H<sub>2</sub>O  
4 is energetically more favorable than by CO<sub>2</sub>. The *in situ* infrared (IR) results of Loring et al.<sup>29-</sup>  
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monolayer amount of H<sub>2</sub>O that props open the interlayer. For these cations, solvation by H<sub>2</sub>O is energetically more favorable than by CO<sub>2</sub>. The *in situ* infrared (IR) results of Loring et al.<sup>29-31</sup> for Na-montmorillonite confirmed that a similar minimum content of co-adsorbed H<sub>2</sub>O is necessary to facilitate CO<sub>2</sub> intercalation and demonstrated that at 323 K and 90 bar maximum CO<sub>2</sub> intercalation occurs when the amount of co-adsorbed H<sub>2</sub>O corresponds to a monolayer (1L) hydrate structure. More recently, the *in situ* XRD, IR and nuclear magnetic resonance (NMR) results of Bowers et al.<sup>17</sup> at 323K and 90 bar showed that the solvation properties of the exchangeable cation (Na<sup>+</sup>, Cs<sup>+</sup> or Ca<sup>2+</sup>) significantly affect the structure, dynamics, and energetics of intercalated CO<sub>2</sub> in the similar smectite mineral, hectorite. The results show that interlayers containing large, monovalent cations that have similar solvation energies for H<sub>2</sub>O and CO<sub>2</sub> (such as Cs<sup>+</sup>)<sup>58</sup> intercalate CO<sub>2</sub> even under experimentally dry conditions after vacuum drying. In contrast, with Na<sup>+</sup> and Ca<sup>2+</sup> CO<sub>2</sub> intercalation requires at least a sub-1L of H<sub>2</sub>O to prop open the interlayers. For all these hectorites, the interlayer CO<sub>2</sub> content increases up to the 1L structure and decreases at higher H<sub>2</sub>O contents, as for montmorillonite at the same conditions.<sup>18,26,29</sup> These results emphasize the importance of having molecular scale understanding of the structure, dynamics, and energetics of H<sub>2</sub>O and CO<sub>2</sub> in the interlayers of smectites with exchangeable cations spanning a range of solvation energies with H<sub>2</sub>O and CO<sub>2</sub>.

Computational molecular modeling studies for Na-smectites are in good agreement with the experimental results showing that CO<sub>2</sub> intercalation requires the presence of at least a sub-1WL H<sub>2</sub>O layer.<sup>33-37,40</sup> Grand Canonical Monte Carlo (GCMC) simulations by Botan et al.<sup>33</sup> also suggest a stable bilayer (2L) hydrate structure (basal spacing ~15.0Å) for Na-montmorillonite at 348 K and 125 bar in contact with H<sub>2</sub>O-saturated scCO<sub>2</sub>. The GCMC simulations of Rao et al.<sup>37</sup> reported a higher interlayer CO<sub>2</sub> mole fraction for Na-montmorillonite with lower structural charge than with higher ones (-0.75 |e| vs. -1.0 |e|) at a given relative humidity (R.H.) at 323 K and 90 bar. Gibbs Ensemble Monte Carlo studies of

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3 Makaremi et al.<sup>36</sup> showed how the location of the structural charge sites in the smectite  
4 framework T-O-T layer structure alters the equilibrium basal spacing and energetics of Na-  
5 smectites at 348 K and 125 bar. Our previous grand canonical molecular dynamics (GCMD)  
6 simulations showed that temperature (323-368 K) and pressure (90-150 bar) have little impact  
7 on the structure and dynamics of interlayer CO<sub>2</sub> in Na-hectorite in contact with H<sub>2</sub>O saturated  
8 scCO<sub>2</sub>.<sup>40</sup>  
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17 There are, however, few computational modeling studies that examine the effect of  
18 cation solvation energy on the partitioning of H<sub>2</sub>O and CO<sub>2</sub> between smectite interlayers and  
19 bulk fluid and its interlayer structure, dynamics, and energetics in the supercritical regime. To  
20 our knowledge, the only such study is that of Kadoura et al.,<sup>34</sup> who explored the influence of  
21 Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> on CO<sub>2</sub> intercalation in montmorillonite at 323 K and 90 bar using GCMC.  
22 The results show that the interlayer CO<sub>2</sub> mole fraction is very similar with all these cations at  
23 R.H.s  $\geq$  60%, consistent with their high affinity for H<sub>2</sub>O. In contrast, our recent *in situ* XRD,  
24 IR and NMR experiments and GCMD simulations with montmorillonite and hectorite have  
25 shown that cations with low hydration energies (e.g., Cs<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) permit CO<sub>2</sub> intercalation  
26 even in the absence of H<sub>2</sub>O at 323 K and 90 bar in smectites, whereas those cations with higher  
27 hydration energies (e.g., Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) do not.<sup>41,42</sup> Energetically, the results show that the  
28 clay-cation interactions play a dominant role in determining the overall intercalation behavior,  
29 suggesting that further studies should be performed for cations with a greater range of size,  
30 CO<sub>2</sub> and H<sub>2</sub>O solvation energies.<sup>41,42</sup>  
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49 We address this gap here by examining the intercalation behavior of H<sub>2</sub>O and CO<sub>2</sub> in  
50 hectorite containing a cation with a low hydration energy (Cs<sup>+</sup>) and one with a high hydration  
51 energy (Ca<sup>2+</sup>) at 323 K and 90 bar in equilibrium with H<sub>2</sub>O-saturated scCO<sub>2</sub> using GCMD  
52 simulations.<sup>40-42</sup> Cs<sup>+</sup> and Ca<sup>2+</sup> are representative of cations with greatly different hydration  
53 energies and charge/radius ratios,<sup>48,53,58</sup> and they have greatly different CO<sub>2</sub>/H<sub>2</sub>O intercalation  
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3 behavior.<sup>17</sup> The results here are in excellent agreement with experimental data of Bowers et  
4 al.<sup>17</sup> and provide a basis for their detailed molecular scale structural, dynamic, and energetic  
5 interpretation and understanding.  
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10 The primary reason for using hectorite rather than montmorillonite is that samples of  
11 natural hectorite with a very low Fe content are available, and such samples were used in NMR  
12 experiments to reduce paramagnetic effects on the probe nuclei.<sup>17</sup> Both hectorite and  
13 montmorillonite develop their layer charge dominantly in the octahedral layer, and previous  
14 experimental NMR, IR, XRD, neutron scattering and simulation studies have shown that their  
15 intercalation behavior is very similar when fully hydroxylated and possessing identical layer  
16 charge.<sup>17-23, 25-54</sup>  
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## 26 **Simulation Details**

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28 Hectorite is a 2:1 trioctahedral smectite that develops its negative structural layer charge  
29 by isomorphic substitution of  $\text{Li}^+$  for  $\text{Mg}^{2+}$  in the octahedral layer. The simulated hectorite  
30 model has a structural formula of  $\text{M}^+(\text{Mg}_5\text{Li})\text{Si}_8\text{O}_{20}(\text{OH})_4$ . There are no tetrahedral  
31 substitutions in this model, in accordance with the experimental sample that contains a  
32 negligible fraction (0.25%) of isomorphic  $\text{Al}^{3+}/\text{Si}^{4+}$  substitution.<sup>59</sup> However, there are two  
33 important differences between the natural sample used in our experiments and the simulated  
34 model: (i) the model has 30% higher layer charge, and (ii) the simulated octahedral layer has  
35 only  $\text{OH}^-$  groups, whereas the natural sample has  $\sim 55\%$   $\text{F}^-$  for  $\text{OH}^-$  substitution.<sup>17,46,47</sup> The  
36 hydration behavior of synthetic fluoro-hectorite has been discussed previously.<sup>60</sup>  
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49 The simulation supercells for the Cs- and Ca-hectorite models consist of 16  
50 crystallographic unit cells of hectorite ( $4 \times 2 \times 2$ ) and include two interlayer galleries with  
51 surface areas of  $\sim 20.9 \text{ \AA} \times 18.2 \text{ \AA}$  ( $a=b=c: 90^\circ$ ) that are large enough to overcome any finite  
52 size effects. The isomorphic  $\text{Li}^+$  for  $\text{Mg}^{2+}$  substitutions were introduced only after constructing  
53 the supercell. This procedure provides a quasi-disordered pattern with different arrangements  
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3 of  $\text{Li}^+$  ions in the octahedral layer. Li-O-Li linkages are forbidden in this procedure in  
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5 accordance with the generalization of Lowenstein's rule.<sup>61</sup> The initial structure has the charge  
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7 compensating cations placed randomly in the interlayer region. Further details about this  
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9 hectorite model are described elsewhere.<sup>40,42,49,51</sup>

