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1 **Determination of layer charge density in expandable phyllosilicates with alkylammonium ions:**
2 **A combined experimental and theoretical assessment of the method**

3

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18

19 ABSTRACT

20 Layer charge deficit is a key crystal-chemical parameter for the classification and nomenclature of
21 2:1 phyllosilicates that also controls some of their fundamental properties such as cation exchange
22 capacity, expandability, water content, or rheology. The clay community has thus devoted
23 significant efforts to determine this parameter either from the smectite/vermiculite chemical
24 composition (the structural formula method) or experimentally using the alkylammonium method,
25 that theoretically allows the determination of the mean layer charge density and of its distribution.
26 In the present study density functional theory (DFT) and molecular dynamics (MD) simulations are
27 compared to experimental X-ray diffraction data for a series of synthetic saponites with layer charge
28 ranging from medium-charge smectite to medium-charge vermiculite. Consistency of computed and
29 measured layer-to-layer distances confirms the ability of computational approaches to accurately
30 predict the organization of alkylammonium cations in smectite interlayers. Thermalization of DFT-
31 optimized structure models through MD simulations allows probing possible alternative interlayer
32 configurations such as the electrostatically-favored location of ammonium heads above/below Al-
33 substituted tetrahedra. X-ray diffraction results showed that layer-to-layer distances intermediate
34 between those corresponding to the stable h1, h2, etc interlayer configurations described in the
35 literature result from the interstratification of different stable configurations. The overall
36 consistency of computational and experimental results confirms also the ability of the
37 alkylammonium method to accurately determine a mean value of layer charge density consistent
38 with smectite structural formula when using the revised equations proposed by Laird et al. (1989).
39 The validity of the method appears however limited to smectite-group minerals [layer charge
40 density ranging from ~ 0.5 to ≤ 1.2 per $O_{20}(OH)_4$] most likely owing to the coexistence of both stable
41 "layered" and paraffin-like interlayer configurations for higher values of layer charge. In addition,
42 this consistency challenges the ability of the method to quantitatively describe distributions of layer
43 charge in expandable phyllosilicates even when using the complete series of alkylammonium
44 cations.

45

46 1. Introduction

47 Classification and nomenclature of 2:1 phyllosilicates rely to a large extent on their layer
48 charge deficit (Guggenheim et al., 2006). This key crystal-chemical parameter allows indeed
49 differentiating talc-pyrophyllite, smectite, vermiculite, interlayer-deficient mica, true mica, and
50 brittle mica groups of 2:1 phyllosilicates (Guggenheim et al., 2006). Furthermore, layer charge
51 controls fundamental properties of the phyllosilicates such as cation exchange capacity (Jackson,
52 2005; Dohrmann, 2006 and references therein), expandability (Laird, 2006), or water content (Sato
53 et al., 1992; Ferrage et al., 2007). Similarly, layer charge density controls to a large extent clay
54 swelling through the hydration of interlayer cations (Ferrage et al., 2011; Dazas et al., 2015; Vinci et
55 al., 2020), and is thus an essential parameter for the design of engineered clay barriers, including
56 their self-healing ability (Gates et al., 2009), and rheological properties of clay suspensions
57 (Christidis et al., 2006; Paineau et al., 2011a, 2011b). Abundance and nature of expandable 2:1 layer
58 silicates (smectite and vermiculite groups) also have, together with organic matter, a key influence
59 on soil fertility.

60 The pivotal influence of layer charge density on properties of expandable phyllosilicates has
61 induced significant efforts from the clay community to determine theoretically this crystal chemical
62 parameter from the smectite/vermiculite chemical composition (the so-called structural formula
63 method, SFM – Newman and Brown, 1987; Ciel and Komadel, 1994; Laird, 1994) or experimentally.
64 In this context, the so-called alkylammonium method (AAM) initially developed by Lagaly, Weiss,
65 and co-workers (Lagaly and Weiss, 1969, 1971; Lagaly, 1994) appears especially well suited, allowing
66 the determination of the mean layer charge density and of its distribution. The method relies on the
67 experimental determination of unit-cell d_{001} parameter for phyllosilicates intercalated with
68 alkylammonium cations of increasing chain lengths (Lagaly, 1994). As the original method is time
69 consuming for routine analysis, simplified methods have been proposed (Olis et al., 1990; Dohrmann
70 et al., 1999). These methods commonly use a limited number of alkyl chain lengths to determine
71 the mean layer charge density. Considerable efforts have also been devoted to reconcile the results
72 obtained from SFM and AAM (Laird, 1994; Kaufhold, 2006; Kaufhold et al., 2011).

73 In parallel to the experimental AAM, molecular dynamics (MD) has been used to provide
74 insights into the molecular-level interactions responsible for the experimentally observed changes
75 in layer-to-layer distances as a function of alkyl chain length (Heinz et al., 2007; Liu et al., 2007). In
76 these studies, computational results were assessed against experimental literature data obtained

77 on natural smectites whose layer charges scatter essentially over the whole range allowed for
78 smectite (Lagaly and Weiss, 1971; Laird et al., 1989; Vaia et al., 1994). Comparison of MD simulations
79 computed properties with data supported the robustness of the modelling approach and its ability
80 to describe the organization of large organic molecules in smectite interlayers although some
81 specific aspects remained unclear. The first issue is related to the underestimation of layer charge
82 densities derived from the strict application of the AAM compared to those resulting from the SFM,
83 this AAM known bias challenging the consistency between computed and experimental results. A
84 second issue is related to smectite interlayer structure in transition zones between the well-defined
85 configurations described by Lagaly and coworkers (Lagaly and Weiss, 1969, 1971; Lagaly, 1994). In
86 the method description (Lagaly, 1994), layer-to-layer distances intermediate between those of the
87 well-defined configurations correspond to their coexistence/interstratification whereas they
88 correspond to a unique “stable” configuration in the simulations (Heinz et al., 2007; Liu et al., 2007).

