

1 Revision 3

2 Correction Date 08/31/13

3 Structural and dynamical relationships of Ca^{2+} and
4 H_2O in smectite/ $^2\text{H}_2\text{O}$ systems

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12 ABSTRACT

13 We present an X-ray diffraction and multi-nuclear (^2H and ^{43}Ca) NMR study of Ca-exchanged
14 hectorite (a smectite clay) that provides important new insight into molecular behavior at the
15 smectite- H_2O interface. Variable temperature ^{43}Ca MAS NMR and controlled humidity XRD
16 indicate that Ca^{2+} occurs as proximity-restricted outer-sphere hydration complexes between -120
17 °C and +25 °C in a two-layer hydrate and at $T \leq -50$ °C in a 2:1 water/solid paste. Changes in
18 the ^{43}Ca NMR peak width and position with temperature are more consistent with diffusion-

19 related processes than with dynamics involving metal-surface interactions such as site exchange.
20 The ^2H NMR signal between $-50\text{ }^\circ\text{C}$ and $+25\text{ }^\circ\text{C}$ for a two-layer hydrate of Ca-hectorite is similar
21 to that of Na- and other alkali metal hectorites and represents $^2\text{H}_2\text{O}$ molecules experiencing
22 anisotropic motion describable using the ^2H C_2/C_3 jump model we proposed previously. ^2H T_1
23 relaxation results for Ca- and Na-hectorite are well fit with a fast-exchange limit, rotational
24 diffusion model for $^2\text{H}_2\text{O}$ dynamics, yielding GHz-scale rotational reorientation rates compatible
25 with the C_3 component of the C_2/C_3 hopping model. The apparent activation energy for $^2\text{H}_2\text{O}$
26 rotational diffusion in the two-layer hydrate is greater for Ca-hectorite than Na-hectorite (25.1
27 kJ/mol vs. 21.1 kJ/mol), consistent with the greater affinity of Ca^{2+} for H_2O . The results support
28 the general principle that the dynamic mechanisms of proximity-restricted H_2O are only weakly
29 influenced by the cation in alkali metal and alkaline earth metal smectites and provide critical
30 evidence that the NMR resonances of charge-balancing cations in smectites become increasingly
31 influenced by diffusion-like dynamic processes at low temperatures as the charge density of the
32 unhydrated cation increases.

33 KEYWORDS: ^{43}Ca NMR, ^2H NMR, dynamics, interface, clay, water.

34

INTRODUCTION

35 Processes at fluid-solid interfaces influence the behavior of many chemical and natural systems
36 but are difficult to study because of the inherently multi-phase character of the systems and the
37 disordered structure of the interface due to static and dynamic effects. The high surface area,
38 layered structures of clay minerals offer an excellent opportunity to investigate fundamental
39 structural and dynamical questions about the behavior of H_2O molecules, cations, and other
40 fluids at fluid-solid interfaces. In particular, the smectite clay minerals (swelling clays) have
41 been extensively studied because of the ease with which they exchange their charge-balancing

42 cations and their ability to incorporate large amounts of H₂O in their interlayer space, in some
43 cases swelling to many times their initial volume. The interfacial behavior in clay mineral
44 systems has been studied using a wide range of experimental and computational techniques,
45 although most work has focused on systems involving alkali metal cations as the charge-
46 balancing species (Bish et al., 2003; Bowers et al., 2008a; Bowers et al., 2011; Chipera et al.,
47 1997; Fripiat et al., 1982; Gates et al., 2012; Guichet et al., 2008; Loring et al., 2012; McKinley
48 et al., 2001; Park and Sposito, 2004; Pons et al., 1982; Porion et al., 2001a; Porion and Delville,
49 2005; Sposito et al., 1999; Wang et al., 2006; Zachara et al., 2002; Weiss et al., 1990a; Weiss et
50 al., 1990b). Currently, there is consensus from NMR spectroscopy, neutron scattering, and
51 computational molecular dynamics simulations that proximity-restricted H₂O (molecules within
52 5 Å of an external or interlayer surface or cation) in hydrated alkali metal smectites (those with
53 alkali metal charge-balancing cations) cannot be adequately described structurally or
54 dynamically as either bulk liquid H₂O or ice at most temperatures (see Bowers et al., 2011 and
55 the references therein for a more detailed review). In addition, this proximity-restricted H₂O
56 diffuses at rates 4-5 times slower than in bulk H₂O at room temperature. ¹H and ²H NMR results
57 (Bowers et al., 2011; Ishimaru and Ikeda, 1999; Tenorio et al., 2008) provide insight into the
58 reorientation mechanisms of proximity-restricted H₂O molecules, and ²H NMR suggests
59 variability in the geometry of the charge-balancing cation hydration shell for proximity-restricted
60 alkali metal smectites (Bowers et al., 2011). The H₂O content of the system, total permanent
61 charge on the clay layers, and the location of isomorphic substitution sites causing the layer
62 charge (octahedral vs. tetrahedral substitutions) are known to influence H₂O dynamics, cation
63 diffusion and sorption/desorption behavior, and interlayer expansion and delamination (Delville

64 and Laszlo, 1990; Grandjean, 1997; Greathouse and Sposito, 1998; Labouriau et al., 1997;
65 Porion and Delville, 2005; Sposito et al., 1999).

66 NMR spectroscopy is an effective, element-specific probe of structure and dynamics of
67 hydrated alkali metal smectites in the Hz to GHz frequency range (Bowers et al., 2008b; Bowers
68 et al., 2011; Delville et al., 1981; Delville and Porion, 2003; Delville et al., 2000; Kim et al.,
69 1996; Kim and Kirkpatrick, 1997; Labouriau et al., 1997; Porion and Delville, 2005; Porion et
70 al., 2007; Porion et al., 1998; Porion et al., 2001b; Weiss et al., 1990a; Weiss et al., 1990b), but
71 as noted above, has rarely been applied to alkaline earth metal smectite-H₂O systems. The lack
72 of NMR data for alkaline earth smectites is a result of the poor NMR sensitivity of the NMR-
73 active isotopes of these elements due to their low resonance frequencies, frequently large
74 quadrupole couplings leading to broad resonances (up to 100s of kHz in width), and in many
75 cases a low isotopic abundance. We have found only two published ²⁵Mg NMR studies of
76 phyllosilicates, both of which focus on structural Mg²⁺ in the octahedral layers and its evolution
77 with temperature rather than the interfacial behavior of charge-balancing Mg²⁺ (MacKenzie and
78 Meinhold, 1994a; MacKenzie and Meinhold, 1994b). There are no reported ⁴³Ca NMR studies
79 of Ca-phyllosilicates, and the only published ⁸⁷Sr study of Sr-phyllosilicates focuses on the
80 room-temperature structure of bound Sr²⁺ in a synthetic fluoromica and did not examine ⁸⁷Sr
81 dynamic behavior (Bowers et al., 2006). Two published ²H NMR studies examined ²H₂O
82 dynamics in a mixed Ca²⁺/alkali metal smectite (Grandjean, 1997; Weiss and Gerasimowicz,
83 1996). Both of these studies used diffusional exchange/isotropic rotational diffusion models to
84 explain the dynamic behavior. Two recent neutron scattering studies of H₂O diffusion in Ca-
85 montmorillonites (Gates et al., 2012; Gonzalez et al., 2008) reported slower diffusion for
86 proximity-restricted H₂O than in bulk water and show that the identity of the charge-balancing

87 cation exerts a small but detectable influence on H₂O dynamics. Activation energies for H₂O
88 diffusion in several Ca-clays have also been reported from neutron scattering results (Gonzalez
89 et al., 2008) and from ²H NMR relaxation data (Giese and Fripiat, 1979; Weiss and
90 Gerasimowicz, 1996). We are unaware of any published NMR or neutron scattering studies of
91 H₂O dynamics in Mg²⁺, Sr²⁺, or Ba²⁺ smectites and can find only two other neutron scattering
92 studies of smectites with multi-valent transition metals as charge-balancing species (Ni²⁺ and
93 Sm³⁺) (Sobolev et al., 2011; Sobolev et al., 2009).

94 Of the alkaline earth metals, ⁴³Ca is the most promising isotope for examining alkaline earth
95 metal binding structure and dynamics in smectite clays with NMR, because it has a much smaller
96 nuclear electric quadrupole moment than Mg²⁺ or Sr²⁺ [-40 mb vs. 199.4 mb and 335 mb,
97 respectively (Pyykkö, 2001)]. This means that the ⁴³Ca NMR resonances are much narrower
98 than for the other alkaline earth elements, leading to greater sensitivity and allowing greater
99 resolution that may permit identification of multiple ⁴³Ca structural environments. However,
100 ⁴³Ca has the lowest natural abundance of all the NMR-active isotopes of the alkaline earth metals
101 (~0.135%; Holden 1995), making efficient data acquisition challenging and rendering variable
102 temperature/multi-dimensional NMR studies nearly impossible without ⁴³Ca enrichment. This is
103 particularly true of complex structures susceptible to many types of disorder such as smectites.
104 Unfortunately, ⁴³Ca is quite expensive (~ \$US 6,000-10,000 per 100 mg of ~60% ⁴³CaCO₃),
105 limiting the application of ⁴³Ca NMR in glasses and other disordered materials (Bryce, 2010;
106 Laurencin and Smith, 2012). To overcome the abundance-related sensitivity limitations, all ⁴³Ca
107 NMR experiments in this paper were performed on 30% ⁴³Ca-enriched Ca-hectorite.