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12 We performed the GCMD<sup>62</sup> simulations in the grand canonical ensemble at 323 K and  
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14 90 bar using methods described previously.<sup>40,42</sup> Briefly, the interlayer basal spacings were  
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16 varied from 9.2 Å to 18.0 Å at an interval of 0.2 Å. The interlayer galleries were constrained  
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18 to maintain the same interlayer spacing along the  $z$ -dimension in each simulation run. However,  
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20 the simulations allow the lateral movement of the T-O-T layers along the  $x$  and  $y$  directions  
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22 without disrupting the structure or changing the basal spacing. This is because the minimum  
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24 energy interlayer structure depends strongly on the relative positions of adjacent T-O-T layers  
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26 and varies with the nature of the interlayer cation and the number of intercalated fluid  
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28 molecules.<sup>33,40</sup> All the simulations were performed using the GCMD module embedded in the  
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30 simulation package, RASPA.<sup>63</sup> The interatomic interactions for the clay structure and the  
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32 exchangeable cations are calculated using the *CLAYFF* force field,<sup>64</sup> which is widely used in  
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34 clay interfacial simulations. The  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules were represented by the rigid versions  
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36 of the SPC<sup>65</sup> and EPM2<sup>66</sup> models, respectively. Three-dimensional periodic boundary  
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38 conditions were employed with a cutoff of 9.0 Å for short range non-electrostatic interactions,  
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40 and the long-range electrostatic interactions were computed using Ewald summation<sup>67</sup> with an  
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42 accuracy of  $10^{-6}$ .

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45 The composition of the virtual reservoir representing the bulk  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluids  
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47 corresponds to the  $\text{H}_2\text{O}$ -saturated  $\text{CO}_2$ -rich phase at the simulated pressure (90 bar) and  
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49 temperature (323 K). The values were obtained from the experimental solubility data of  
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51 Spycher et al.<sup>68</sup> ( $x_{\text{H}_2\text{O}} = 0.0041$   $x_{\text{CO}_2} = 0.9959$ ). Fugacities required to calculate the probability  
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53 of acceptance and deletion moves of the fluid species ( $f_{\text{H}_2\text{O}} = 0.231$ :  $f_{\text{CO}_2} = 0.654$ ) were obtained  
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3 using the Peng-Robinson equation of state.<sup>69</sup> Further details of the GCMC approach and data  
4 analysis have been discussed in our previous papers.<sup>40,42,49,51,70,71</sup>  
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## 7 **Results and Discussion**

### 8 *Adsorption Profiles and Energetics*

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10 The computed intercalation behavior of CO<sub>2</sub> and H<sub>2</sub>O are very different in the Cs- and  
11 Ca-hectorites (Figures 1a -1c). For both systems, neither H<sub>2</sub>O nor CO<sub>2</sub> intercalate at basal  
12 spacings less than 10.2 Å, but their behaviors are very different as the interlayers expand  
13 (Figures 1a and 1b). For Ca-hectorite, H<sub>2</sub>O adsorption begins at 10.2 Å and reaches a plateau  
14 at ~11.0 Å, where CO<sub>2</sub> intercalation begins (Figure 1a). With increasing basal spacing, the  
15 amount of intercalated CO<sub>2</sub> increases, reaches a maximum at 12.8 Å, gradually decreases at  
16 larger spacings, and finally reaches an approximately constant value of 0.2 CO<sub>2</sub>/unit cell at  
17 spacings > ~16.0 Å. In contrast, the amount of intercalated H<sub>2</sub>O remains almost constant at  
18 spacings between 11.0 Å and 12.8 Å, and then increases almost linearly with further increase  
19 of the interlayer spacing. Based on our previous studies of hydrated Ca-hectorite without CO<sub>2</sub>,<sup>51</sup>  
20 the amount of H<sub>2</sub>O (~3 molecules/unit cell) in the plateau region corresponds to approximately  
21 1/3 of that needed for a full monolayer hydrate structure. This result is in good agreement with  
22 experimental studies that show CO<sub>2</sub> intercalation in Ca-hectorite begins only with H<sub>2</sub>O present  
23 in the interlayer.<sup>17</sup> The decrease in interlayer CO<sub>2</sub> mole fraction with increasing H<sub>2</sub>O content  
24 is consistent with previous IR spectroscopic data for hectorite and similar smectites  
25 (montmorillonite).<sup>17,29-31</sup> The experimentally determined Ca-hectorite basal spacings of  
26 ~12.6 Å and ~15.9 Å correspond to 1L and 2L structures, respectively, and are in very good  
27 agreement with the simulated values of 12.8 Å and 16.2 Å.<sup>17</sup> These 1L and 2L distances are  
28 also comparable to those from our recent MD simulations of hydrated Ca-hectorite without  
29 CO<sub>2</sub> at ambient conditions.<sup>51</sup> Importantly, the adsorption profiles of CO<sub>2</sub> and H<sub>2</sub>O reported here  
30 are similar to our previous studies on Na-hectorite under identical thermodynamic conditions.  
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3 This similarity emphasizes the critical role played by the H<sub>2</sub>O molecules in propping open the  
4 interlayer region to allow CO<sub>2</sub> intercalation when the interlayer cations have relatively high  
5 hydration energies.<sup>40,58</sup>  
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10 In contrast, for Cs-hectorite neither H<sub>2</sub>O nor CO<sub>2</sub> intercalate at basal spacings <11.1 Å.  
11 With increasing basal spacing beyond this value, CO<sub>2</sub> intercalation increases up to 12.5 Å,  
12 decreases at larger values, has a shallow local minimum near 14.2 Å, and reaches a nearly  
13 constant value of ~0.3 CO<sub>2</sub>/unit cell at spacings > 16.0 Å (Figure 1b). Significant H<sub>2</sub>O  
14 intercalation begins only at ~13.0 Å, near the maximum of CO<sub>2</sub> intercalation, and increases  
15 with increasing basal spacing. The amount of intercalated H<sub>2</sub>O at spacings < 13.0 Å is  
16 negligible (1.5%), consistent with the experimentally observed intercalation of CO<sub>2</sub> in Cs-  
17 hectorite under fully dry conditions with a basal spacing of 12.2 Å, indicative of an anhydrous  
18 1L structure.<sup>17</sup> At basal spacings > 13.2 Å, the decrease in CO<sub>2</sub> intercalation is compensated  
19 by increasing H<sub>2</sub>O. The adsorption profiles and the interlayer distance at which CO<sub>2</sub>  
20 intercalation begins reported here are very similar those in our earlier study of Cs-hectorite  
21 exposed to dry scCO<sub>2</sub><sup>42</sup> up to 13.2 Å, suggesting that the intercalation behavior of CO<sub>2</sub> is not  
22 significantly affected by the presence of H<sub>2</sub>O in the bulk fluid phase reservoir. Similar increases  
23 in interlayer H<sub>2</sub>O content at larger spacings have been reported previously in simulations of  
24 hydrated Cs-hectorite and other smectites,<sup>49,54</sup> although such expanded structures are not  
25 observed experimentally.  
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47 The calculated immersion energies for Cs-hectorite (Figure 1c) show a global minimum  
48 at a basal spacing of ~12.5 Å, indicating that the 1L structure is the thermodynamically stable  
49 state for this phase in equilibrium with H<sub>2</sub>O-saturated scCO<sub>2</sub> at 323 K and 90 bar, in agreement  
50 with the experimental results.<sup>17</sup> In contrast, for Ca-hectorite the energy minimum near the 1L  
51 structure is poorly localized. The immersion energies decrease beyond the 1L structure and  
52 reach a minimum at 16.2 Å, corresponding to a 2L structure. Further increase in basal spacing  
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3 shows little variation in energy, consistent with experimental observations that higher  
4 hydration states for Ca-hectorite are possible, depending upon the thermodynamic activity of  
5 H<sub>2</sub>O.<sup>17</sup> Most importantly, these results clearly demonstrate that the thermodynamically stable  
6 state of Ca-hectorite in equilibrium with H<sub>2</sub>O-saturated scCO<sub>2</sub> has a much larger basal spacing  
7 than Cs-hectorite under the same conditions, consistent with experimental XRD  
8 measurements.<sup>17</sup> The qualitative behavior of the immersion energies of Ca-hectorite are also  
9 consistent with our previous MD simulations of hydrated Ca-hectorite without CO<sub>2</sub>.<sup>51</sup> Ideally,  
10 formation of the stable energy structures can be obtained by computing the disjoining pressure  
11 and swelling free energy calculations.<sup>72,73</sup> However, the results of Young et al.<sup>71</sup> for hydrated  
12 smectites indicate that conclusions drawn from the immersion energies and free energies are  
13 comparable to each other. The use of immersion energies to investigate the equilibrium states  
14 of smectites have been discussed elsewhere for H<sub>2</sub>O adsorption and is extended to CO<sub>2</sub> in our  
15 studies.<sup>49,51,70</sup> Importantly, the thermodynamic stable states obtained using the immersion  
16 energy criterion in our earlier studies of Na-hectorite under identical simulated conditions are  
17 comparable with the conclusions based on swelling free energies reported using the similar  
18 smectite mineral, montmorillonite.<sup>33,36,37,40,42</sup> Therefore, we conclude that the energetic features  
19 of the immersion energy plots are good indicators of the thermodynamically stable states.  
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42 The computed interlayer CO<sub>2</sub> mole fractions in Cs- and Ca-hectorite are in good  
43 agreement with the ranges estimated from *in situ* high *T* and *P* experimental studies conducted  
44 at similar *T* and *P* conditions<sup>17</sup> (Table 1). For Cs-hectorite, our simulations indicate a CO<sub>2</sub> mole  
45 fraction of 0.98 at the equilibrium 1L basal spacing of 12.5 Å, in reasonable agreement with  
46 the upper-range experimental value of 0.82 estimated from the intensities of the spinning side  
47 bands (SSBs) in <sup>13</sup>C NMR spectra and the IR observed H<sub>2</sub>O/cation ratio.<sup>17</sup> Similarly, for Ca-  
48 hectorite the computed CO<sub>2</sub> mole fractions of 0.34 for the 1L (12.8 Å) structure and 0.02 for  
49 the 2L (16.2 Å) structure are within the ranges estimated from NMR/IR data, though we note  
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3 that the 2L result is close to what was reported as the minimum interlayer mole fraction for this  
4 sample.<sup>17</sup> The differences between the experimental and computed results for both Cs- and Ca-  
5 hectorite are mostly likely associated with uncertainty in the IR-derived H<sub>2</sub>O/cation ratio due  
6 difficulty in resolving signal from CO<sub>2</sub> sorbed on external surfaces and in interlayers, the layer  
7 charge differences between SHCa-1 and the model (-0.75 |e| vs -1.0 |e|), and the use of a fully  
8 hydroxylated hectorite model in contrast to the extensively fluorinated experimental sample.<sup>17</sup>  
9 Because of the higher structural charge used in the simulations, the model requires more Ca<sup>2+</sup>  
10 ions to charge compensate the surface. Due to the high hydration energy of Ca<sup>2+</sup>,<sup>58</sup> more H<sub>2</sub>O  
11 molecules are adsorbed in the interlayer region to hydrate these Ca<sup>2+</sup> ions leading to less  
12 available space for CO<sub>2</sub> intercalation in the simulation. The effect of charge was been reported  
13 previously by Rao et al.<sup>37</sup> for a similar smectite mineral, montmorillonite. In addition, the XRD  
14 profiles of Dazas et al.<sup>74</sup> clearly indicate that adsorption of H<sub>2</sub>O is less for fluorinated hectorite  
15 compared to hydroxylated hectorite. As a result, there is probably more interlayer space  
16 available for CO<sub>2</sub> intercalation in the experimental sample than in our simulated model.<sup>17</sup>  
17 Because the natural samples inevitably adsorb fluid species on external surfaces, the  
18 simulations provide specific insight into the interlayer fluid composition and dynamics.