89 The present study aims at investigating these two specific aspects. For this purpose the AAM
90 was used on four synthetic samples whose layer charge densities range from medium-charge
91 smectite to medium-charge vermiculite [0.8 to 1.4 per $O_{20}(OH)_4$]. The use of synthetic samples
92 aimed at minimizing the heterogeneity of layer charge density for a given sample and at improving
93 crystallinity to minimize experimental bias related to peak broadening (Stanjek and Friedrich, 1986;
94 Stanjek et al., 1992; Mermut, 1994). Simulations were performed with both density functional
95 theory (DFT) to determine interlayer configurations most symmetrical and most stable at 0 K and
96 MD approaches that allow calculation of more realistic configurations after thermalization at 300 K.

97

98 **2. Materials and Methods**

99 *2.1 Smectite synthesis*

100 A set of expandable phyllosilicates with a common structural formula
101 $inter[Na_x]^{oct}[Mg_6]^{tet}[Si_{8.0-x}Al_x]O_{20}(OH)_4$ and a layer charge (x) varying from 0.8 to 1.4 per $O_{20}(OH)_4$ were
102 synthesized hydrothermally from gel precursors in an externally heated Morey-type pressure vessel
103 with an internal silver tubing (Hamilton and Henderson, 1968; Robert et al., 1993; Bergaoui et al.,
104 1995), as described previously (Dazas et al., 2015). A temperature of 400 °C, a water pressure of 1
105 kbar, and a duration of 4 weeks were used for synthesis. After synthesis, all samples were Na-
106 saturated at room temperature by contact with 1 mol·L⁻¹ aqueous solutions of NaCl. Excess NaCl

107 was removed by rinsing the solid by immersion for 24 h in deionized water (Siemens UltraClear, 18.2
108 M Ω .cm) and separation of the solid fraction by centrifugation. Resulting monomineralic synthetic
109 saponites are hereafter referred to as Sap-OH-x. Previous studies of samples prepared using the
110 same experimental protocols for gel preparation and synthesis supported, from nuclear magnetic
111 resonance and Ar adsorption data, an homogeneous distribution of Al substitutions in saponites,
112 whatever the layer charge (Sanz and Robert, 1992; Michot and Villieras, 2002; Sanz et al., 2006).

113 *2.2 Alkylammonium method*

114 *2.2.1. Preparation of alkyl chains*

115 Homoionic saturation of saponites with alkylammonium cations having different carbon chain
116 lengths required the preparation of solutions with these cations from alkylamines of proper chain
117 length (Table S1). Preparation of alkylammonium cation solutions was described by Lagaly (1994).
118 In brief, the required amount of alkylamine (Table S2) was weighted and stirred and dissolved in
119 100mL of ethanol in a 1000 mL beaker. Next, 400 mL of ultrapure water were added to the solution
120 while maintaining the stirring, commonly leading to the formation of a precipitate. Suspension was
121 then titrated with hydrochloric acid to pH 7.0. Concentrations and approximate volumes of
122 hydrochloric acid solutions required for the titration are reported in Table S2. For short chain
123 lengths, heat production during titration of the solutions required controlling temperature with a
124 water bath. For chain lengths ranging 14-18 carbons, the precipitate did not disappear when acid
125 was added; ethanol (approximate volumes listed in Table S2) was then added to the stirred
126 suspension to allow for a complete dissolution of the precipitate. If necessary, precipitate
127 dissolution was enhanced by heating the suspension to ~50 °C using a water bath. When clear and
128 pH neutral solutions were obtained, ultrapure water was added to a final volume of 1000 mL of
129 appropriate alkylammonium cation concentrations (Table S2).

130 *2.2.2. Smectite saturation with alkylammonium cations*

131 Homoionic saturation of saponites with alkylammonium cations having different carbon chain
132 lengths was performed in 10 mL Teflon tubes using ~100 mg of synthetic saponite. After addition of
133 2 mL of the appropriate alkylammonium solution (4 mL for chains longer than 13 C atoms), the
134 suspension was shaken vigorously. Tubes were shaken until foam, that may contain clay particles,
135 disappeared. Tubes were then heated to 65 °C in an oven for 24 hrs, tube caps remaining slightly
136 open. The cation-exchanged smectites were then centrifuged and rinsed with ethanol (2 mL per
137 rinsing step). Rinsing steps were repeated 8-10 times until the ethanol supernatant did not leave

138 white traces when dried on a glass slide. Alkylammonium-exchanged smectites were then finally air
139 dried at room temperature overnight.