108 The data presented here show that the dynamical processes that influence the NMR resonances
109 of charge-balancing metal ions at smectite/H₂O interfaces become progressively more dominated

110 by diffusion-related effects relative to metal-surface interactions at lower temperatures as the
111 charge density of the unhydrated metal ion increases. This statement is more general than in our
112 previous paper (Bowers et al., 2011), which focused on ionic radius in the series of alkali metal
113 smectites. Here we evaluate this hypothesis by comparing new variable temperature ^{43}Ca NMR
114 results for Ca-hectorite equilibrated at atmospheric humidity and in a $\sim 2:1$ by mass
115 $^2\text{H}_2\text{O}$:smectite paste with similar ^{23}Na NMR results for Na-hectorite published previously
116 (Bowers et al., 2011). This comparison is an effective test, because Na^+ and Ca^{2+} have similar
117 Pauling ionic radii (1.02 \AA vs. 1.00 \AA , respectively, for six-fold coordination; Shannon, 1976).
118 Thus, Ca^{2+} has a larger charge density than Na^+ due only to its larger charge. The data show that
119 the resulting greater affinity of Ca^{2+} for H_2O [hydration energy = -1592 kJ/mol vs. -405 kJ/mol
120 for Na^+ (Burgess, 1978)] dominates the larger electrostatic attraction between Ca^{2+} and the
121 mineral surface, leading to diffusion-dominated dynamic averaging of the ^{43}Ca NMR resonances
122 at temperatures $< -20 \text{ }^\circ\text{C}$ (the onset of fast diffusion effects in Na-hectorite pastes). Analysis of
123 companion ^2H NMR experiments shows that the C_2/C_3 jump motion model developed for
124 proximity-restricted $^2\text{H}_2\text{O}$ motion in alkali metal smectites (Bowers et al., 2011) also applies to
125 the two-layer hydrate of Ca-hectorite, that isotropic rotational diffusion of $^2\text{H}_2\text{O}$ adequately
126 accounts for the C_3 -type motion in the model, and that the deviation from ideal octahedral
127 symmetry of the metal hydration shell along the surface normal/ C_3 symmetry axis is only slightly
128 reduced when Ca^{2+} is substituted for Na^+ . New ^2H T_1 relaxation data also support the hypothesis
129 that the greater affinity of Ca^{2+} for H_2O vs. Na^+ leads to larger activation energy for fast
130 rotational diffusion of $^2\text{H}_2\text{O}$ in two-layer hydrates of Ca-hectorite versus Na-hectorite.

131

132

MATERIALS AND METHODS

133 *Samples*

134 The isotopically enriched ^{43}Ca -hectorite samples were prepared by ion exchange with a Na-
135 saturated hectorite prepared from the $< 1 \mu\text{m}$ fraction isolated from the standard San Bernardino
136 hectorite (SHCa-1) available from the Clay Mineral Society's Source Clays Repository.
137 Hectorite is a trioctahedral smectite clay with a permanent negative charge of -0.36/formula unit
138 due to substitution of Li^+ for Mg^{2+} in the octahedral sheet. The chemical composition of the
139 specific hectorite fraction used in this study, the procedure for isolating this fraction, and Na-
140 exchange procedures were published previously (Bowers et al., 2011; Weiss et al., 1990a). The
141 30% ^{43}Ca -enriched CaCO_3 starting material was prepared by grinding the appropriate amount of
142 62% ^{43}Ca CaCO_3 (Isoflex USA) and unenriched, reagent grade CaCO_3 in an agate pestle and
143 mortar. This material was dissolved in HCl to produce a 0.1 M solution of CaCl_2 (pH of 6-6.5) at
144 roughly 30% ^{43}Ca using previously published procedures (Singer et al., 2012). For the Ca-
145 exchange, two 500 mg aliquots of Na-saturated hectorite were suspended in ~ 50 mL of the ^{43}Ca -
146 enriched CaCl_2 solution in 80 mL centrifuge tubes, shaken vigorously, and placed on a
147 mechanical rocker for 12 hours. During rocking, the suspended hectorite formed weak
148 agglomerates that settled to the bottom of the tubes. The agglomerates were re-suspended as
149 much as possible by vigorous shaking and separated from the solution by centrifugation at 5000
150 rpm (~ 2100 g) for 15 minutes. The supernatant solutions were decanted, combined, and saved
151 for recovery of the ^{43}Ca . The clay fractions were washed by re-suspension in ~ 50 mL of
152 deionized H_2O followed by centrifuging at 5000 rpm for two cycles. After the second rinse, the
153 clay was freeze-dried and one fraction was gently ground by mortar and pestle and sieved to
154 collect the $< 106 \mu\text{m}$ fraction. Gentle grinding of the Ca-hectorite was critical to avoid smearing.
155 Similar smearing behavior was not observed for the Na-saturated form. The second ^{43}Ca -

156 exchanged sample was stored without grinding after the freeze-drying procedure. The ground
157 sample was held at room conditions for subsequent NMR analysis. We denote any sample with
158 ^{43}Ca enrichment as “ ^{43}Ca -hectorite” in the remainder of the text. Table 1 provides a listing of
159 sample names and compositions.

160 A sample of Ca-hectorite without ^{43}Ca enrichment was prepared for X-ray diffraction (XRD)
161 and ^2H NMR analysis using the same ion exchange procedure. After freeze-drying and grinding,
162 the split for XRD was held at room conditions prior to analysis. A second split of this non- ^{43}Ca
163 enriched smectite was placed into a desiccator over K_2CO_3 -saturated $^2\text{H}_2\text{O}$ [H_2O activity
164 equivalent to ~43% relative humidity (RH)] and allowed to equilibrate for several days. The
165 equilibrated sample was removed from the desiccator and immediately loaded into a cut 5 mm
166 quartz NMR tube. After packing, the tube was sealed with water-tight epoxy, weighed, and
167 placed on the benchtop. The tube packing/sealing procedure was repeated several times until a
168 sealed sample was obtained that exhibited no weight gain or loss for at least three days. This
169 sealed sample was shipped to the Pennsylvania State University for ^2H NMR analysis. The ^2H -
170 equilibrated, non- ^{43}Ca enriched hectorite will be called “(^2H)Ca-hectorite” in the remainder of
171 the discussion.

172 Use of non- ^{43}Ca enriched material for XRD and ^2H NMR analysis was motivated by a desire to
173 minimize loss of the expensive isotopically enriched sample. Although we cannot rule out some
174 effects on the results due to Ca-related isotope effects, Ca^{2+} has a sufficiently large mass that
175 isotope effects on its binding structure and interfacial dynamic behavior should be minimal.

176 *XRD*

177 The Ca-hectorite fraction with no isotopic enrichment (Ca-hectorite) was examined by
178 controlled-humidity X-ray powder diffraction using an automated Bruker D8 powder

179 diffractometer mated with a SolX detector. Samples were deposited as aqueous slurries on an
180 off-axis cut quartz plate. The relative humidity was stepped from 0% to 90% and back to 0% in
181 10% increments using an InstruQuest V-Gen dew point/RH generator and a custom-built
182 humidity control stage. All other conditions were the same as in our previous work on Na-
183 hectorite (Bowers et al., 2011). The d values reported here were calculated using center-of-mass
184 methods for each basal (001) reflection.

185 ^{43}Ca NMR

186 Variable temperature (VT) ^{43}Ca Bloch-decay NMR experiments were performed using the
187 20.0 T (850 MHz ^1H frequency) Agilent DD2 NMR spectrometer at the William R. Wiley
188 Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National
189 Laboratory. Magic angle spinning (MAS) spectra were obtained for the ^{43}Ca -hectorite
190 equilibrated at atmospheric conditions using an Agilent 4mm HXY probe. The atmospheric
191 conditions at EMSL were well within the range of H_2O activities that produce a two-layer
192 hydrate based on the controlled RH XRD results (see results below). Static and MAS ^{43}Ca NMR
193 spectra were also obtained for an ~2:1 by mass $^2\text{H}_2\text{O}/^{43}\text{Ca}$ -hectorite paste. This (^2H) ^{43}Ca -
194 hectorite paste was prepared by adding the appropriate amount of $^2\text{H}_2\text{O}$ to the room RH
195 equilibrated ^{43}Ca -hectorite directly on a balance. The water/hectorite mixture was then
196 mechanically kneaded to bread-dough like consistency with no separate liquid-rich phase or dry
197 material visible. The paste was loaded into an open-top NMR rotor within five minutes of
198 preparation and the pre- and post-weight of each sample was monitored to evaluate H_2O
199 gain/loss during the NMR experiments. Actual paste $^2\text{H}_2\text{O}$ content varied such that the
200 $^2\text{H}_2\text{O}$:clay ratios were between 2:1 and 1.8:1 by mass over the course of the NMR experiments.

201 ^{43}Ca NMR spectra were obtained at sample temperatures between -120°C and $+25^{\circ}\text{C}$ using a
202 standard Agilent VT stack and liquid nitrogen-cooled dry nitrogen cooling gas stream. MAS
203 spectra for the 2WL- ^{43}Ca -hectorite sample were acquired using a 10 kHz rotation rate, 350
204 transients, a 60 s pulse delay, and a 3 μs pulse ($\pi/2$ pulse width for CaO was 9 μs at the power
205 levels employed). All spectra for this sample are referenced to 1 M CaCl_2 (aq) via a secondary
206 standard of CaO as suggested by Gervais and colleagues (Gervais et al., 2008). All other data
207 acquisition and processing conditions were identical to those of our previously published ^{43}Ca
208 NMR spectra of amorphous calcium carbonates (Singer et al., 2012). Based on the MAS results,
209 static spectra of (^2H)- ^{43}Ca -hectorite paste and 2WL- ^{43}Ca -hectorite were obtained using a pulse
210 delay of 5 s and a central transition selective $\pi/2$ pulse width of 5 μs . The number of transients
211 varied from 650 to 6500 with decreasing temperature due to the need to maintain similar
212 signal/noise ratios in the face of increasing peak widths with decreasing temperature and
213 potential temperature-dependent relaxation effects discussed in greater detail below. Static
214 spectra are referenced with respect to 1 M CaCl_2 (aq) via a secondary standard of calcite using
215 the left-hand singularity (21.6 ppm). The spectra in our figures were processed using a left-shift
216 of four data points to remove artifacts from probe ringing and received apodizations equivalent
217 to 20, 50, or 100 Hz depending on the natural linewidth (the largest linewidths received the
218 greatest apodization). The resonance line shapes were fit with Lorentzian and stretched
219 Lorentzian (Bowers et al., 2011) functions using the Abscissa software written by Rudiger Bruhl.
220 Attempts to fit the spectra to MAS quadrupolar lineshapes in DMFit (Massiot et al., 2002) did
221 not improve the fit quality.