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Importantly, for the 1L structures, which for each cation have the greatest interlayer CO<sub>2</sub> contents, both Cs- and Ca-hectorite have more interlayer CO<sub>2</sub> than Na-hectorite, as also observed in the experimental high *T* and *P* IR results.<sup>17,40</sup> Recent GCMC simulation studies by Kadoura et al.<sup>34</sup> show similar behavior, with Ca- and Mg-montmorillonite having higher CO<sub>2</sub> mole fractions than Na- montmorillonite at a given R.H. The interlayer CO<sub>2</sub> mole fractions from our studies for Ca-hectorite are similar to the reported values by Kadoura et al.<sup>34</sup> for Ca-montmorillonite, despite our simulations having a higher layer charge.

### *Interlayer Structure*

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As for the adsorption isotherms, the atomic density profiles (ADPs) of the intercalated species as functions of distance normal to the basal surface are greatly different for Cs- and Ca-hectorite (Figures 2a-2c). For the 1L structures, the presence of H<sub>2</sub>O in Ca-hectorite leads to a more complex interlayer structure than for Cs-hectorite, which has only ~1.5% interlayer H<sub>2</sub>O and, thus, does not yield an observable H<sub>2</sub>O ADP. For both 1L phases, the ADPs of the cation (Ca<sup>2+</sup> or Cs<sup>+</sup>), C<sub>CO2</sub> and O<sub>CO2</sub> are characterized by single peaks located at the mid-plane of the interlayer (Figures 2a and 2c) coordinating directly with the basal surface. This arrangement is the same as in Cs-hectorite exposed to dry scCO<sub>2</sub> at the same T and P.<sup>42</sup> For the 1L structure of Ca-hectorite, the nearest neighbor Ca<sup>2+</sup> coordination shell (Figure 3d) consists of 6.0 H<sub>2</sub>O (3 associated with each surface) and 2.0 O<sub>b</sub> (one from each surface), and the ADPs of O<sub>H2O</sub> and H<sub>H2O</sub> are characterized by 4 and 5 peaks respectively. As shown in our previous simulations of hydrated Ca-hectorite without CO<sub>2</sub>,<sup>51</sup> these distributions indicate two different adsorption environments for H<sub>2</sub>O, one close to the basal surface and the other near the mid-plane of the interlayer. The H<sub>2</sub>O molecules closer to the surface are coordinated to the oxygen atoms of the basal surface, O<sub>b</sub>, through both of their H<sub>H2O</sub>. Those near the mid-plane are coordinated to the O<sub>b</sub> atoms through only one H<sub>H2O</sub> at a time. The H<sub>2</sub>O ADPs have been discussed in more detail in our earlier study.<sup>51</sup> Although the 2L structure is the thermodynamically stable state for Ca-hectorite in contact with H<sub>2</sub>O-saturated scCO<sub>2</sub> at our conditions, the structure and dynamics for the 1L state are relevant, because experimental XRD studies show that it occurs in the presence of H<sub>2</sub>O-undersaturated scCO<sub>2</sub> (low R.H. conditions).<sup>17</sup> We use the basal spacing of 12.8 Å to represent the 1L structure because it has the maximum amount of interlayer CO<sub>2</sub> and a complete 1L structure. This 1L structure is comparable to the experimental structure of Ca-hectorite upon exposure to dry scCO<sub>2</sub> (0 % R.H.), in which the interlayer spacing corresponds to 1L regime and has a maximum CO<sub>2</sub> content.<sup>17</sup>