140 *2.3 XRD data collection and processing (alkylammonium method)*

141 For all samples, oriented slides were prepared by drying at room temperature a clay
142 suspension in ethanol on glass slides. XRD patterns were then recorded using a Bruker D8
143 diffractometer equipped with a MHG Messtechnik humidity controller coupled to an Anton Paar
144 CHC+ chamber. Intensities were measured with a SolXE Si(Li) solid-state detector (Baltic Scientific
145 Instruments) for 4 s per 0.04° 2θ step over the 2–50° 2θ Cu Kα angular range. Divergence slit, the
146 two Soller slits, the antiscatter, and resolution slits were 0.3°, 2.3°, 0.3°, and 0.1°, respectively.
147 Samples were kept at 23 °C in the CHC+ chamber during the whole data collection. Samples were
148 kept also under a constant flow of mixed dry/saturated air to maintain a 5% relative humidity (RH)
149 to minimize hydration of smectite interlayers. RH was continuously monitored with a hygrometer
150 (uncertainty of ~2% RH) located close to the sample.

151 The alkylammonium method was performed assuming a systematic surface area of the unit
152 cell of 49 Å² within the **ab** plane and no correction for particle size [$A_c = 5.67 \times N_c + 14$; $\sigma' = 49 / (2 \times$
153 $A_c)$ in which A_c is the average planar area associated with each alkylammonium cation of carbon
154 chain length N_c , σ' being the layer charge corresponding to the critical carbon chain length causing
155 the transition from h1 to h2 configurations – (Lagaly, 1981)]. The revised equation ($\sigma'' = 1.672 \times \sigma'$
156 $- 0.156$) proposed by Laird et al. (1989) was preferred however to ease the comparison with layer
157 charge density determined from the structural formula, that is in the present case with layer charge
158 density determined from the stoichiometry of the synthetic products. In addition, the use of
159 synthetic smectites with an enhanced homogeneity and extent of coherent layer stacking along the
160 c^* axis allowed minimizing reflection broadening and no correction of peak position was performed
161 (Stanjek and Friedrich, 1986; Stanjek et al., 1992; Mermut, 1994).

162 *2.4 Density functional theory (DFT) simulations*

163 Crystal models defined with general structural formula $Mg_6Si_{8.0-x}Al_xO_{20}(OH)_4.NH_3(CH_2)_nCH_3$,
164 $x = 1.0$ and 1.5 , and $n = 1, 2$, etc were used for DFT simulations. Simulations were performed using
165 a $2a \times 1b \times 1c$ super-cell for $x = 1.0$, and a $2a \times 2b \times 1c$ super-cell for $x = 1.5$. Interlayer displacement
166 was allowed to vary during the simulations. Within these super-cells, distributions of Al-substituted
167 tetrahedra and of interlayer alkylammonium cations were generated to obey Löwenstein rule (no

168 adjacent Al-substituted tetrahedra) and to be as regular as possible, consistent with the
169 homogeneous distribution of Al substitutions in saponites reported in the literature (Sanz and
170 Robert, 1992; Michot and Villieras, 2002; Sanz et al., 2006). Periodic DFT calculations were
171 performed with the Siesta 4.0b-485 code (Soler et al., 2002) using a generalized gradient
172 approximation and a Perdew-Burke-Ernzerhof correlation-exchange functional with a mesh cut-off
173 of 500Ry and 6 and 9 k-points in the Monkhorst Pack grid (Hernández-Haro et al., 2016). Troullier-
174 Martins norm-conserving pseudopotentials (Troullier and Martins, 1991) and numerical atomic
175 orbital and double ξ plus polarization basis sets were also used for calculations. DFT methods are
176 well suited to described systems containing cations as interlayer species as the present ones
177 (Hernández-Haro et al., 2016).

178 *2.5 Molecular dynamics (MD) simulations*

179 Classical MD simulations were performed for saponites having layer charges similar to those
180 of the synthetic products: $x = 0.8, 1.0, 1.2,$ and 1.4 per $\text{O}_{20}(\text{OH})_4$. Initial atomic positions for both the
181 clay layer and interlayer were derived by replicating the DFT optimized configurations in a $6a \times 4b \times$
182 $1c$ super-cell, and using the DFT-optimized layer displacement. For $x = 0.8$ and $x = 1.0$, initial
183 positions were obtained from DFT configurations optimized for $x = 1.0$; and for $x = 1.2$ and $x = 1.4$,
184 DFT configurations optimized for $x = 1.5$ were used. Owing to the replication of DFT optimized cells,
185 substitutions are regularly distributed in the super-cells used for MD simulations. When necessary,
186 layer charge was decreased by switching Al-substituted tetrahedral sites back to Si occupancy and
187 removing the associated alkyl molecule (total number of substitutions in **Table S3**). Charge
188 adjustments were performed to maintain the distribution of Al-substituted tetrahedra as regular as
189 possible.

190 MD simulations were performed using ClayFF force field for the clay model (Cygan et al., 2004)
191 whereas alkylammonium parameters were obtained from DFT calculations at the B3LYP/6-31G*
192 level performed with the Gaussian software. Alkylammonium molecules were optimized in the gas
193 phase and RESP (restrained electrostatic potential) partial atomic charges, that allow reproducing
194 the electrostatic potential of molecular boundaries, were used as molecular net charges in the force-
195 field simulations (Woods and Chappelle, 2000). The general Amber force field (Wang et al., 2004),
196 which is extensively used for organic molecules modelling and reproduces well their structure and
197 dynamics (Hobza et al., 1997; Young et al., 1997; Thyveetil et al., 2008; Swadling et al., 2013;
198 Szczerba et al., 2014; Szczerba and Kalinichev, 2016; Corbin et al., 2021), was used to generate

199 alkylammonium molecular parameters. Lorentz-Berthelot rules were applied for Lennard-Jones
200 inter force fields parameters. Amber and ClayFF force fields are rather simple to combine as they
201 both use harmonic potential for bond terms, although ClayFF does not use angle and dihedral terms.
202 This approach has already been successfully used in various theoretical studies (Thyveetil et al.,
203 2008; Swadling et al., 2010, 2013; Mignon et al., 2020; Corbin et al., 2021). Periodic boundary
204 conditions were applied in all three spatial directions.