222 A room-temperature double frequency sweep (DFS, Kentgens, 1991) Bloch-decay ^{43}Ca MAS
223 NMR spectrum of 2WL- ^{43}Ca -hectorite was also collected using the Varian Inova 21.1 T NMR

224 spectrometer at EMSL and a home-built 5 mm HX high-temperature MAS probe in order to
225 estimate the ^{43}Ca quadrupolar parameters. These 21.1 T experiments used a 3.5 μs central
226 transition selective $\pi/2$ pulse width, a 60 s pulse delay, and 40 kHz spectral width to acquire
227 2064 data points. The DFS conditions were optimized using a ^{43}Ca -enriched sample of CaCO_3
228 and swept a frequency region from 15 kHz to 1.4 MHz from the transmitter frequency over a
229 period of 600 μs using a 12 kHz rf field strength. The zero filling, exponential apodization, and
230 other processing conditions were identical to those used for the ^{43}Ca spectra acquired at 20.0 T.
231 The room temperature peak maximum of the resonances at 20.0 and 21.1 T were compared to
232 estimate the isotropic chemical shift and quadrupolar product according to the procedure of
233 Mueller et al. (1991). All spectra at 21.1 T are referenced to 1 M CaCl_2 (aq) via a secondary
234 standard of CaO .

235 ^2H NMR

236 Variable temperature ^2H NMR spectra were obtained for 2WL- $(^2\text{H})\text{Ca}$ -hectorite using a wide-
237 line ^2H NMR probe, a Tecmag HF-3 Apollo console, and a 7.6 T magnet at the Pennsylvania
238 State University NMR facility. Spectra were acquired at -80°C , -50°C , -35°C , -20°C , -10°C ,
239 0°C , $+10^\circ\text{C}$, $+25^\circ\text{C}$, and $+40^\circ\text{C}$ with the quadrupolar echo pulse sequence and a 40 μs echo
240 delay. The temperature measured by the VT stack thermocouple was within $\pm 0.1^\circ\text{C}$ of the
241 temperature given by a thermocouple placed in the sample coil during a calibration test. All other
242 ^2H NMR experimental conditions and data processing parameters were identical to those in our
243 previous work (Bowers et al., 2011), including referencing the spectra to the ^2H signal of 99%
244 $^2\text{H}_2\text{O}$.

245 ^2H inversion-recovery T_1 experiments were conducted at -50°C , -30°C , -20°C , and 0°C for
246 2WL- $(^2\text{H})\text{Ca}$ -hectorite and a sample of Na-hectorite equilibrated in $\sim 43\%$ RH $^2\text{H}_2\text{O}$ to gain

247 insight into the dynamics of proximity-restricted $^2\text{H}_2\text{O}$ in the vicinity of the ^2H Larmor
248 frequency, which is 45.653 MHz at this field. Both of these samples are predominantly 2-layer
249 hydrates at this humidity. Thirty-five points were acquired for the T_1 curve using a 5 s pulse
250 delay and 16 dummy scans. Sixty-four transients were acquired at each T_1 point. All other
251 conditions were identical to the quadrupolar echo experiments described in the previous
252 paragraph. The T_1 data were fit with a single exponential function involving a parameter to
253 account for incomplete inversion of the equilibrium magnetization by the π pulse. Variability in
254 T_1 over the width of the ^2H NMR resonance was also calculated at each temperature for the
255 2WL-(^2H)Na-hectorite and proved to be within the limits of uncertainty for these calculations.
256 The associated fast-exchange limit correlation times for $^2\text{H}_2\text{O}$ rotational diffusion were
257 calculated using the methods of Grandjean and Laszlo (1989) and Weiss and Gerasimowicz
258 (1996) assuming a 230 kHz quadrupole coupling constant and an asymmetry parameter of 0.1 for
259 ^2H in $^2\text{H}_2\text{O}$ (Wittebort et al., 1988). Arrhenius plots were constructed from these data to
260 determine the activation energy for rotational diffusion analogous to the procedure of Weiss and
261 Gerasimowicz (1996).

262

263

RESULTS

264 *XRD*

265 The controlled-RH XRD data show that Ca-hectorite can be well described as predominantly a
266 two-layer hydrate (containing two full layers of H_2O molecules between each clay layer) at most
267 RH values near room temperature and imply that the Ca-hectorite paste is probably a mixture or
268 interstratification of two-layer, three-layer, and more-expanded hydrates, most likely including a
269 small fraction of delaminated T-O-T layers (Fig. 1). While the specific basal spacings at each

270 temperature do not agree precisely with similar previous studies of a synthetic hectorite by
271 Karmous et al. (2007, 2009), our conclusions regarding the number of water layers and RH
272 stability range for two-layer Ca-hectorite hydrate are in close agreement. The (001) spacing at
273 0% RH was $\sim 12.8 \pm 0.2 \text{ \AA}$, statistically identical to the Karmous et al. results at 10% RH
274 (Karmous et al., 2009). This value shows that Ca-hectorite exists primarily as a one-layer hydrate
275 with a small fraction of two-layer hydrates even in a dry atmosphere. Basal spacings of $\sim 9.6 \text{ \AA}$
276 represent collapsed clay interlayers (analogous to talc and pyrophyllite), spacings of $\sim 12.5 \text{ \AA}$ are
277 associated with a single layer of H_2O molecules in the interlayer (one-layer hydrates), and that
278 basal spacings of $\sim 15 \text{ \AA}$ are associated with two layers of H_2O in the interlayer space (two-layer
279 hydrates). With increasing RH, the (001) spacing of our sample increases to $\sim 15 \text{ \AA}$ at 30% RH,
280 showing that essentially all interlayers contain two H_2O layers at this RH. We are aware of no
281 experimental evidence of distinct non-integer H_2O layers in studies of hectorite hydration. Thus,
282 the intermediate (001) spacings at lower RH values most likely reflect a mixture or
283 interstratification of one- and two-layer hydrates, with the two-layer hydrate fraction increasing
284 with increasing RH. The (001) spacing continues to increase with increasing RH, but the two-
285 layer hydrate fraction dominates between 30% RH and 60% RH, as reported by Karmous et al.
286 (2009). The widths and maxima of the reflections are quite similar in this RH range. At 70% RH
287 and above, the (001) spacing is greater than 16.5 \AA , indicating that a substantial fraction of the
288 sample enters the osmotic swelling regime or becomes a three-layer hydrate. These observations
289 are supported by the presence of XRD intensity between 2° and $12^\circ 2\theta$ (Fig. 1). Note that there
290 is minor hysteresis in the hydration/dehydration curve above 70% RH that is absent at lower RH
291 values that can also be observed in the XRD patterns directly. This results contrasts with the
292 hysteresis observed over the full RH range for Na-hectorite (Bowers et al., 2011).

293 ⁴³Ca NMR

294 The variable temperature ⁴³Ca MAS NMR spectra of the room humidity 2WL-⁴³Ca-hectorite
295 are dominated by narrow, featureless, and symmetric resonances with maxima near 0 ppm, the
296 value for Ca²⁺ in dilute aqueous CaCl₂ solution (Fig. 2, Table 2). The peaks narrow progressively
297 and their maxima shift slightly to lower resonance frequencies (more negative peak positions or
298 more shielded chemical environments) with increasing temperature. They are well-fit with
299 single Lorentzian functions at -100 °C and above. Use of quadrupolar MAS lineshapes did not
300 improve the quality of the fits, consistent with small ⁴³Ca quadrupolar couplings and suggesting
301 that the resonance widths are dominated by chemical shift dispersion and dynamic effects. The
302 small temperature-dependent shift to lower resonance frequency with increasing temperature is
303 similar to that observed in ²³Na MAS NMR spectra of a 1.5:1 water:solid ratio Na-hectorite
304 paste, which show a symmetric resonance that moves to lower resonance frequency with
305 increasing temperature above -20 °C (Bowers et al., 2011). The ⁴³Ca linewidths at all
306 temperatures are always broader than those of Ca²⁺ in aqueous solution at room temperature and
307 20.0 T (28 ± 2 Hz), indicating a strong surface association. At -120 °C, there is also observable
308 intensity to the high-frequency edge (more positive chemical shift values) of the symmetric ⁴³Ca
309 resonance that may indicate resolution of a second local Ca²⁺ environment at this temperature.