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3 In the 2L structure of Ca-hectorite (Figure 2b),  $\text{Ca}^{2+}$  occurs at the mid-plane of the  
4 interlayer  $\sim 4.8$  Å from the two basal surfaces and is coordinated by 8.0  $\text{H}_2\text{O}$  (4 associated with  
5 each basal surface) in a square antiprism arrangement (Figure 3f), consistent with recent high  
6  $T$ - $P$  NMR studies.<sup>17</sup> In contrast, the  $\text{C}_{\text{CO}_2}$  and  $\text{O}_{\text{CO}_2}$  ADP peaks at 3.0 Å and 6.7 Å show that  
7 the  $\text{CO}_2$  molecules are in direct coordination with the basal surfaces. In addition, the broad  
8 shoulders for  $\text{O}_{\text{CO}_2}$  at  $\sim 2.2$  Å and  $\sim 7.5$  Å, even closer to the nearest basal surface, shows that  
9 the  $\text{CO}_2$  molecules probe more orientations and are less dynamically restricted in the 2L  
10 structure than in the 1L structure. As in the 1L structure, the  $\text{H}_2\text{O}$  molecules at 2.8 Å from each  
11 basal surface are coordinated to the  $\text{O}_b$  atoms through one H-atom. In contrast,  $\text{H}_2\text{O}$  molecules  
12 in the mid-plane region (at  $\sim 5.0$  Å) are coordinated only to other  $\text{H}_2\text{O}$  molecules and the  $\text{Ca}^{2+}$ ,  
13 and not to the basal surfaces. The  $\text{Ca}^{2+}$  and  $\text{CO}_2$  distributions are in reasonable agreement with  
14 previous simulations of Ca-montmorillonite in contact with  $\text{scCO}_2$  under similar conditions.<sup>34</sup>  
15 However, our hectorite simulations show only one ADP peak for  $\text{Ca}^{2+}$  in the 1L and 2L  
16 structures, and consequently different  $\text{H}_2\text{O}$  profiles. This difference is probably due to the  
17 presence of tetrahedral charge resulting from Al for Si substitution in the montmorillonite  
18 model used by Kadoura et al.<sup>34</sup> and to the smaller layer charge ( $-0.8 |e|$ ) compared to our model  
19 ( $-1.0 |e|$ ). The presence of tetrahedral charge can greatly change the interlayer adsorption,  
20 structure, and dynamics of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules, as discussed by Makaremi et al.<sup>36</sup> It should  
21 be noted that the interlayer arrangements of  $\text{CO}_2$  molecules in Ca-hectorite in both the 1L and  
22 2L structures are similar to the comparable systems with  $\text{Na}^+$ , although the  $\text{H}_2\text{O}$  distributions  
23 are different because the larger  $\text{H}_2\text{O}$  content in the present study leads to a more ordered  
24 interlayer  $\text{H}_2\text{O}$  structure than in Na-hectorite.<sup>40</sup>