205 The large-scale atomistic/molecular massively parallel simulator (LAMMPS – Plimpton, 1995)
206 was used for all simulations, which were performed at 300 K and 1 atm. A 12 Å cutoff was used for
207 electrostatic and Lennard-Jones interactions. Coulombic interactions were computed by Ewald
208 summation and the particle-particle-particle-mesh method at a 0.0001 accuracy. The equilibration
209 procedure consisted first in warming up the system in the NVT ensemble. The system was then
210 allowed to relax along all directions in the NPT ensemble to model the interlayer space in real
211 conditions and density. The system was then equilibrated through a two-step procedure increasing
212 time steps from 0.1 to 0.5 fs. The initial equilibration run included a total of 1,200,000 time steps. A
213 second NPT simulation was then run for 600,000 time steps during which the average d_{001} was
214 determined to be compared with experimental results. A final NVT simulation (600,000 time steps)
215 was run to compute structural data. Octahedral Mg atoms were kept fixed during all simulations by
216 imposing forces to be null. This allowed minimizing translations within the layer plane and induced
217 systematic location of Mg atoms at the origin of the unit cell (Mignon et al., 2020; Corbin et al.,
218 2021).

219

220 **3. Results and discussion**

221 *3.1 X-ray diffraction*

222 As expected for smectites hosting interlayer alkylammonium cations, positions of reflections
223 present in the XRD patterns of Sap-OH-0.8 indicated an increase of the layer-to-layer distance (LLD)
224 with increasing chain length (Figs. 1-2). For Sap-OH-0.8, two “plateaus” corresponding to LLDs of
225 ~ 13.4 and ~ 17.6 Å were observed for $n = 3-9$, and $n = 16-18$, respectively. The two “plateaus”
226 correspond to the LLDs of monolayers and bilayers of alkylammonium cations [defined as interlayer
227 h1 and h2 configurations, respectively at 13.4 and 17.6 Å by Lagaly (1994)], for which alkyl chains
228 are essentially parallel to the layer surface. Between these two plateaus, the apparent basal distance
229 increased steadily as described by Lagaly (1994). When increasing the charge density from $x=0.8$ to

230 $x = 1.0, 1.2,$ and $1.4,$ h1 and h2 configurations were observed for decreasing chain lengths (Figs. 2,
231 1, S1-S3), consistent with the basics of the method (Lagaly, 1994). A third plateau at $\sim 22 \text{ \AA}$, typical
232 for the pseudotrimolecular layers of alkylammonium cations (h3 interlayer configuration – Lagaly,
233 1994) was observed for high-charge samples and long alkylammonium chains ($x = 1.2-1.4$ and $n =$
234 $16-18$ – Figs. 2, S2-S3).

235 When plotting the full width at half-maximum intensity (FWHM) as a function of peak position,
236 three local minima were visible (Fig. 3). Minimum FWHM values were observed for apparent LLDs
237 corresponding to h1, h2, and h3 configurations. The significant increase in FWHM between these
238 three minima results from the interstratification of different stable configurations within the same
239 crystals (Méring, 1949; Moore and Reynolds, 1997; Aristilde et al., 2013), consistent with the
240 prediction of Lagaly (1994). Apparent LLDs intermediate between those of the stable configurations
241 thus correspond to the coexistence within the same crystals (interstratification) of two stable
242 configurations rather than to intermediate configurations as consistently observed for smectite
243 hydration (Ferrage et al., 2005, 2010; Ferrage, 2016) and cation/anion exchange in clays and layer
244 double hydroxides (Glaeser and Méring, 1954; Méring and Glaeser, 1954; Feng et al., 2006; Möller
245 et al., 2010; Taviot-Guého et al., 2010; Lanson, 2011 and references therein).

246 Layer charge densities deduced from the evolution of XRD peak position with alkylammonium
247 chain length increased consistently with the stoichiometry of the synthetic products. When using
248 the original equation of Lagaly (1994), experimentally determined charge densities were 0.52, 0.69,
249 0.86, and 0.88 for Sap-OH- x with $x = 0.8, 1.0, 1.2,$ and $1.4,$ respectively. As shown previously by Laird
250 et al. (1989), values deduced from the original alkylammonium method (Lagaly, 1994) are
251 systematically and significantly shifted towards lower values compared to those deduced from
252 smectite stoichiometry and may be corrected to minimize this discrepancy. When using the revised
253 equation proposed by Laird et al. (1989), layer charge densities determined using the modified
254 alkylammonium method became 0.72, 0.99, 1.28, and 1.31 for Sap-OH- x with $x = 0.8, 1.0, 1.2,$ and
255 $1.4,$ respectively. Corrected values were significantly closer to those deduced from smectite
256 stoichiometry, consistent with the conclusions of Laird et al. (1989). No significant difference was
257 observed between Sap-OH-1.2 and Sap-OH-1.4, however, possibly indicating a limited sensitivity of
258 the method for high layer charge densities.