310 The ⁴³Ca nutation behavior of the room humidity 2WL-⁴³Ca-hectorite under MAS conditions
311 is intermediate between rigid ⁴³Ca in crystalline CaCO₃ and Ca²⁺ in a saturated aqueous CaCl₂
312 solution at 25 °C, but it is more similar to the rigid limit throughout the temperature range of this
313 study (Fig. 3). Some of the nutation patterns have an unusual appearance (developing a constant
314 intensity near zero at longer pulse widths) suggestive of varying degrees of saturation and
315 potentially temperature-dependent variations in the ⁴³Ca T₁. However, since an identical pulse

316 delay value of 60 s was used for all of the nutation experiments, we would expect to observe
317 identical effects of T_1 on the shape of the room-temperature nutation patterns of ^{43}Ca -hectorite,
318 calcite, and $\text{CaCl}_2(\text{aq})$ if the local molecular-scale ^{43}Ca environments were the same in these
319 materials. The intermediate behavior of the 2WL- ^{43}Ca hectorite is consistent with the idea that
320 the proximity-restricted ^{43}Ca in this sample at room humidity is intermediate between a rigid
321 solid and a dynamically averaged solution, in agreement with the linewidth observations (Fig. 3).
322 In most rigid solids only the central (1/2, -1/2) nuclear transition is excited and observed, whereas
323 for fully dynamically averaged species in solution, all transitions are excited and observed. For
324 these data, dynamical averaging occurs but is incomplete, which leads to a partial intensity
325 contribution in the observed resonance from the satellite transitions and the intermediate nutation
326 behavior observed.

327 The multiple field ^{43}Ca data at room temperature for room humidity 2WL- ^{43}Ca -hectorite reveal
328 little regarding the role of quadrupolar interactions on the observed resonances, but indicate that
329 any quadrupolar contribution to the lineshape is relatively small. Assuming the center-of-mass
330 at 21.1 T corresponds to the observed chemical shift at this field, the ^{43}Ca quadrupolar product
331 ($P_Q = C_Q \sqrt{1 + \eta^2/3}$) is 1.4 ± 1.4 MHz. The large uncertainty spans the range of ^{43}Ca
332 quadrupolar products determined from computation and experiment for Ca compounds with
333 predominantly oxygen in the nearest neighbor Ca coordination sphere (Gervais et al., 2008) and
334 occurs because the peak maximum at 20.0 T falls within the peak maximum uncertainty at 21.1
335 T (Fig. 4). The resonance obtained at 21.1 T is quite broad and asymmetric because of field
336 inhomogeneity resulting from an inability of the shim stack to overcome field distortions
337 generated by the specialized materials in the high-temperature probe that was used to acquire
338 these data. However, the presence of small quadrupolar couplings for ^{43}Ca in ^{43}Ca -hectorite is

339 consistent with the lack of features in the ^{43}Ca NMR spectra, the fit quality obtained using single
340 Lorentzian rather than quadrupolar MAS patterns for these ^{43}Ca spectra, and the idea of a quite
341 symmetrical, fully hydrated interlayer Ca^{2+} coordination indicated by the XRD data. Data for
342 this sample from a lower field, where a greater difference in the observed resonance frequency
343 will result if the quadrupolar interactions are significant, are required to resolve the issue.

344 The observed resonances in the static ^{43}Ca NMR spectra of 2WL- ^{43}Ca -hectorite and (^2H) ^{43}Ca -
345 hectorite paste are also symmetrical and featureless and have decreasing widths with increasing
346 temperature (Fig. 5). At all temperatures, the static peak maxima of the paste occur at higher
347 resonance frequencies than for the room humidity sample, and the peak widths are smaller. The
348 static peak maxima for the room humidity sample are at slightly lower frequencies than the peak
349 maxima for this sample under MAS conditions, and the static peak widths are considerably
350 greater. The static spectra show no evidence for multiple Ca^{2+} sites or quadrupolar lineshapes,
351 supporting the existence of small ^{43}Ca quadrupolar coupling constants in these systems.

352 ^2H NMR

353 The ^2H NMR spectra of the 2WL-(^2H)Ca-hectorite sample are dominated by one ^2H resonance
354 indicative of anisotropic motional averaging that varies little between $-50\text{ }^\circ\text{C}$ and $+25\text{ }^\circ\text{C}$ (Fig. 6,
355 Table 3). These spectra are very similar to the ^2H NMR spectra for a predominantly two-layer
356 mixed one-layer/two-layer Na-hectorite published previously (Bowers et al., 2011). As for Na-
357 hectorite, the quadrupolar dominated ^2H line shape and the similarity of the linewidths and
358 splittings over a wide temperature range is the result expected for a system in which the $^2\text{H}_2\text{O}$ is
359 closely associated with the clay layers (so-called proximity restricted $^2\text{H}_2\text{O}$), where little bulk or
360 “free” $^2\text{H}_2\text{O}$ is present in the system, and when the rates of the motions responsible for the line
361 shape are at least an order of magnitude greater than the static peak widths over the entire

362 temperature range. These proximity-restricted $^2\text{H}_2\text{O}$ molecules may be located either in the
363 interlayer region or on external crystallite surfaces. The ^2H spectra of the 2WL-(^2H)Ca-hectorite
364 at 0 °C and +25 °C do contain a small, narrow central feature indicative of $^2\text{H}_2\text{O}$ undergoing
365 rapid isotropic motion analogous to that of bulk water, probably due to external, surface-
366 adsorbed $^2\text{H}_2\text{O}$ or $^2\text{H}_2\text{O}$ in pores. The integrated intensity of this peak is only 1-2% of the total,
367 as expected for a sample equilibrated at ~43% RH. At temperatures below 0 °C, the rapid
368 motion of this population appears to be frozen out and the resulting low intensity, broadened
369 signal is not resolvable above the noise.

370 The ^2H quadrupolar splitting for the 2WL-(^2H)Ca-hectorite is approximately 3-4 kHz less than
371 for the 2WL-(^2H)Na-hectorite at all temperatures (Table 3), and as for the Na-hectorite, the
372 spectral line shapes at -50 °C and above are well-fit by the combined C_2/C_3 jump motion model
373 derived from a Na-hectorite paste sample (Bowers et al., 2011) (See discussion below.)

374 The most prominent difference between the 2WL-(^2H)Ca-hectorite and 2WL-(^2H)Na-hectorite
375 ^2H NMR spectra occur at the lowest temperature studied (-80 °C). At this temperature, the Na-
376 hectorite resonance retains its dynamically averaged, quadrupolar peak shape, whereas the Ca-
377 hectorite resonance experiences a dramatic loss in both observable intensity and definition of the
378 quadrupolar powder pattern. These differences suggest that the frequency of the dynamical
379 process causing the well-defined anisotropic line shape is approaching the static peak width for
380 the Ca-hectorite at -80 °C, but that the frequency of these processes in Na-hectorite exceeds that
381 of the peak width by at least an order of magnitude at this temperature. This observation is
382 consistent with the greater affinity of Ca^{2+} for H_2O as reflected in the cation hydration energies,
383 causing the H_2O molecules to be more tightly bound to the Ca^{2+} and thus hopping between sites
384 in and outside the cation hydration shell at lower frequencies.

385 The variable temperature ^2H T_1 relaxation times for 2WL-(^2H)Na- and 2WL-(^2H)Ca-hectorites
386 decrease with decreasing temperature and are of a similar magnitude, but at a given temperature
387 the values for Ca-hectorite are always smaller than for Na-hectorite (Table 3). To characterize
388 the dynamical processes at frequencies of the order of the ^2H Larmor frequency (~ 48 MHz), we
389 followed the approach of Weiss and Gerasimowicz (1996) to calculate rotational correlation
390 times for ^2H diffusional exchange in the fast-exchange limit. The resulting rotational correlation
391 times for both our samples fall on linear Arrhenius relationships between -50 $^\circ\text{C}$ and $+25$ $^\circ\text{C}$, as
392 previously observed in a different Na-hectorite/ H_2O system (Weiss and Gerasimowicz, 1996)
393 (Table 3; Fig. 7). This result suggests that the fast-exchange limit diffusional exchange model for
394 $^2\text{H}_2\text{O}$ is appropriate for the 2WL-(^2H)Na- and 2WL-(^2H)Ca-hectorite systems examined in this
395 study. The apparent activation energies for ^2H diffusional exchange are larger for 2WL-(^2H)Ca-
396 hectorite than for 2WL-(^2H)Na-hectorite (25.1 kJ/mol vs. 21.1 kJ/mol; Fig. 7), consistent with
397 the greater affinity of Ca^{2+} for H_2O . Reorientation of the $^2\text{H}_2\text{O}$ molecules at the calculated
398 correlation times ($\tau_c = 10^{-11}$ to 10^{-9} s) is intermediate between the correlation times for librational
399 motions captured in infrared spectroscopy (10^{-14} to 10^{-15} s) and the correlation times for fast-limit
400 motion based on the static $^2\text{H}_2\text{O}$ peak width in ice (10^{-6} to 10^{-7} s), as required for the C_3 hopping
401 component of the fast C_2/C_3 jump motion model (Bowers et al., 2011). Thus, the T_1 results
402 provide additional validation of the fast C_2/C_3 hopping model and support the existence of fast
403 C_2/C_3 jump motion at many temperatures in two-layer smectite hydrates regardless of the charge-
404 balancing cation present.