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54 In the 1L structure of Cs-hectorite and the 1L and 2L structures of Ca-hectorite, the  
55 computations show that intercalated  $\text{CO}_2$  molecules are oriented with the average position of  
56 their O-C-O vectors parallel to the basal surface (Figure 2d) and that they undergo librational  
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3 motion around an axis perpendicular to their O-C-O axis. The values 0 and  $\pm 1$  for  $P(\cos \vartheta)_{\text{CO}_2}$   
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5 correspond to parallel and perpendicular orientation of  $\text{CO}_2$  with respect to the plane of the  
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7 basal surface, respectively. These results are in full agreement with the interpretation of  
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9 spinning sideband patterns in *in situ* experimental  $^{13}\text{C}$  MAS NMR spectra.<sup>17</sup> In addition, the  
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11 calculations show that the O-C-O axes probe a range of angles, demonstrating wobbling  
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13 motion with respect to the basal surfaces. For Ca-hectorite, the angular distribution is larger for  
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15 the 2L structure (between  $\sim\pm 0.8$ ) than for the 1L structure (between  $\sim\pm 0.6$ ). The range of  
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17 orientations probed by the O-C-O vectors in the 1L structure of Cs-hectorite is essentially  
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19 identical to that of the same hectorite model exposed to dry  $\text{scCO}_2$  under similar conditions.<sup>42</sup>  
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21 This is as expected due to the very low  $\text{H}_2\text{O}$  content of the structure here. In contrast, the range  
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23 of angles explored by the O-C-O vector in the 1L structure of Ca-hectorite is larger than in the  
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25 1L structure of the same model exposed to dry  $\text{scCO}_2$  at the same  $P$  and  $T$ .<sup>42</sup> This difference is  
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27 most likely due to the combination of a slightly larger basal spacing ( $0.4\text{\AA}$ ) and a higher  
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29 interlayer  $\text{CO}_2$  mole fraction (1.0) with dry  $\text{scCO}_2$  compared to our 1L simulations here (0.34)  
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31 caused by the presence of interlayer  $\text{H}_2\text{O}$ . In the current study, the  $\text{Ca}^{2+}$  ions are coordinated  
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33 by only  $\text{H}_2\text{O}$  molecules and basal oxygen atoms, which permits the intercalated  $\text{CO}_2$  molecules  
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35 to occupy the volume between hydrated metal cations. As also found in molecular simulations  
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37 of Na-hectorite,<sup>40</sup> the intercalated  $\text{CO}_2$  molecules in the Cs- and Ca-hectorite simulations do  
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39 not undergo isotropic reorientation, as shown by the lack of peaks or shoulders near -1 and +1  
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41 for the O-C-O vectors. The average angles probed by the  $\text{H}_2\text{O}$  dipole vectors for the 1L and 2L  
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43 structures of Ca-hectorite are similar to those in Na-hectorite, demonstrating two different  $\text{H}_2\text{O}$   
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45 orientations, consistent with the presence of two different types of interlayer  $\text{H}_2\text{O}$  (Figure S1  
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47 and related discussion in the Supporting Information).<sup>40</sup>  
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56 The radial distribution functions (RDFs) and running coordination numbers (RCNs;  
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58 Figures 3a, 3c, 3e) clearly show that the intercalated  $\text{CO}_2$  directly coordinates  $\text{Cs}^+$  in the 1L  
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3 Cs-hectorite structure (Figure 3b) and that it does not coordinate  $\text{Ca}^{2+}$  in either the 1L or 2L  
4 structures, even for short times (Figures 3d and 3f). For the Cs-hectorite 1L structure, the mean  
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6  $\text{Cs}^+ - \text{O}_{\text{CO}_2}$  and  $\text{Cs}^+ - \text{O}_b$ , interatomic distances are both  $\sim 3.2 \text{ \AA}$ . The  $\text{Cs}^+ - \text{O}_b$  RCN is 8.3, and  
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8 the  $\text{Cs}^+ - \text{O}_{\text{CO}_2}$  RCN is 4.5, resulting in a total ion coordination number of  $\sim 12.8$ . Each  $\text{Cs}^+$  ion  
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10 is in inner sphere (IS) coordination at the center of a ditrigonal cavity of one surface and above  
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12 a Si tetrahedron on the other (Figure 3b), as well as being surrounded by 4-5  $\text{CO}_2$  molecules.  
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14 The  $\text{Cs}^+ - \text{O}_{\text{CO}_2}$  RCNs are essentially identical to those of Cs-hectorite exposed to dry  $\text{scCO}_2$   
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16 under same thermodynamic conditions, as expected due to the low  $\text{H}_2\text{O}$  content here.<sup>42</sup>  
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18 Importantly, the  $\text{Cs}^+ - \text{O}_{\text{CO}_2}$  RCN here is very similar to that of  $\text{Cs}^+ - \text{O}_{\text{H}_2\text{O}}$  in Cs-hectorite in  
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20 equilibrium with pure  $\text{H}_2\text{O}$ .<sup>49</sup> This result is in good agreement with our recent experimental  
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22 results, which suggest that replacement of  $\text{H}_2\text{O}$  by  $\text{CO}_2$  in the 1L structure of Cs-hectorite under  
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24 the conditions here requires only a small energy change.<sup>17</sup> The mean non-bonded  $\text{O}_{\text{CO}_2} - \text{O}_b$   
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26 and  $\text{O}_{\text{CO}_2} - \text{O}_{\text{CO}_2}$  interatomic distances in Cs-hectorite are centered at  $3.4 \text{ \AA}$  and  $3.2 \text{ \AA}$ ,  
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28 respectively, and the  $\text{O}_{\text{CO}_2} - \text{O}_b$  RCN is  $\sim 7.7$  (Figure 4a). The average local structure of the  $\text{CO}_2$   
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30 molecules is best characterized as having the  $\text{O}_{\text{CO}_2}$  atoms located above a silica tetrahedron of  
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32 one basal surface and above the center of a ditrigonal cavity of the other basal surface (Figure  
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34 3b). The  $\text{O}_{\text{CO}_2} - \text{O}_{\text{CO}_2}$  RCN is  $\sim 4.6$ , and their mutual arrangement is dominated by a slipped  
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36 parallel arrangement (parallel  $\text{CO}_2$  with slight offset) with only a small fraction of T-shaped  
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38 arrangements (Figure 3b).<sup>38</sup> The rapid reorientation of  $\text{CO}_2$  perpendicular to the O-C-O  
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40 molecular axis is well illustrated by the dispersed contours for  $\text{O}_{\text{CO}_2}$  in the 1L structure (Figure  
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42 S2).  
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51 In both the 1L and 2L structures of Ca-hectorite, the mean  $\text{Ca}^{2+} - \text{O}_{\text{H}_2\text{O}}$  distance is  $2.5 \text{ \AA}$ ,  
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53 similar to the value in bulk aqueous solutions (Figure 3c and 3e),<sup>75</sup> and the absence of nearest  
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55 neighbor cation- $\text{O}_{\text{CO}_2}$  coordination is the same as in Na-hectorite.<sup>40</sup> This later result is  
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57 consistent with the expectation that cations with large hydration energies and smaller  $\text{CO}_2$   
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3 solvation energies prefer to be coordinated by H<sub>2</sub>O at all R.H.s.<sup>58,75</sup> In Ca-hectorite, the  
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5 intercalated CO<sub>2</sub> molecules occur in small clusters between the hydrated Ca<sup>2+</sup> ions (Figure 3d),  
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7 as also observed in previous MD simulations of Na-montmorillonite.<sup>38</sup> The adsorption  
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9 environment of the Ca<sup>2+</sup> ions is very similar to our previous results of hydrated Ca-hectorite  
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11 without CO<sub>2</sub>.<sup>51</sup>  
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15 The local coordination environment of CO<sub>2</sub> in the 1L structure of Ca-hectorite is  
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17 significantly different than in Cs-hectorite, with one O<sub>CO2</sub> at the center of a ditrigonal cavity of  
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19 one surface and the other directly above an O<sub>b</sub> of the opposite basal surface (Figure 3d). The  
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21 adsorption environment of CO<sub>2</sub> molecules reported here is in good agreement with earlier  
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23 calculations for Na-hectorite under identical simulated conditions.<sup>40</sup> This structure is also in  
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25 agreement with the O<sub>CO2</sub>-O<sub>b</sub> RCN of ~7.0 (Figure 4b). The aggregation of CO<sub>2</sub> is mostly in  
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27 trimers (O<sub>CO2</sub>-O<sub>CO2</sub> RCN = 3.6) with a slipped parallel orientation. There is no evidence of T-  
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29 shaped arrangements, as is also observed in the 1L structure of Cs-hectorite. The total non-  
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31 bonded coordination of CO<sub>2</sub> in Ca-hectorite increases from 10.3 (7.1 O<sub>b</sub> : 3.2 O<sub>H2O</sub>) in the 1L  
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33 structure to 12.3 (4.0 O<sub>b</sub> : 8.3 O<sub>H2O</sub>) in the 2L structure, but the H<sub>2</sub>O coordination to O<sub>b</sub> atoms  
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35 in the 1L and 2L structures is nearly the same as in hydrated Ca-hectorite without CO<sub>2</sub>.<sup>51</sup> This  
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37 result demonstrates that the H<sub>2</sub>O to O<sub>b</sub> H-bonding is not significantly affected by the presence  
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39 of CO<sub>2</sub>. The mean O<sub>b</sub>-O<sub>CO2</sub> distances decrease from 3.6 Å to 3.3 Å as the basal spacing  
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41 increases from the 1L to 2L structures, suggesting a more compact arrangement in the 2L  
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43 structure. Despite having similar mean O<sub>CO2</sub>-O<sub>b</sub> and O<sub>CO2</sub>-O<sub>H2O</sub> interatomic distances, the RCN  
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45 values in Ca-hectorite are significantly smaller than in the simulations of Ca-montmorillonite  
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47 exposed to wet CO<sub>2</sub> fluid at 323 K and 90 bar due to the differences in layer charge and  
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49 location, as discussed above.<sup>34</sup> The average adsorption environments of the intercalated species  
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51 for cations, H<sub>2</sub>O and CO<sub>2</sub> in the 1L and 2L structures of Cs- and Ca-hectorites are further  
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3 validated by the planar atomic density distributions discussed in the supporting information  
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5 (Figures S2-S6).  
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8 *Coordination times and dynamics of the interlayer species*  
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10 The mean nearest neighbor coordination times among the different intercalated species  
11 (H<sub>2</sub>O, CO<sub>2</sub>, cations) and with surface O<sub>b</sub> atoms show that the charge compensating cations play  
12 a crucial role in dictating the overall interlayer dynamics (Table 2). For the 1L structures, the  
13 intermittent and continuous coordination times for the Ca<sup>2+</sup>-O<sub>b</sub> pair are an order of magnitude  
14 longer than for the Cs<sup>+</sup>-O<sub>b</sub> pair, in good agreement with previous MD simulations of hydrated  
15 hectorites under ambient conditions.<sup>51</sup> In the 1L structures of both Cs- and Ca-hectorite, the  
16 cation-O<sub>b</sub> coordination times are significantly longer than the O<sub>CO2</sub>-O<sub>b</sub> coordination times,  
17 reflecting the weaker interaction of the CO<sub>2</sub> with the clay surface compared to cations. In  
18 contrast, the O<sub>CO2</sub> spend similar times near O<sub>b</sub> and Cs<sup>+</sup> in the 1L structure, suggesting a constant  
19 exchange among these coordination environments. This exchange may be due to the  
20 reorientation of the CO<sub>2</sub> parallel to the surface, which is consistent with the delocalized PADD  
21 contours for CO<sub>2</sub> molecules (Figure S2). The O<sub>CO2</sub>-O<sub>H2O</sub> and O<sub>CO2</sub>-O<sub>b</sub> residence times are  
22 similar for both the 1L and 2L structure of Ca-hectorite, but these times are much shorter than  
23 those for Ca-O<sub>H2O</sub> and Ca-O<sub>b</sub>, indicating that the interactions of CO<sub>2</sub> with the surface and H<sub>2</sub>O  
24 are weaker than those of Ca<sup>2+</sup>. The longer coordination times of Ca<sup>2+</sup> with H<sub>2</sub>O than with O<sub>b</sub> is  
25 consistent with its large hydration energy.<sup>58</sup> For Ca-hectorite, all the coordination times for the  
26 2L structure are shorter than for the 1L structure, reflecting the higher probability for H<sub>2</sub>O  
27 molecules to exchange between the 1<sup>st</sup> and 2<sup>nd</sup> coordination spheres of Ca<sup>2+</sup> with CO<sub>2</sub> librating  
28 and hopping between surface sites. There are no residence time values for Ca-O<sub>CO2</sub> for the 1L  
29 and 2L structures of Ca-hectorite and O<sub>H2O</sub> coordination around Cs<sup>+</sup> and O<sub>CO2</sub> in 1L structure  
30 of Cs-hectorite, because such coordination does not occur, even for short periods of time  
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(Figures 3c-3f). Similarly, because  $\text{Ca}^{2+}$  is present in outer sphere coordination in the 2L structure, there are no  $\text{Ca-O}_b$  values for it.