259 3.2 DFT and MD simulations

260 In the present work, DFT simulations allowed determining interlayer configurations most
261 stable at 0 K. These optimal configurations, highly symmetrical owing to the limited system size,
262 were then used to derive initial inputs for MD simulations that allowed calculation of more realistic
263 configurations after thermalization at 300 K. As a result, layer-to-layer distances computed from
264 both DFT and MD simulations were essentially similar for a given layer charge and alkyl chain length
265 (Fig. 4b,d), although thermal expansion was noticeable. Specifically, the two computational
266 approaches used in the present study allowed describing the three stable configurations initially
267 proposed by Lagaly (h1, h2, h3 – 1994), consistent with previous computational studies (Heinz et
268 al., 2007; Liu et al., 2007).

269 3.2.1 Interlayer structure of the different stable configurations

270 Figure 4 also shows that LLDs derived from both DFT and MD simulations were close to the
271 values obtained experimentally for a given layer charge and alkyl chain length. Slightly larger LLDs
272 were systematically obtained from MD simulations compared to DFT however. Unit-cell expansion
273 most likely results from thermal motion which is implicit in MD simulations performed at 300 K,
274 compared to the initial structures optimized at 0 K in DFT calculations. Computed LLDs were also
275 consistent with those computed from classical MD simulations by Heinz et al. (2007), although
276 systematically lower (by ~ 0.50 - 1.25 Å – Fig. 4a,c), possibly as the result of different charge location
277 (tetrahedral substitutions in the present case) and of the induced contrasting undersaturation of
278 surface O atoms. In addition, the starting model used in the present study for MD simulations was
279 derived from DFT simulations optimized at 0 K and thus corresponding to minimal LLD. In their study
280 Heinz et al. (2007) compared their results with LLDs from the literature that are systematically higher
281 than those obtained experimentally in the present study. As a result, the apparent discrepancy
282 between computed and experimental values was larger in the present study although calculated
283 LLDs were lower, and closer to experimental LLDs obtained in the present work. This may be due to
284 the improved crystallinity of the synthetic smectite used in the present study that allowed
285 minimizing positional shifts of diffraction peaks related to size-broadening (Stanjek and Friedrich,
286 1986; Stanjek et al., 1992; Mermut, 1994).

287 Alkylammonium cations located in saponite interlayers were distributed with the ammonium
288 heads pointing towards layer surfaces to compensate efficiently for the layer charge deficit through
289 H-bonding (Figs. 5a, 6a, 7a, S4a, S5a). In DFT-optimized structures, ammonium NH_3^+ heads were
290 located essentially above/below the ditrigonal cavity and bound to the layer through N-H \cdots O-H and
291 N-H \cdots O-(Si,Al) H-bonds (see inset in Fig. 5b). Location of R-NH $_3^+$ head groups above the ditrigonal

292 cavity is consistent with results obtained by Heinz et al. (2007) and allows for a maximum
293 compression of the system at 0 K.

294 DFT-computed N-H••O-(Si,Al) bond lengths between H atoms of the ammonium head and
295 surface O atoms from (Si,Al)O₄ tetrahedra scattered from 1.7-1.8 Å to 1.85-1.95 Å for Al and Si
296 tetrahedra, respectively. These distances were consistent with the long N••Al distances (3.45-
297 3.55 Å) obtained from thermalized MD simulations (Fig. S6) but significantly larger than the 1.5 Å
298 reported by Heinz et al. (2007) for O••H distances, despite the shorter LLDs obtained in the present
299 study, consistent with XRD data. In the model used by Heinz et al. (2007), only octahedral
300 substitutions were considered and electrostatic forces may be over-estimated. Indeed, ammonium
301 head charges were adjusted arbitrarily to +0.7 e⁻ charge per ammonium head for all alkyl chains
302 whereas parameters DFT computed RESP charges obtained in the present study indicated lower
303 positive charges. Despite the induced longer H-bonds observed in our models compared to those
304 reported by Heinz et al. (2007), shorter LLDs were obtained for stable h1 and h2 domains, consistent
305 with experimental LLDs (Fig. 4). In addition to the position above/below the ditrigonal cavity, MD
306 simulations performed in the present study indicated that in thermalized systems ammonium heads
307 may also be located above/below Al-substituted tetrahedra leading to shorter N••O-(Si,Al)
308 distances (2.85-2.95 Å – Fig. S6), consistent with previous reports (Chen et al., 2017). This alternative
309 configuration allows for an improved local charge compensation of undersaturated surface O atoms
310 from Al-substituted tetrahedra and for an improved electrostatic stabilization but results in slightly
311 larger LLD values, as computed for thermalized systems. From the present MD simulations, this
312 configuration appeared to be favored for saponites having the lowest charge (x = 0.8 – data not
313 shown) owing to the presence of localized tetrahedral charges and to minimum steric constraints.
314 Increasing layer charge density results in a layer charge distribution that is more homogeneous and
315 in the sole location of ammonium heads above/below ditrigonal cavities thus allowing a stronger
316 steric compression in the interlayers of higher charge saponites. Although no specific simulations
317 were performed, location of ammonium heads above/below the ditrigonal cavity is thus most likely
318 favored by the presence of multiple Al-substituted tetrahedra among those defining this cavity. As
319 a consequence, such a distribution of Al-substituted tetrahedra that could result, for example, from
320 a non-homogeneous distribution of isomorphic Al-for-Si substitutions does not appear to challenge
321 the validity of the alkylammonium method which relies primarily on steric constraints. Consistently,
322 the alternative configuration of ammonium heads above/below Al-substituted tetrahedra was
323 absent from the simulations performed by Heinz et al. (2007) whatever the layer charge considered,

324 most likely as the result of the octahedral substitutions present in their clay layer that induced a
325 more diffuse undersaturation of surface oxygen, compared to saponites. Consistently, Chen et al.
326 (2017) reported only a minor contribution of ammonium heads located above/below Al-substituted
327 tetrahedra from MD simulations performed for a model equivalent to Sap-OH-1.2, although a non-
328 homogeneous distribution of tetrahedral substitutions and initial random location of
329 alkylammonium cations were assumed. The actual location of ammonium heads above Al-
330 substituted tetrahedral or ditrigonal cavities thus appears to result from the balance between local
331 charge compensation and steric hindrance.