405 DISCUSSION

406 *Ca²⁺ Structure and Dynamics*

407 The ^2H and ^{43}Ca NMR data and the XRD data presented here are consistent with the
408 hypothesis that the vast majority of Ca^{2+} in a two-layer hydrate of Ca-hectorite is present on
409 proximity-restricted sites, i.e. those within 5 Å of a surface in the interlayer or on particle
410 exteriors. XRD shows that a majority of hectorite layers exist as two-layer hydrates at
411 atmospheric RH values of 30-60%, putting interlayer Ca^{2+} at a maximum distance of ~ 2.5 Å
412 from an interlayer surface in these phases. The very small amount of water showing bulk
413 behavior (1-2%) observed in the higher temperature ^2H spectra under these conditions shows that
414 there is not enough bulk H_2O to develop a significant Ca^{2+} population at > 5 Å from the external
415 surfaces. A metal ion can only desorb from a smectite surface into a free state (one with no
416 restrictions on mobility) if excess H_2O is present in inter-particle domains, if the clay layers are
417 highly expanded, or if the hectorite particles are in a dilute suspension. In addition, there is no
418 evidence for a narrow component in the ^{43}Ca spectra that would indicate Ca^{2+} in an isotropically
419 averaged, solution-like environment in the 2WL- ^{43}Ca -hectorite.

420 For the (^2H) ^{43}Ca -hectorite paste, the ^{43}Ca NMR data suggest that both proximity-restricted and
421 free Ca^{2+} environments are present at some temperatures. At the lowest temperatures of the
422 study (-120 °C and -100 °C), the ^{43}Ca NMR resonances for the 2WL- ^{43}Ca -hectorite and
423 (^2H) ^{43}Ca -hectorite paste are essentially identical (Fig. 5), suggesting that the Ca^{2+} is present in
424 the paste only in proximity restricted domains at these temperatures. This is expected based on
425 the known ability of ice to exclude solvated ions. The ^2H NMR data for Na-hectorite pastes
426 (Bowers, et al., 2011) shows the presence of bulk ice-1h domains at low temperatures, and the
427 Ca-hectorite system should behave in the same way. Ice in inter-particle pores or between highly
428 expanded hectorite layers forces the Ca^{2+} ions to the hectorite surfaces, where they are required
429 for charge-balance, leading to only proximity-restricted Ca^{2+} at these temperatures. However, as

430 the temperature increases, the static linewidths of the (^2H) ^{43}Ca -hectorite paste become narrower
431 than those of the room humidity 2WL- ^{43}Ca -hectorite (Table 2), and are nearly fully liquid-like at
432 0 °C and +25 °C [$\sim 80 \pm 35$ Hz vs. 28 ± 2 Hz for Ca^{2+} in a saturated CaCl_2 (aq) solution]. The
433 very narrow resonances at and above the freezing point of bulk ice-1h with a slightly greater
434 residual linewidth than Ca^{2+} in bulk aqueous solution suggest desorption of Ca^{2+} from the surface
435 into a “free” solution-like state and, given the need for balance of the negative layer charge of the
436 clay, probably indicate rapid exchange between bulk solution and surface-sorbed environments
437 (although other dynamic averaging mechanisms are possible; see discussion below). The “free”
438 Ca^{2+} may occur in bulk liquid domains in highly expanded interlayers (the layers may even be
439 fully delaminated) and/or in liquid-rich pores between particles. Significant layer expansion at
440 high $^2\text{H}_2\text{O}$ activity is supported by the XRD results, which show a large fraction of basal
441 spacings well in excess of 15 Å at 90% RH. Similar desorption and potential delamination at
442 high temperatures has been reported previously in (^2H)Na-hectorite pastes (Bowers et al., 2011).

443 The ^{43}Ca NMR spectra and XRD results suggest that the proximity-restricted Ca^{2+} is present as
444 principally outer-sphere complexes in both the two-layer hydrate and paste, consistent with the
445 idea that Ca^{2+} - H_2O interactions dominate the direct Ca^{2+} -smectite surface interactions in
446 hectorite. Based on the similar ionic radii of Ca^{2+} and Na^+ but the larger charge of Ca^{2+} , one
447 might anticipate that Ca^{2+} would have a stronger attraction to the hectorite surface than Na^+ and
448 may even prevent interlayer expansion via stronger electrostatic bridging across the interlayer
449 space. However, the hydration energy of Ca^{2+} is nearly four times the value of Na^+ , reflecting
450 the much greater affinity of Ca^{2+} for H_2O . The XRD results clearly indicate that direct Ca^{2+} -
451 hectorite surface interactions do not present a significant barrier to layer expansion. In addition,
452 there is no evidence in the ^{43}Ca static or MAS NMR spectra for broad quadrupolar signals

453 associated with a rigid, asymmetrical Ca^{2+} environment expected for Ca^{2+} on inner-sphere
454 sorption sites. For example, the ^{43}Ca NMR parameters reported for ackermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$;
455 an anhydrous phase with Ca^{2+} layers located between two 2-D magnesium silicate layers)
456 based on quantum chemical calculations show a small, positive isotropic chemical shift (7 ppm)
457 and a quadrupolar product of 2.2 MHz (Gervais et al., 2008). It is likely that if Ca^{2+} were
458 associated with the mineral surface as an inner-sphere complex in a two-layer hydrate, the
459 resulting nearest-neighbor coordination sphere would be highly asymmetric, suggesting larger
460 values of the quadrupolar product via increased quadrupolar coupling, quadrupolar asymmetry,
461 or both. However, the resonances from the Ca^{2+} in both the 2WL- ^{43}Ca -hectorite and (^2H) ^{43}Ca -
462 hectorite paste at +25 °C are on the low end of ^{43}Ca linewidths typically observed at +25 °C and
463 at 20.0 T for inorganic solids in which the Ca^{2+} atoms are rigidly held and directly coordinated to
464 the anions (Fig. 8) (Bryce, 2010; Gervais et al., 2008; Lin et al., 2004; Wong et al., 2006). The
465 width appears to be most similar to those of calcite and aragonite at this field, which have some
466 of the smallest reported ^{43}Ca quadrupolar products (1.4 MHz and <0.68 MHz, respectively) and
467 are structurally ordered, in contrast to hectorite interlayers. A full hydration shell for Ca^{2+} in
468 ^{43}Ca -hectorite and lack of inner-sphere complex formation is also supported by the ^{43}Ca
469 chemical shifts, which are similar to those of Ca^{2+} in dilute aqueous CaCl_2 solutions at all
470 temperatures at both moisture contents. The large hydration energy for Ca^{2+} , the basal spacings
471 observed by XRD, and the variations in the XRD results with respect to Na-hectorite suggest that
472 hydration of the Ca^{2+} ions dominates the overall hectorite hydration behavior at water activities
473 <70% RH, lending additional weight to the idea of predominantly outer-sphere complex
474 formation and weak direct Ca^{2+} -hectorite surface interactions at all humidity levels above 30%
475 RH.

476 There is no evidence in the NMR results suggesting that Ca^{2+} occupies preferred surface or
477 interlayer binding sites. Preferential siting of strongly hydrated metal cations near specific
478 tetrahedral sites has only been observed in Monte Carlo and MD simulations for smectites with
479 layer charge due to isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet, which can
480 also lead to inner-sphere complex formation (Chang et al., 1995; Greathouse and Sposito, 1998;
481 Sposito et al., 1999). In contrast, the hectorite layer charge is developed predominantly by
482 octahedral substitution, and only Cs^+ with its large ionic radius and small hydration energy has
483 been observed to occur as inner-sphere complexes in octahedrally substituted clays (Weiss et al.,
484 1990a; Weiss et al., 1990b). Based on the XRD and NMR results, it appears that smaller, higher
485 charge cations with large hydration energies (such as Ca^{2+}) probably do not have a strong
486 preference for specific sorption sites.

487 The ^{43}Ca NMR spectra at both hydration levels also contain evidence of dynamic averaging via
488 a process involving diffusional motion of the Ca^{2+} ions, diffusional motion of $\text{H}_2\text{O}/^2\text{H}_2\text{O}$ in the
489 Ca^{2+} hydration shell, or a combination of the two. The decreasing peak widths for the static and
490 MAS ^{43}Ca NMR spectra of 2WL- ^{43}Ca -hectorite with increasing temperature demonstrate an
491 increasing rate of dynamical averaging, as also observed for ^{23}Na in Na-hectorite paste (Bowers
492 et al., 2011). For rigidly held ^{43}Ca under static conditions, possible line broadening mechanisms
493 include homonuclear and heteronuclear dipole-dipole interactions, chemical shift anisotropy
494 (CSA), and quadrupolar interactions along with dispersion of these parameters and the isotropic
495 chemical shift due to structural or dynamical disorder. Increasing motion at frequencies on the
496 order of and greater than the static linewidth decreases the contributions of these interactions to
497 the observed linewidth, and the observed narrowing of the static peak widths with increasing
498 temperature must be due to full or partial averaging of these interactions by dynamical processes.