## Conclusions

Our GCMD simulation studies indicate that the intercalation behavior of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the interlayers of hectorite when in contact with a binary  $\text{H}_2\text{O}$ -saturated  $\text{scCO}_2$  fluid at 323 K and 90 bars strongly depends on the hydration and solvation properties of the exchangeable, charge compensating cations. The adsorption profiles provide direct evidence for  $\text{CO}_2$  intercalation in Cs-hectorite even under anhydrous conditions, as observed in recent experimental studies.<sup>17</sup> In contrast,  $\text{CO}_2$  intercalation in Ca-hectorite occurs only when there is at least a sub-monolayer of  $\text{H}_2\text{O}$  present in the interlayers, as is also the case for Na-smectites.<sup>17,25</sup> The maximum interlayer mole fraction for  $\text{CO}_2$  occurs near the 1L structure for both Cs- (12.5 Å) and Ca-hectorites (12.8 Å) and decreases with increasing basal spacing. The negligible  $\text{H}_2\text{O}$  content (~1.5%) present at the maximum  $\text{CO}_2$  content in Cs-hectorite clearly indicates that  $\text{Cs}^+$  has similar affinities for both  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , in good agreement with experiments.<sup>17,58</sup> The calculated immersion energies show that at the simulated conditions the 1L (12.5 Å) and 2L (16.2 Å) structures represent the stable equilibrium states for Cs- and Ca-hectorite, respectively.

The structural and dynamical behavior of the  $\text{CO}_2$  molecules in the 1L and 2L structures are in full agreement with previous interpretations of  $^{13}\text{C}$  NMR SSB patterns.<sup>17</sup> The simulations show that  $\text{CO}_2$  molecules in the 1L structures are located at the interlayer midplane, have a mean O-C-O axis orientation parallel to the basal surface (though they wobble around this mean value), and undergo librational motion about an axis perpendicular to their O-C-O axis. The observed  $^{13}\text{C}$  MAS NMR CSA patterns demonstrate rapid reorientation about an axis perpendicular to their O-C-O axis and because they probe the time-averaged structure are consistent with wobbling around this axis.<sup>17</sup> In contrast, simulations show that the intercalated

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3 CO<sub>2</sub> molecules in the 2L structure of Ca-hectorite are adsorbed closer to one of the basal  
4 surfaces and experience less restricted dynamics than in the 1L structure. The computations  
5 show that direct, nearest neighbor coordination of CO<sub>2</sub> with Cs<sup>+</sup> in the 1L structure, but no  
6 nearest neighbor CO<sub>2</sub>-Ca<sup>2+</sup> coordination in either the 1L or 2L structures of Ca-hectorite.  
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8 Again, these results are in full agreement with *in situ* experimental NMR observations.<sup>17</sup> In the  
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10 1L structure of Cs-hectorite Cs<sup>+</sup> ions are adsorbed in a 9-fold IS coordination with respect to  
11 the basal surfaces and are also coordinated to 4-5 CO<sub>2</sub>. In contrast, in the 1L structure of Ca-  
12 hectorite CO<sub>2</sub> molecules occur exclusively in small clusters between hydrated Ca<sup>2+</sup> ions, where  
13 they assume a predominantly slipped parallel orientation with respect to each other. In the 1L  
14 structure of Cs-hectorite, the CO<sub>2</sub> molecules have one O<sub>CO2</sub> above a Si tetrahedron of one  
15 surface and the other above the center of a ditrigonal cavity of the opposite surface. This  
16 arrangement is slightly altered in both the 1L and 2L structures of Ca-hectorite, in which one  
17 O<sub>CO2</sub> is above the center of a ditrigonal cavity but the other is above an O<sub>b</sub> on the opposite  
18 surface and not on top of a Si tetrahedron.

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21 Overall, the computed intercalation structure, dynamics and compositions are in good  
22 agreement with the recent *in situ* XRD, IR and NMR experimental data of Bowers et al.<sup>17</sup>,  
23 highlighting the complementarity of spectroscopy and molecular modeling. The agreement  
24 between the experimental interpretations and those observed in the GCMD simulations  
25 suggests that GCMD methods can be broadly applicable in future studies of binary and more  
26 complex fluids in complex nanoconfined environments.

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## 20 **Notes**

21  
22 The authors declare no competing financial interest.  
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## 26 **Supporting Information**

27  
28 A brief discussion of residence time definitions, orientations of H<sub>2</sub>O dipole with respect  
29 to surface normal of Ca-hectorites for 1L and 2L structures. Details of the planar atomic density  
30 distributions of interlayer species for the 1L and 2L structures of Cs- and Ca-hectorites.  
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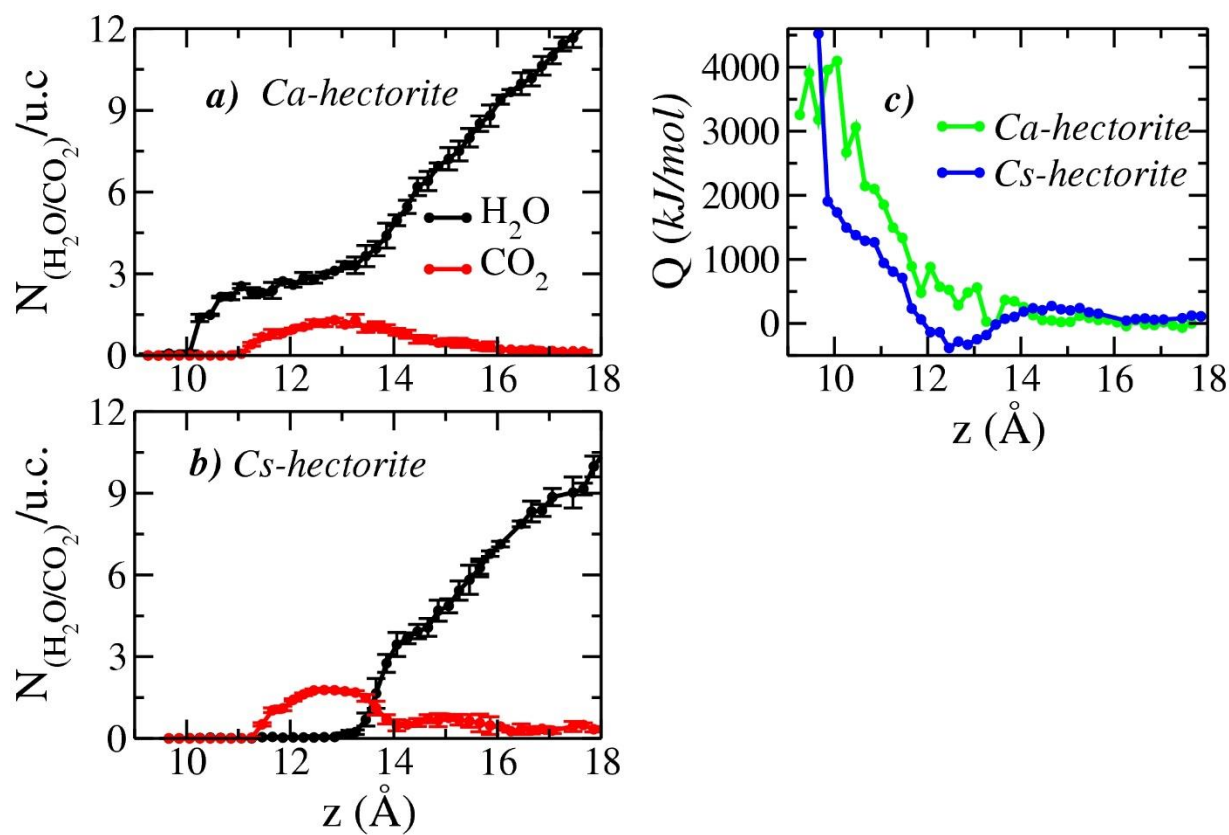
**Table 1.** CO<sub>2</sub> mole fraction at equilibrium interlayer distances for Cs- and Ca-hectorites at 323 K and 90 bar in comparison to experimental results.