332 Alkyl chains forming the tails of the alkylammonium cations were essentially parallel to the
333 basal surface of the 2:1 layers to optimize steric constraints. Consequently, h1 and h2 configurations
334 essentially correspond to 1 and 2 planes of C atoms from the alkyl chains bound to adjacent layers
335 as initially proposed by Lagaly (1994 – Figs. S4b, S5b). These interlayer configurations were also
336 consistent with the ones reported by Heinz et al. (2007) for stable h1 and h2 configurations
337 computed for C10 and C22 chain lengths (NH₃ head groups) and a CEC 91meq/100g (see Fig. 1a in
338 Heinz et al., 2007). Finally, MD calculations suggested that the h3 configuration proposed by Lagaly
339 (1994 – Fig. 7), included two major planes of C atoms similar to those observed for the h2
340 configuration. An intermediate and apparently less organized zone sandwiched in between these
341 two planes hosted sections of the alkyl chains that were not accommodated in the two main planes,
342 similar to the organization of interlayer H₂O molecules in highly hydrated smectites (Dazas et al.,
343 2014).

344 3.2.2. Stability domains for the different stable configurations

345 As LLDs calculated from both DFT and classical MD simulations were close to experimentally
346 determined ones, the number of carbon atoms in the alkyl chains corresponding to the experimental
347 transition from one stability domain to another also corresponded nicely to simulation results (Fig.
348 4). For example, the stability domain of the h1 configuration (apparent LLD within the 12.8-13.7 Å
349 range) extended experimentally from short chain lengths to C10, C7, C5, and C5 for x = 0.8, 1.0, 1.2,
350 and 1.4, respectively. Similar LLD values (12.8-13.7 Å – Fig. 4) were computed for the h1
351 configuration from both DFT and classical MD simulations. The decrease of the maximum (critical)
352 chain length allowing this h1 configuration with increasing layer charge density was consistent with
353 the initial model (Lagaly and Weiss, 1971; Lagaly, 1994). Except for DFT calculations that were
354 performed for x = 1.5, these chain lengths corresponded to the maximum alkyl chain length allowing
355 the h1 interlayer configuration in the simulations performed. Similarly, the shortest alkyl chains

356 leading experimentally to the h2 configuration comprised 16, 12, 9, and 9 carbon atoms for $x = 0.8$,
357 1.0, 1.2, and 1.4, respectively (Fig. 4). These chain lengths were consistent with those determined
358 using computational approaches and leading to LLDs typical for the h2 configuration. For MD
359 simulations, the LLD typical of the h2 configuration was slightly higher (18.0-18.7 Å – Fig. 4b) than
360 the distance usually reported experimentally for the h2 configuration. Similar LLDs exceeding 18.0 Å
361 were also reported by Heinz et al. (2007) for the h2 configuration. Compared to the maximum chain
362 length leading experimentally to a stable h2 configuration (18, 15, 11, and 11 C atoms for $x = 0.8$,
363 1.0, 1.2, and 1.4, respectively), the stability domain computed for the h2 configuration was extended
364 slightly towards longer alkyl chain lengths (e.g., 16-17 C atoms for $x = 1.0$), possibly as the result of
365 the larger LLD computed for this h2 configuration. The stability domain of the h2 configuration
366 computed for lower charge density extended also towards shorter alkyl chain lengths however, as
367 a LLD of 17.7 Å, consistent with this interlayer configuration was computed for $x = 0.8$ and C12 (Fig.
368 4a).

369 *3.3 Interstratification of different stable configurations and heterogeneity of layer charge density*

370 The extents of the stability domains corresponding to the stable configurations defined by
371 Lagaly and coworkers (Lagaly and Weiss, 1971; Lagaly, 1994) and of the transition zones were
372 essentially similar in both experimental and computational approaches (Fig. 4). LLD evolutions
373 within the transition zones differed strongly in both cases, however. Experimentally determined LLD
374 values increased steadily from those corresponding to one stability domain to the next one,
375 consistent with the random interstratification of different stable interlayer configurations within the
376 same crystals (Méring, 1949; Lanson, 2011 and references therein). This steady evolution is also
377 consistent with the initial definition of the method. XRD data, and more especially the observed
378 broadening of XRD maxima located between these LLDs (Fig. 3) supports such interstratification.
379 Lagaly and coworkers (Lagaly and Weiss, 1971; Lagaly, 1994) related the coexistence of different
380 interlayer configurations within a given crystal to the heterogeneity of layer charge density. The use
381 of synthetic smectites for the experimental section of the present study was expected to reduce
382 significantly this heterogeneity but no specific decrease of the extent of these intermediate domains
383 was observed compared to natural smectites (Lagaly and Weiss, 1970, 1971; Laird et al., 1989;
384 Lagaly, 1994).