499 MAS at a 10 kHz spinning frequency provides mechanical averaging of the dipole-dipole, CSA
500 interactions, and first-order quadrupolar interactions; partial averaging of the second-order
501 quadrupolar interaction; and no averaging of static chemical shift dispersion. The data suggest
502 that the MAS linewidths for 2WL-⁴³Ca-hectorite are dominated by chemical shift dispersion due
503 to a range of local Ca²⁺ structural environments, and thus the narrowing of the MAS resonances
504 with increasing temperature demonstrates dynamical averaging by atomic hopping of the Ca²⁺
505 among environments with different chemical shifts and different second order quadrupole
506 couplings (if present) or to rapid averaging of the local Ca²⁺ environments due to hopping of
507 coordinating ²H₂O molecules, or a combination of the two. These conclusions are supported by
508 the ⁴³Ca nutation data that show behavior intermediate between rigid and liquid-like character for
509 this sample. The progressive change of the peak maxima to lower resonance frequencies with
510 increasing temperature in the MAS spectra of this sample indicates a progressive weakening of
511 the interactions of Ca²⁺ with its coordination shell, as also observed for ²³Na⁺ in (²H)Na-hectorite
512 paste above -20 °C (Bowers et al., 2011). If site exchange due to strong ion-surface interactions
513 were the source of dynamic averaging, a single narrow resonance should appear at the weighted-
514 average position between the exchange sites at all temperatures above the fast exchange limit,
515 and this peak would not shift with increasing temperature. In addition, separate resonances for
516 the different sites at temperatures sufficiently low to freeze out the exchange motion would be
517 observed. There is no evidence of this in the data for either the 2WL-⁴³Ca-hectorite or (²H)⁴³Ca-
518 hectorite paste at temperatures as low as -120 °C. This observation does not completely rule out
519 the possibility of exchange, because colder temperatures may be required to freeze out the site
520 exchange dynamics, but the results down to -120 °C are fully consistent with diffusion-related
521 dynamic processes as the dominant dynamic averaging mechanism. We also note that obtaining

522 lower temperature data would require the use of specialized cryogenic NMR probes. The onset
523 temperature for the progressive shift to more negative resonance frequencies for the 2WL-⁴³Ca-
524 hectorite is much lower than for the Na-hectorite paste (Bowers et al., 2011), in agreement with
525 our proposal that diffusional dynamic effects influence the low temperature cation NMR signal
526 more than surface effects for cations with larger charge densities. The observation that the static
527 peak widths for the room humidity sample are always narrower under MAS than without
528 spinning shows that even at room temperature, interactions other than dispersion of the chemical
529 shift are present and are not fully averaged by atomic motion. As noted earlier, the peak widths
530 for the paste sample under static conditions are narrower than the MAS peak widths for the room
531 humidity sample at 0 °C and near room temperature, consistent with more rapid atomic motion
532 occurring in larger interlayer galleries and/or free ²H₂O domains between hectorite particles in
533 the paste. The dynamic source of this line narrowing may be faster Ca²⁺ diffusion among surface
534 sites, more rapid ²H₂O hopping between coordinating and non-coordinating environments,
535 desorption and diffusion of Ca²⁺ to a non-proximity-restricted state, or any combination of these
536 mechanisms. For the (²H)⁴³Ca-hectorite paste, these processes are all facilitated by excess ²H₂O.
537 It is difficult to distinguish among these mechanisms based on the NMR data alone; molecular
538 dynamics simulations at a variety of H₂O contents and neutron scattering studies of ²H₂O
539 diffusion are needed for a more detailed analysis.

540 *²H NMR and H₂O Dynamics*

541 Recently, we proposed a model for ²H₂O dynamics in alkali metal hectorites that involves
542 simultaneous fast-motion limit libration and site hopping of water molecules (Bowers et al.,
543 2011). This model is supported by computational molecular dynamics simulations (Morrow et
544 al., 2013) and also provides an accurate description of the observed ²H NMR spectra of the

545 2WL-(²H)Ca-hectorite generated in the current study. The so-called C₂/C₃ hopping model
546 requires that the rate of libration or rotation of ²H₂O molecules about the C₂ symmetry axis of the
547 ²H₂O must be at least an order of magnitude faster than hopping of the water molecules among
548 sites with C₃ symmetry with respect to the surface normal. The model also requires that the rate
549 of the C₃ hopping must be at least an order of magnitude faster than the observed static ²H
550 linewidth (~230 kHz). From an NMR perspective, these rates are in the fast-motion regime,
551 meaning that their influence on the observed spectrum is independent of the specific rates of
552 motion as long as they meet these criteria. Water librational motion about the orientation of the
553 dipole moment occur at about around 500 cm⁻¹ in conventional IR spectra, meaning the rate of
554 C₂ hopping is expected to be in the range of 10s of THz. Thus, the range of rates for C₃ hopping
555 that could lead to fast-motion limit ²H NMR spectra is very large, spanning from ~1 MHz to ~1
556 THz. The rotational correlation times obtained by applying the isotropic rotational diffusion
557 model discussed above to the room humidity (²H)Na-hectorite and (²H)Ca-hectorite show ²H
558 motion are in the narrower range of 1 to 100 GHz. Geometrically, if the time-averaged
559 orientation of the O-²H vector with respect to the layer normal [the surface normal (SN)-O₂H₂O-
560 ²H angle] is at the octahedral angle (54.7°, also the NMR MAS magic angle), the ²H resonance
561 appears as a single sharp peak. If, however, the time averaged value of this angle is different
562 than 54.7°, there is a residual quadrupolar broadening that results in observable spectral features
563 characteristic of integer spin quadrupolar powder patterns. Both positive and negative difference
564 in orientation from the octahedral angle yield the same spectra due to symmetry, and thus two
565 angular values are reported. Interlayer ²H₂O can be part of the interlayer cation coordination
566 shell, occupy an empty ditrigonal ring, or occur in a transient orientation between these stable
567 states at any instant in time. The presence of a single resonance in the ²H NMR spectra of the

568 2WL-(²H)Na- and 2WL-(²H)Ca-hectorites shows that during the NMR T₂ observation time all
569 ²H₂O molecules occupy all types of sites that are present. The SN-O_{2H2O}-²H angle determined
570 from the ²H NMR spectra is, thus, the average over all the ²H₂O populations in the hectorite
571 interlayers and on external surfaces, which includes ²H₂O molecules in the cation hydration shell
572 and those occupying other types of sites. Exchange between interlayer and external surface sites
573 does not appear to be significant on the ms to 10s of ms timescales for these samples.

574 The ²H NMR results for the 2WL-(²H)Ca-hectorite sample show that substitution of Ca²⁺ for
575 Na⁺ in hectorite does not greatly affect the types of motion that the proximity-restricted H₂O
576 molecules undergo in the two-layer hydrates or how these motions affect the observed ²H
577 lineshape. The ²H NMR spectra of the 2WL-(²H)Na- and 2WL-(²H)Ca-hectorites (Fig. 6) are
578 very similar between -80 °C and +25 °C, and both are well fit by the model described above
579 (Fig. 9). A similar independence of H₂O motion with respect to the charge balancing cation has
580 been reported for montmorillonites based on neutron scattering results (Gonzalez et al., 2008).

581 The data do show that Ca²⁺ for Na⁺ substitution in hectorite has only a small effect on the time
582 averaged orientation of the ²H₂O molecules with respect to the clay surface. For the room
583 humidity Ca-hectorite, the ²H spectra from -50 to +25 °C are well fit with surface normal (SN)-
584 O_{2H2O}-²H angles of either 51.5° or 58.5°, which are closer to the octahedral angle than for Na-
585 hectorite, for which the spectra are best fit using angles of 51 or 59°. The ²H splittings are very
586 sensitive to the angle with respect to the surface normal (Bowers et al., 2011), and the
587 differences reported here are significant. Computational molecular dynamics studies suggest that
588 the dipole moment of H₂O adjacent to the muscovite mica surface has an average SN-O_{H2O}-H
589 angle of 150-160° and that the average H₂O molecule is donating two H-bonds to the surface
590 (Wang et al., 2005), making the expected SN-O_{2H2O}-²H angle in an ion-free ring ~ +25 ± 5°.

591 Although the SN-O_{2H₂O}-²H angle is likely to be smaller in hectorite because it has effectively no
592 layer charge originating from tetrahedral substitutions, if we assume a similar orientation of
593 ²H₂O at the Ca-hectorite interface and account for the fact that the number of ring-sorbed H₂O
594 molecules should be greater in Ca-hectorite than in Na-hectorite due to fewer Ca²⁺ being
595 required for charge balance, these data suggest that the nearest neighbor hydration shell around
596 Ca²⁺ in the two-layer hydrate of hectorite may be closer to ideal octahedral geometry than that
597 around Na⁺. Thus, the angle θ_A , the SN-Ca²⁺-O_{2H₂O} angle (Fig. 9), may be closer to 54.7° in
598 2WL-(²H)Ca-hectorite. This geometry is easily obtained in the interlayer with the ²H₂O
599 molecules located next to the basal oxygens and the Ca²⁺ in the center of the interlayer
600 equidistant from the basal surfaces.

601 *²H₂O Rotational Diffusion and Activation Energies*

602 The activation energies for ²H₂O rotational diffusion reported here [25.1 kJ/mol for (²H)Ca-
603 hectorite vs. 21.1 kJ/mol for (²H)Na-hectorite] are in good agreement with those in the literature
604 for other Na- and Ca-smectites, suggesting that the isotropic rotational diffusion model is
605 applicable to ²H₂O in both alkali metal and Ca-hectorites. The values in this work are slightly
606 lower than the activation energies for ²H₂O rotational diffusion reported for other Na-smectites
607 and vermiculites based on ²H NMR (37.8 kJ/mol for Na-hectorite, 35.5 kJ/mol for Na-
608 vermiculite) (Giese and Fripiat, 1979; Weiss and Gerasimowicz, 1996) and higher than those
609 reported for H₂O diffusion in one- and two-layer hydrates of Na- and Ca-montmorillonite from
610 neutron scattering (11-12 kJ/mol) (Gonzalez et al., 2008). However, direct comparison and
611 interpretation of the absolute values of apparent activation energies for complex processes is
612 difficult, and sample differences such as smectite composition, layer charge, type of isomorphic
613 substitution (tetrahedral vs. octahedral), and H₂O content are likely to influence the relaxation

614 times and apparent activation energies. Gonzalez-Sanchez et al. (2008) show that different types
615 of phyllosilicates have different activation energies for H₂O diffusion, supporting this
616 conclusion. In addition, the activation energies for H₂O diffusion in Na- and Ca-
617 montmorillonites based on neutron scattering results relate to motion in the temperature range of
618 27-95 °C, which may result in different values if the Arrhenius behavior is not strictly
619 exponential (Gonzalez et al., 2008).