	Interlayer distance	Interlayer mole fraction of CO <sub>2</sub>	
		(Simulations)	(Experiments) <sup>17</sup>
<b>Cs – hectorite</b>	Monolayer (12.5 Å)	0.98	0.34 - 0.82 (12.2 Å)
<b>Ca – hectorite</b>	Monolayer (12.7 Å)	0.34	0.13 - 0.54 (12.0 Å)
	Bilayer (16.2 Å)	0.02	0.02 - 0.42 (15.8 Å)
<b>Na – hectorite</b>	Monolayer (12.5 Å) <sup>40</sup>	0.18	0.05 - 0.14
	Bilayer (15.5 Å) <sup>40</sup>	0.03	

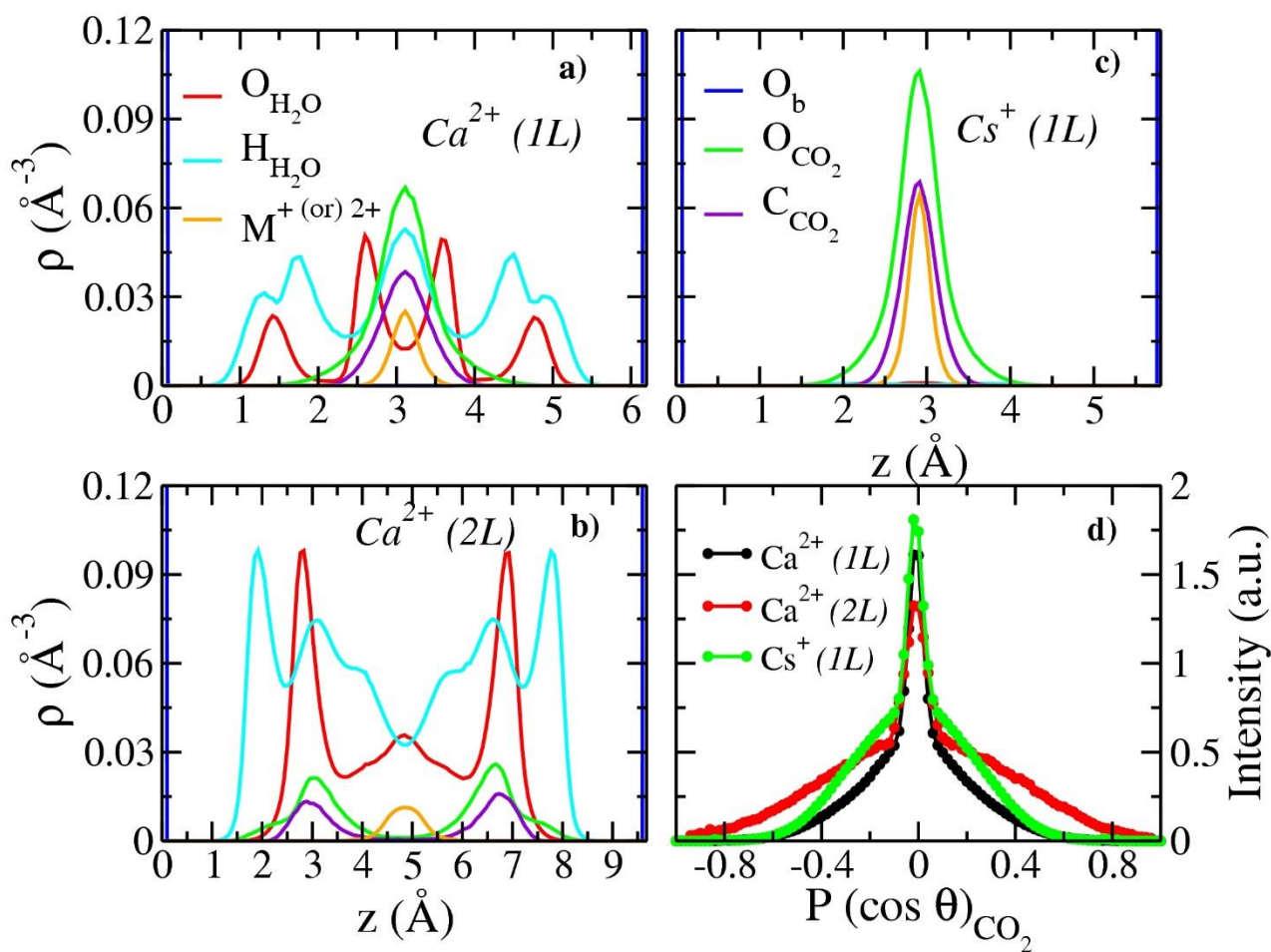
**Table 2.** Calculated intermittent and continuous residence times (*ns*) for the listed atomic pairs in the interlayers of Cs- and Ca-hectorite at 323 K and 90 bar.

basal spacing (Å)	Ion-O <sub>H2O</sub>	Ion-O <sub>b</sub>	Ion-O <sub>CO2</sub>	O <sub>H2O</sub> -O <sub>b</sub>	O <sub>b</sub> -O <sub>CO2</sub>	O <sub>H2O</sub> -CO <sub>2</sub>
<b><math>\tau_{int}</math> (res): <math>\tau_{cont}</math> (res)</b>						
<i>Ca-hectorite</i>						
1L (12.8Å)	21 : 3	12 : 1	- : -	2 : 0.4	0.5 : 0.05	0.5 : 0.1
2L (16.2Å)	1.9 : 0.5	- : -	- : -	0.4 : 0.1	0.1 : 0.03	0.1 : 0.02
<i>Cs-hectorite</i>						
1L (12.5Å)	- : -	0.9 : 0.05	0.4 : 0.02	- : -	0.5 : 0.03	- : -