385 Simulation results indicated also the existence of LLDs intermediate between those
386 corresponding to stable configurations (Fig. 4). In contrast to the experimental steady evolution

387 however, computed LLD values usually exhibited a major increase for a small increase of the alkyl
388 chain length typical of the destabilization of one configuration. The rapid LLD evolution possibly
389 results from the lower stability of configurations having LLD values intermediate between those of
390 the stable h1, h2, and h3 configurations. Similarity of experimental and computed transition
391 domains challenges however the original assumption of Lagaly concerning the origin of the
392 interstratification of different interlayer configurations since DFT and MD simulations were
393 systematically performed for homogeneous charge distributions within successive layers and within
394 a given layer. In the present theoretical calculations, the distribution of Al-for-Si substitutions was
395 periodic and thus maximized the homogeneity of layer charge distribution within the layer plane.
396 The mixture (interstratification) of Lagaly's stable configurations is thus likely energetically more
397 favorable than an intermediate configuration to "average" the interlayer space required to
398 compensate for a given layer charge density using a single alkyl chain length.

399 *3.4 Implications for the layer charge determination method using alkylammonium cations*

400 The overall consistency observed in the present study between the stability domains (in terms
401 of alkyl chain length) calculated for h1 and h2 configurations using computational approaches and
402 those determined from XRD data for smectites having well-defined layer-charge deficit confirms the
403 validity of the method that relies mainly on the extent (in terms of alkyl chain length) of these
404 stability domains. The ability of the alkylammonium method to provide layer charge densities
405 consistent with those derived from smectite structural formula was strongly improved however by
406 using the revised equation proposed by Laird et al. (1989). In the present case, layer charge densities
407 deduced from the alkylammonium method and this revised equation were 0.72, 0.99, 1.28, and 1.31
408 for Sap-OH-x with x = 0.8, 1.0, 1.2, and 1.4, respectively. Note that layer charge density values
409 obtained using the alkylammonium method may provide a more realistic description of smectite
410 properties, and in particular of their cation exchange capacity however (Kaufhold, 2006; Kaufhold
411 et al., 2011). Adequate corrections to measured cation exchange capacity values may however allow
412 improving the agreement with layer charge densities obtained using the structural formula method
413 (Środoń and McCarty, 2008).

414 The similar layer charge density values obtained for Sap_OH_1.2 and Sap_OH_1.4 challenge
415 however the ability of the alkylammonium method to accurately determine the layer charge density
416 of high-charge expandable phyllosilicates (vermiculites). For the two samples investigated, the
417 evolution of the position of the first basal reflection as a function of alkyl chain length was typical

418 for low-to-medium charge vermiculites ($x \leq 1.5$ per $O_{20}(OH)_4$), with stepwise, or wave-like, changes
419 of the apparent basal distance with alkyl chain length (Lagaly, 1994). The reduced extension of the
420 domains corresponding to stable h1 and h2 configurations possibly limits the applicability of the
421 routine alkylammonium method. The non-linearity of this evolution allows rejecting also a paraffin-
422 like configuration of alkylammonium cations in these low-to-medium charge vermiculites (Lagaly,
423 1994). Consistently, the α angle determined from a linear fit to the data ($\text{pos.} = 10.172 + 0.744 \times n$,
424 $R^2 = 0.9865$) was unrealistically low (36.2°) to allow layer-charge determination using the various
425 empirical curves proposed for high-charge vermiculites (Lagaly and Weiss, 1969; Ghabru et al., 1989;
426 Mermut, 1994). For these low-to-medium charge vermiculites ($1.2 \leq x \leq 1.5$ per $O_{20}(OH)_4$),
427 interstratification of interlayers exhibiting stable h1/h2 configurations and paraffin-like
428 configuration of alkylammonium cations thus appears as a possible alternative hypothesis for the
429 inefficiency of both methods, thus hampering the use of the alkylammonium method for such
430 expandable phyllosilicates. The stability of paraffin-like configurations for a layer charge $x = 1.5$ (per
431 $O_{20}(OH)_4$) and short alkyl chain lengths (4-5 carbons – Fig. 8) evidenced by DFT calculations supports
432 this hypothesis. The reported modification of interlayer alkylammonium configuration from h1/h2
433 to paraffin-like with increasing layer charge density may be due to contrasting ordering of
434 isomorphic substitutions in smectites and vermiculites (random and ordered distributions,
435 respectively) or to the contrasting layer charge densities. The alkylammonium method does not
436 hypothesize however on the ordering, or location, of isomorphic substitutions and Dazas et al.
437 (2015) did not evidence any direct relationship between ordering of isomorphic substitutions and
438 that of interlayer cations.

439 Finally, both DFT and MD simulations showed that even for highly homogeneous layer charge
440 densities, a significant range of carbon chain lengths allowed the presence of LLDs intermediate
441 between those of stable configurations. These intermediate distances correspond experimentally
442 to the interstratification of different stable configurations that were initially thought to be
443 characteristic of layer charge heterogeneity (Lagaly and Weiss, 1971; Lagaly, 1994). Simulations
444 show that intermediate distances, and thus interstratification of different stable configurations,
445 occur also for homogeneous layer charge distributions, thus challenging the ability of the
446 alkylammonium method to describe quantitatively layer charge distributions. Similarity of peak
447 position evolution as a function of alkylammonium chain length determined in the present study
448 from synthetic smectites with those determined from natural smectite of similar layer charge
449 supports this limitation. As a consequence, the benefice expected from the use of the complete

450 series of alkylammonium cations is vanishing. The use of simplified methods using a reduced
451 number of alkyl chain lengths (Olis et al., 1990; Mermut, 1994) is thus to be preferred as their main
452 drawback was supposed to be their inability to provide layer charge distribution (Kaufhold, 2006).