620 The calculated rotational correlation times for ²H₂O rotational diffusion (10-1000 ps) are also
621 similar to those determined in other NMR experiments with smectites and vermiculites, but are
622 larger than those determined from neutron scattering studies. Like our results, the rotational
623 correlation times determined for Na-hectorite and Na-saponite by Weiss and Gerasimowicz
624 (1996) also fall between 10 and 1000 ps between -35 °C and +25 °C and decrease with
625 increasing temperature. For Na- and Ca-montmorillonites, the rotational correlation times
626 determined by neutron scattering are 1-2 ps and the average residence times of ²H₂O in a
627 particular site determined from neutron scattering are between 10 and 20 ps (Gates et al., 2012;
628 Gonzalez et al., 2008). Based on these results, it appears that both NMR and neutron scattering
629 support the idea that the motion with C₃ symmetry in the C₂/C₃ hopping model is closely related
630 to hopping diffusion of ²H₂O, in good agreement with our conclusion that the importance of
631 diffusion-based dynamic averaging of metal ions in hydrated smectites at lower temperatures
632 increases as the metal ion charge density increases.

633 *High-frequency ⁴³Ca Shoulder*

634 The presence of a small, second ⁴³Ca resonance with signal toward higher frequencies than the
635 main resonance (more positive chemical shifts) in the -120°C MAS spectrum of the 2WL-⁴³Ca-
636 hectorite sample (Fig. 2) may be due to the presence of Ca²⁺ on external surfaces, but this

637 interpretation is not certain. It is possible that the rates of the processes causing dynamical line
638 narrowing may be sufficiently slow or different in the interlayers and external surfaces at this
639 temperature to allow resolution of these signals. The resonances are not separable in the static
640 spectra at any temperature, and experiments at even lower temperatures are required to explore
641 this observation in more detail. It does not seem likely that this second site would be inner-
642 sphere Ca^{2+} , as this would suggest that full or partial dehydration of Ca^{2+} becomes easier at lower
643 temperatures, in contrast to what one might expect based on conventional thermodynamic
644 arguments. If the second site were an alternate preferred sorption site for outer-sphere Ca^{2+} , we
645 would expect to observe the influence of exchange between several unique outer-sphere Ca^{2+}
646 environments on the higher temperature NMR spectra. It is also possible that this feature
647 represents a second interlayer Ca^{2+} site. This is not likely, because it would most likely undergo
648 dynamical averaging with the main peak at higher temperatures, causing a shift of the peak
649 maximum to more positive values, which is not observed. In addition, as noted above, the
650 observed ^{43}Ca MAS NMR spectra for 2WL- ^{43}Ca -hectorite are not consistent with exchange type
651 behavior, where one would initially expect a shift to more positive resonance frequency with
652 increasing temperature if exchange between the two resolvable sites were occurring. It is
653 possible that such evidence is present at temperatures between $-120\text{ }^{\circ}\text{C}$ and $-100\text{ }^{\circ}\text{C}$ that were not
654 explored, however it is difficult to support a site exchange model between these two
655 environments using this data set. A true evaluation of the role of site exchange on the ^{43}Ca
656 spectra will best be evaluated using NMR data from lower temperatures, which once again
657 requires use of a specialized cryogenic NMR probe. For completeness, we also note that the
658 high-frequency feature cannot be described using quadrupolar MAS lineshapes, as they produce
659 “tails” on the low-frequency side of the resonance.

660

IMPLICATIONS

661 The ^2H NMR results presented in this study support the increasingly accepted notion that H_2O
662 within $\sim 5 \text{ \AA}$ of a mineral surface has a structure and dynamical behavior unlike either ice-1h or
663 bulk liquid H_2O . For hectorite, the molecular-scale dynamical behavior of the proximity-
664 restricted $^2\text{H}_2\text{O}$ is similar whether the charge-balancing cation is Na^+ , K^+ or Ca^{2+} , and in all the
665 cases we have explored, it is not possible to distinguish between proximity-restricted H_2O in the
666 interlayer galleries and on the external surface using ^2H NMR. Together, the Ca-hectorite results
667 in this paper combined with the alkali metal hectorite results published previously are consistent
668 with the hypothesis that H_2O motion in any smectite dominated by isomorphic substitution in the
669 octahedral sheet can be described using the C_2/C_3 jump motion model over some range of
670 temperatures regardless of the valence of the charge-balancing cation. The general applicability
671 of this statement and details of the molecular-scale motion observable using ^2H NMR associated
672 with the type (Mg^{2+} for Al^{3+} vs. Fe^{2+} for Al^{3+} , for example) or density of octahedral charge
673 substitution in smectites or for clays with tetrahedral substitution remain to be evaluated.
674 Combined MD and neutron spectroscopic results suggest that both H_2O translational diffusion
675 rates and slow rotations of hydrated charge balancing cation clusters are sensitive to the total
676 layer charge and charge location between 300 K and 350 K, which support the need for ^2H NMR
677 investigations of similar samples over a broader range of temperatures (Marry et al., 2011;
678 Michot et al., 2012; Michot et al., 2007; Sanchez et al., 2009). The rates of ^2H isotropic
679 rotational diffusion determined from ^2H T_1 experiments reported here correlate well with the C_3
680 process in the C_2/C_3 jump motion model for proximity-restricted $^2\text{H}_2\text{O}$, provide further validation
681 of this model, and correlate well with similar measurements made in other smectites using
682 neutron scattering techniques.

683

684 The charge density of the anhydrous metal cation correlates with the onset temperature for
685 diffusion-dominated dynamic averaging of that cation's NMR resonance (whether due to motion
686 of the ions or H₂O of hydration) based on our data for Cs⁺, K⁺, Na⁺, and Ca²⁺ (Bowers et al.,
687 2008b; Bowers et al., 2011; Weiss et al., 1990), implying that one can qualitatively predict the
688 dominant type of molecular-scale motion leading to averaging of the NMR signal for alkali and
689 alkaline earth metal ions in smectites and smectite-rich earth materials over a wide range of
690 temperatures based on the anhydrous cation charge density. For example, the charge densities of
691 Sr²⁺ and Ba²⁺ in six-fold coordination fall within the correlation limits and bracket the value for
692 Na⁺ (+0.387/Å³ for Sr²⁺ and +0.259/Å³ for Ba²⁺ vs. +0.300/Å³ for Na⁺), suggesting that Ba²⁺ will
693 require a temperature above 253 K before diffusion-type dynamic averaging of the ¹³⁷Ba NMR
694 resonance will dominate the character of the NMR spectrum. The higher charge density of Sr²⁺
695 suggests that the ⁸⁷Sr NMR spectrum will be dominated by diffusion-type dynamic averaging at
696 a lower temperature than Na⁺. Unfortunately, the rapid modulations of the ⁸⁷Sr quadrupolar
697 interaction (which is much larger than Na⁺) due to this type of dynamic process may lead to
698 unobservable resonances near room temperature due to lifetime broadening, consistent with the
699 inability to observe charge-balancing ⁸⁷Sr in a smectite to date. While the correlation currently
700 contains data points only from alkali and alkaline earth metals where electrostatic interactions
701 with the mineral surface dominate, if the correlation between Z/r^3 holds in general across the
702 periodic table, one may be able to predict the type of dynamic averaging affecting the NMR
703 resonance of heavy metal pollutants within and beyond the transition metals such as Pb²⁺ or Hg²⁺
704 (charge densities of +0.378/Å³ and +0.600/Å³, respectively, which are within the limits of this
705 correlation). However, extreme caution is required when predicting the behavior of the

706 transition metals from a simple Z/r^3 correlation, since other factors such as the ion polarizability,
707 hydrated radius, effective charge, and coordination number may play a more significant role for
708 elements outside the alkaline and alkaline earth metals. NMR-accessible nuclei such as ^{207}Pb
709 (spin $I = 1/2$), ^{199}Hg (spin $I = 1/2$), and ^{201}Hg (spin $I = 3/2$) can and should be used for additional
710 testing of the correlation between cation properties and diffusion-type motion onset temperature
711 and are likely to be more amenable to VT NMR than the other alkaline earth metals such as
712 Mg^{2+} , Sr^{2+} , and Ba^{2+} . Comparing the spin $1/2$ and quadrupolar isotopes of the same element (e.g.
713 ^{199}Hg vs. ^{201}Hg) may also help to determine whether cation or H_2O motion is principally
714 responsible for the observed dynamic averaging of the NMR signal and provide new insight as to
715 how the dynamics of the cations and H_2O molecules are related.

716

717 The data presented here also provide an important baseline for understanding the behavior of
718 cations, H_2O , and organic compounds in hydrated organo-clay complexes. Natural organic
719 matter (NOM) and NOM coatings on minerals alter the mobility of many species, and Ca^{2+} is
720 thought to play an important role in the non-covalent aggregation of NOM. Its role in NOM-
721 smectite complexes is less clear, and it may provide bridges between NOM molecules and
722 mineral surfaces, facilitate formation of surface coatings, or impact the coating density.
723 Comparing data from the NOM-free systems in this study to those obtained in smectite-NOM
724 complexes may allow us to determine the relative roles of the organic matter and inorganic
725 mineral surface in the more complex OM-bearing system. Our group is currently undertaking
726 NMR and computational molecular modeling studies of such smectite-OM complexes to
727 evaluate how organic material alters the solid-fluid interfacial structure and dynamics.