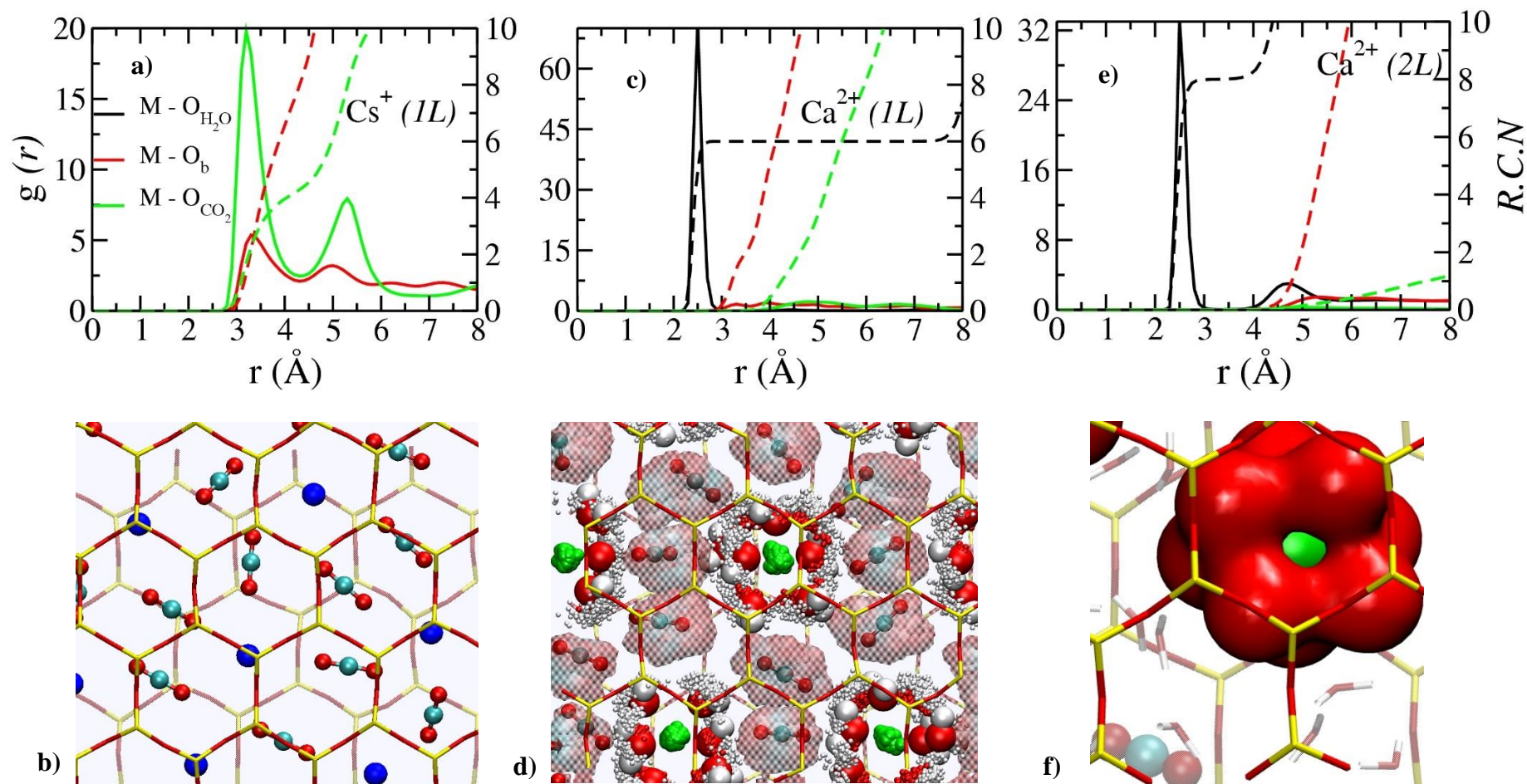
## FIGURES



**Figure 1.** a) and b): Average number of intercalated  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules per unit cell in Ca- and Cs-hectorite as functions of interlayer basal spacing at 323 K and 90 bar. c): The computed immersion energies for the same systems.



**Figure 2.** a), b), c): Computed atomic density profiles (ADPs) of  $\text{O}_b$  (dark blue vertical lines), the exchangeable cation (orange),  $\text{O}_{\text{H}_2\text{O}}$  (red),  $\text{H}_{\text{H}_2\text{O}}$  (cyan),  $\text{O}_{\text{CO}_2}$  (green) and  $\text{C}_{\text{CO}_2}$  (violet) in Cs- and Ca-hectorite as functions of distance from the basal clay surface at 323 K and 90 bar. a) and b) 1L and 2L structures of Ca-hectorite. The ADPs of  $\text{O}_{\text{CO}_2}$  and  $\text{C}_{\text{CO}_2}$  in 2b are enhanced 5 times than their original values to improve visibility. c) 1L structure of Cs-hectorite. d) Computed orientation distributions of intercalated  $\text{CO}_2$  molecules in the interlayers of Ca- and Cs-hectorite at 323 K and 90 bar.  $P(\cos \theta)_{\text{CO}_2}$  is the cosine of the angle between the O-O vector of the  $\text{CO}_2$  molecules and the normal to the hectorite basal surface. The intensity of the distribution for the 2L Ca-hectorite is enhanced 10X for better illustrations.

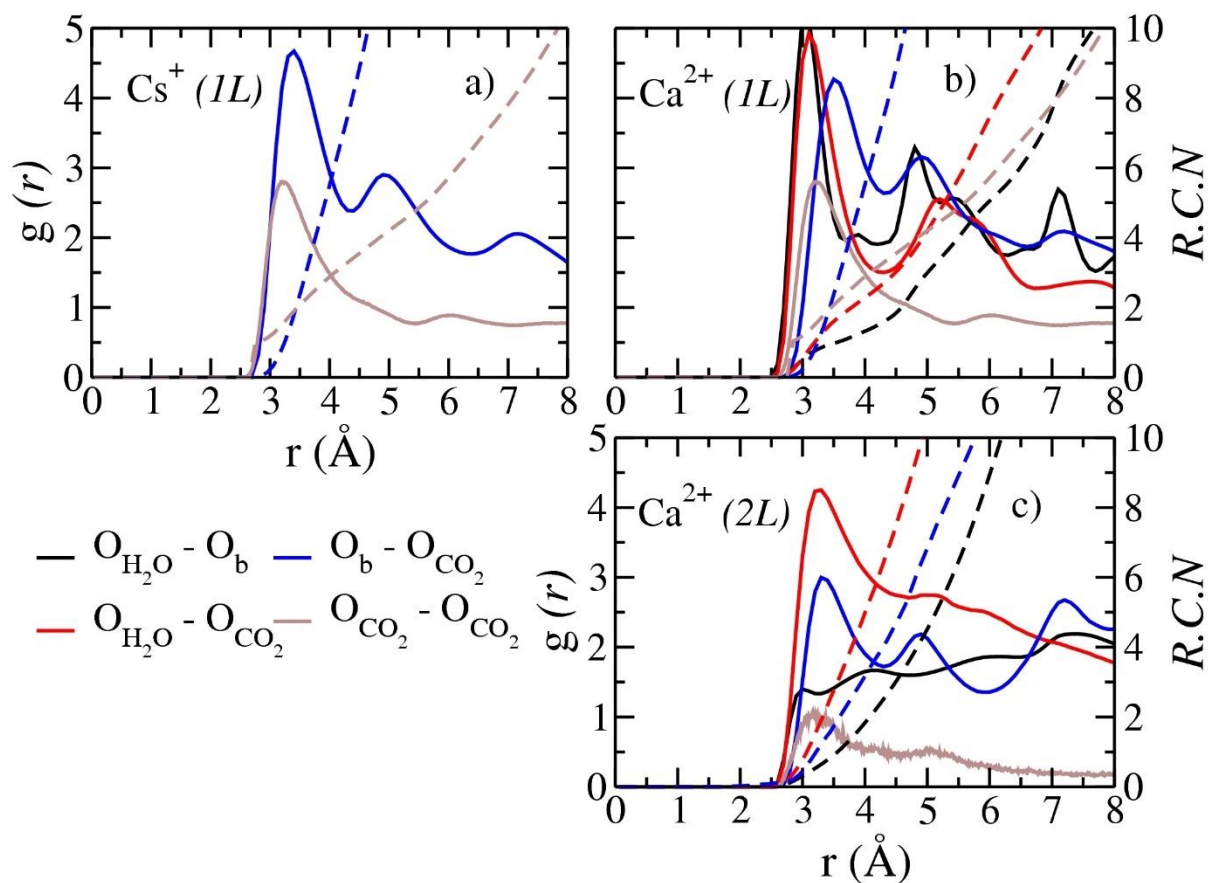


**Figure 3.** a), c), e): Radial distribution functions (RDFs, solid lines) and corresponding running coordination numbers (RCNs, dashed lines) for the indicated atomic pairs involving Cs<sup>+</sup> and Ca<sup>2+</sup> ions in the interlayers of hectorite at 323 K and 90 bar. a) 1L of Cs-hectorite. b) 1L of Ca-hectorite. c) 2L of Ca-hectorite. M – Cation. b) pictorial representation of intercalated CO<sub>2</sub> and Cs<sup>+</sup> in 1L structure of Cs-hectorite; d) pictorial



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3 representation of average positions for CO<sub>2</sub>, H<sub>2</sub>O and Ca<sup>2+</sup> in 1L Ca-hectorite; f) pictorial representation of nearest neighbour H<sub>2</sub>O around Ca<sup>2+</sup>  
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5 ions in 2L Ca-hectorite. Color codes: blue – Cs<sup>+</sup>; green – Ca<sup>2+</sup>; red – O<sub>H2O</sub>/O<sub>CO2</sub>; cyan – C<sub>CO2</sub>; white – H<sub>H2O</sub>; Bright and shaded red and yellow  
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7 sticks corresponds to surface oxygen (O<sub>b</sub>) and silicon atoms.  
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**Figure 4.** Radial distribution functions (RDFs, solid lines) and corresponding running coordination numbers (RCNs, dashed lines) for non-bonded O atomic pairs in Cs- and Ca-hectorites at 323 K and 90. a) 1L of Cs-hectorite. b) 1L of Ca-hectorite. c) 2L of Ca-hectorite.

**TOC Graphic**