728

729

ACKNOWLEDGMENTS

730 This work was supported by the United States Department of Energy, Office of Basic
731 Energy Science through grants DE-FG02-10ER16128 and DE-FG02-08ER15929. The ^{43}Ca
732 NMR spectra were obtained using the High Field Magnetic Resonance User Facility housed at
733 the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored
734 by the Department of Energy's Office of Biological and Environmental Research and located at
735 Pacific Northwest National Laboratory. The authors thank Dr. Alan J. Benesi for acquiring the
736 ^2H NMR using facilities at Penn State University and for helpful consultations regarding the
737 dynamic interpretations of the ^2H NMR spectra. They also thank Ms. Arielle Polakos and Dr.
738 Andrew Eklund for assistance in devising the ^{43}Ca -enriched solution preparation procedure.

739

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925

926

FIGURE CAPTIONS

927 **Figure 1.** Controlled relative humidity (RH) XRD results for Ca-hectorite. The top image
928 shows the basal spacings of Ca-hectorite determined from the peak center-of-mass as a function
929 of RH. All values have an uncertainty between 0.15 and 0.25 Å. This sample occurs dominantly
930 as a two-layer hydrate over the RH range between 30% and 60% and exhibits negligible
931 hysteresis upon dehydration except at the highest RH values. The bottom image presents the
932 observed XRD patterns between 2° and 12° 2θ, showing again a lack of hysteresis and nearly
933 identical widths and peak maxima as humidity is increased (blue lines in both figures) and
934 decreased (black lines in both figures). The red line in the bottom image is 90% RH pattern, the
935 maximum value used.

936 **Figure 2.** Variable temperature ⁴³Ca MAS NMR spectra of 2WL-⁴³Ca-hectorite acquired at 20.0
937 T. The featureless and symmetric resonances progressively narrow and shift to more negative
938 peak maxima with increasing temperature. There is some intensity indicative of a second ⁴³Ca
939 environment on the left side of the dominant resonance at -120 °C that is not visible at any other
940 temperature or in the static ⁴³Ca results.

941 **Figure 3.** ⁴³Ca nutation curves for CaCO₃ (grey), saturated CaCl₂ (aq) (black), and the 2WL-
942 ⁴³Ca -hectorite at 20 °C (blue/dotted), -50 °C (red/dashed), and -120 °C (green/long dash)
943 obtained at 20.0 T under MAS conditions. The ⁴³Ca nutation behavior of this hectorite sample is
944 between that expected for “rigid” ⁴³Ca in CaCO₃ and Ca²⁺ in concentrated aqueous solution at all
945 temperatures. These observations are consistent with the Ca²⁺ being in close association with the
946 surface at all temperatures, as expected for proximity-restricted (< 5 Å from a surface or ion)
947 interlayer and external surface sites.

948

949 **Figure 4.** Comparison of the room temperature ^{43}Ca MAS NMR spectra for 2WL- ^{43}Ca -hectorite
950 at 21.1 T (top) and 20.0 T (bottom). Both peaks are narrow and featureless, and the maximum of
951 the spectrum at 20.0 T falls within the uncertainty of the value at 21.1 T, suggesting only a small
952 contribution from a time-averaged quadrupolar interaction to the line shape ($P_Q = 1.4 \pm 1.4$
953 MHz). The larger peak width and peak shape at 21.1 T is a result of uncorrectable magnetic
954 field inhomogeneities due to the material requirements of the high temperature 5 mm MAS
955 probe used at this field.

956 **Figure 5.** Variable temperature ^{43}Ca static NMR spectra of the 2WL (left) and paste (right)
957 samples of ^{43}Ca -hectorite acquired at 20.0 T. See text for discussion of the peak shapes, positions
958 and intensities.

959 **Figure 6.** Variable temperature ^2H NMR spectra for 2WL-(^2H)Ca-hectorite compared to the ^2H
960 spectra for Na-Hectorite at -80° and 25°C (top and bottom spectra). See text for interpretation.

961 **Figure 7.** An Arrhenius plot of the $^2\text{H}_2\text{O}$ rotational correlation time determined from the ^2H
962 NMR T_1 relaxation times for 2WL-(^2H)Na-hectorite (red) and 2WL-(^2H)Ca-hectorite (blue). The
963 activation energy for rotational diffusion is larger for Ca-hectorite, as expected based on the
964 greater affinity of Ca^{2+} for H_2O with respect to Na^+ , as expressed in their hydration energies.
965 The red point not included in the Arrhenius fit is likely part of the positively sloped region in the
966 classic “V” shape in correlation times versus inverse temperature plots for NMR T_1 data.

967 **Figure 8.** The room temperature ^{43}Ca MAS NMR spectrum of 2WL- ^{43}Ca -hectorite at 20.0 T
968 (top) compared to simulated resonances of crystalline Ca compounds with Ca coordinated by
969 oxygen at this field using the parameters reported in the literature (Bryce, 2010; Gervais et al.,
970 2008). Most of the spectra for phases with Ca directly coordinated by structural oxygen atoms
971 have line shapes dominated by quadrupolar interactions, whereas the hectorite does not. This

972 difference is consistent with the Ca^{2+} in hectorite being in outer sphere complexes. The ^{43}Ca
973 linewidth in the ^{43}Ca -hectorite is most similar to calcite and aragonite, which have the smallest
974 quadrupolar products of the phases shown (1.4 MHz and 0.68 MHz, respectively), making it
975 likely that the quadrupolar product in ^{43}Ca -hectorite is also small. Simulations were performed
976 using the SIMPSON simulation software (Bak et al., 2000) with the same MAS conditions and
977 line broadening that were applied to the experimental spectrum.

978 **Figure 9.** A visual representation of the important angles in the C_2/C_3 hopping model for the ^2H
979 NMR spectra for Ca- and Na-hectorite. θ_A is the surface normal- Ca^{2+} - $\text{O}_{\text{H}_2\text{O}}$ angle that is related
980 to the compression or extension of the Ca^{2+} hydration shell along the C_3 symmetry axis. θ_B is the
981 surface normal- $\text{O}_{\text{H}_2\text{O}}$ - ^2H angle to which the ^2H NMR line shape is sensitive. Two different H_2O
982 sites (H_2O in the Ca^{2+} hydration shell and H_2O sorbed at the center of a hexagonal ring) are
983 represented with different θ_B values. The ^2H NMR line shape reflects the time averaged θ_B value
984 and represents the probability-weighted average of all θ_B values in the sample assuming rapid
985 exchange of $^2\text{H}_2\text{O}$ molecules among all sites. Calcium ions are orange, oxygen is red, and
986 hydrogen/deuterium are white.

987

988

TABLES

989 **Table 1.** Summary of sample designation, experiments, and compositional characteristics.

Designation	Experiment(s)	Characteristics
Ca-hectorite	XRD	Natural abundance of ^{43}Ca and ^2H
2WL-(^2H)Ca-hectorite	^2H NMR	Natural abundance of ^{43}Ca , equilibrated at ~43% RH $^2\text{H}_2\text{O}$ (99.9% ^2H)
2WL- ^{43}Ca -hectorite	^{43}Ca NMR	30% ^{43}Ca , equilibrated at atmospheric RH with natural abundance of ^2H
(^2H) ^{43}Ca -hectorite paste	^{43}Ca NMR	30% ^{43}Ca , mixed at 2:1 mass ratio of 99.9% $^2\text{H}_2\text{O}$:smectite
2WL-(^2H)Na-hectorite	^2H NMR	Natural abundance of ^{23}Na , equilibrated at ~43% RH $^2\text{H}_2\text{O}$ (99.9% ^2H)

990

991 **Table 2.** Fit results for the variable temperature ^{43}Ca NMR of 30% ^{43}Ca enriched Ca-hectorites.

T (°C)	Type ^a	2WL- ^{43}Ca - hectorite MAS		2WL- ^{43}Ca - hectorite static		^{43}Ca -hectorite paste static	
		δ_{CS} (± 0.35 ppm)	FWHM (± 20 Hz)	δ_{CS} (± 0.09 ppm)	FWHM (± 35 Hz)	δ_{CS} (± 0.09 ppm)	FWHM (± 35 Hz)
25/20 ^b	1L	-1.33	139	-1.77	322	-0.56	81.2
0	1L	-0.80	141	-1.51	340	0.12	85.8
-30	1L	-0.04	153	-0.30	362	0.39	151
-50	1L	0.42	214	0.24	435	1.09	281
-75	1L	0.96	284	0.20	506	1.33	366
-100	1L	1.61	310	1.70	946	2.88	971
-120	1L	2.07	450	3.25	1705	4.65	1330
	2L	0.82	265				
		3.10	506				

992 δ_{CS} = observed chemical shift, FWHM = full width at half maximum

993 ^aType of function used to fit the data. 1L is a fit to one pure Lorentzian and 2L is a fit to two
 994 Lorentzian functions

995 ^bThe highest temperature for the static VT experiments was 20°C

996

997 **Table 3.** ²H NMR and T₁ relaxation parameters, including the calculated rotational correlation
 998 times (τ_C) for 2WL-(²H)Ca-hectorite and 2WL-(²H)Na-hectorite.

T (K)	2WL-(² H)Ca-hectorite			2WL-(² H)Na-hectorite		
	Splitting (kHz)	T ₁ (ms)	τ _C (10 ⁻¹⁰ s)	Splitting (kHz)	T ₁ (ms)	τ _C (10 ⁻¹⁰ s)
298	21.48	-	-	24.44	67.0 ± 0.5	0.190
273	21.48	29.9 ± 1.3	0.425	25.62	40.1 ± 0.5	0.318
253	23.44	14.0 ± 0.7	0.910	26.56	19.3 ± 0.2	0.660
238	23.44	6.18 ± 0.41	2.06	27.02	8.94 ± 0.11	1.42
223	25.4	2.55 ± 0.25	5.00	26.87	4.01 ± 0.05	3.17
193	N/A	-	-	35.54	4.87 ± 0.06	2.61

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