453

454 **4. Conclusion**

455 Layer-to-layer distances computed from DFT and MD simulations are consistent with those
456 determined experimentally on a series of synthetic saponites with layer charge ranging from
457 medium-charge smectite to medium-charge vermiculite over the whole range of alkyl chain length
458 considered in the present study. Despite minor differences, this consistency confirms the ability of
459 computational methods to accurately predict the organization of large organic molecules in
460 smectite interlayers and to unravel the molecular interactions ruling this organization. DFT
461 simulations allow high-precision predictions of structure models but computational costs do not
462 always allow probing a model with proper stoichiometry. By deriving DFT-optimized models of
463 similar stoichiometry, MD simulations allow describing structure models for all possible layer
464 compositions. MD simulations also implies thermalization of the system and allows probing
465 alternative configurations allowed by thermal expansion of DFT-optimized models. For example,
466 location of ammonium heads above/below Al-substituted tetrahedra is not observed in DFT
467 simulations owing to the limited interlayer space, whereas the slight increase of LLD values upon
468 thermalization allow these electrostatically-favored configurations. In addition, although LLD values
469 intermediate between those corresponding to the stable h1, h2, etc configurations described by
470 Lagaly (1994) may be computed, experimentally determined intermediate distances rather result
471 from the interstratification of different stable configurations, as proposed initially.

472 The overall consistency of computed and experimental LLD values confirms further the ability
473 of AAM to accurately determine a mean value of layer charge density consistent with smectite
474 structural formula when using the revised equations proposed by Laird et al. (1989). The validity of
475 AAM appears however limited to smectite-group minerals, that is to 2:1 phyllosilicates with layer
476 charge density ranging from ~ 0.5 to ≤ 1.2 per $O_{20}(OH)_4$. For high-charge smectite to medium-charge
477 vermiculites ($1.2 \leq x \leq 1.5$ per $O_{20}(OH)_4$), the coexistence of both stable "layered" and paraffin-like
478 configurations in phyllosilicate interlayers most likely hampers a proper use of the method. Finally,
479 the alkylammonium method is most likely unable to describe quantitatively layer charge
480 distributions even when using the complete series of alkylammonium cations thus questioning the

481 interest of the original method compared to simplified methods involving the use of a reduced
482 number of alkyl chain lengths.

483

484 **Supporting information**

485 Supporting information includes 3 Tables and 6 Figures (X-ray diffraction data and simulation
486 results)

487

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494

495 **Declaration of competing interest**

496 The authors declare that they have no known competing financial interests or personal
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498

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666

667 **Figure captions**

668 **Fig. 1.** X-ray diffraction patterns recorded on Sap-OH-08 as a function of the alkyl chain length of the
669 interlayer alkylammonium cation (expressed as the number n of carbon atoms in the alkyl
670 chain). Data were collected at 5 %RH. Dashed lines indicate the layer-to-layer distances typical
671 for monolayers and bilayers of interlayer alkylammonium cations [h1 and h2 configurations of
672 Lagaly (1994), respectively].

673 **Fig. 2.** Evolution of the position of the first experimental basal reflection as a function of the alkyl
674 chain length. Greyed zones correspond to the layer-to-layer distances typical for monolayers,
675 bilayers, and pseudotrimolecular layers of interlayer alkylammonium cations [h1, h2, and h3
676 configurations of Lagaly (1994) at ~ 13.4 , 17.6 , and 22 \AA , respectively].

677 **Fig. 3.** Evolution of the full width at half maximum intensity (FWHM) of the first low-angle
678 reflection as a function of its position. Greyed zones as in **Fig. 2.**

679 **Fig. 4.** Comparison of the position of the layer-to-layer distance as a function of the alkyl chain
680 length obtained experimentally (**Fig. 2**) with those derived from density functional theory (DFT) or
681 molecular dynamics (MD) simulations. Patterns as in **Fig. 2.**

682 **Fig. 5a** DFT optimized configuration of saponite interlayer hosting a monolayer of
683 alkylammonium cations [interlayer h1 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl
684 chain length of the interlayer alkylammonium cation: 6 carbons. Left and right, views along a and b
685 axes, respectively. Snapshots generated using Materials studio.

686 **Fig. 5b** DFT optimized configuration of saponite interlayer hosting a monolayer of
687 alkylammonium cations [interlayer h1 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl
688 chain length of the interlayer alkylammonium cation: 6 carbons. View along the c^* axis. Inset: Close-
689 up on N-H \cdots O-(Si,Al) bonding. Snapshots generated using Materials studio.

690 **Fig. 6a** DFT optimized configuration of saponite interlayer hosting a bilayer of alkylammonium
691 cations [interlayer h2 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl chain length of the
692 interlayer alkylammonium cation: 14 carbons. From top to bottom, view along the a axis. Snapshots
693 generated using Materials studio.

694 **Fig. 6b** DFT optimized configuration of saponite interlayer hosting a bilayer of alkylammonium
695 cations [interlayer h2 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl chain length of the

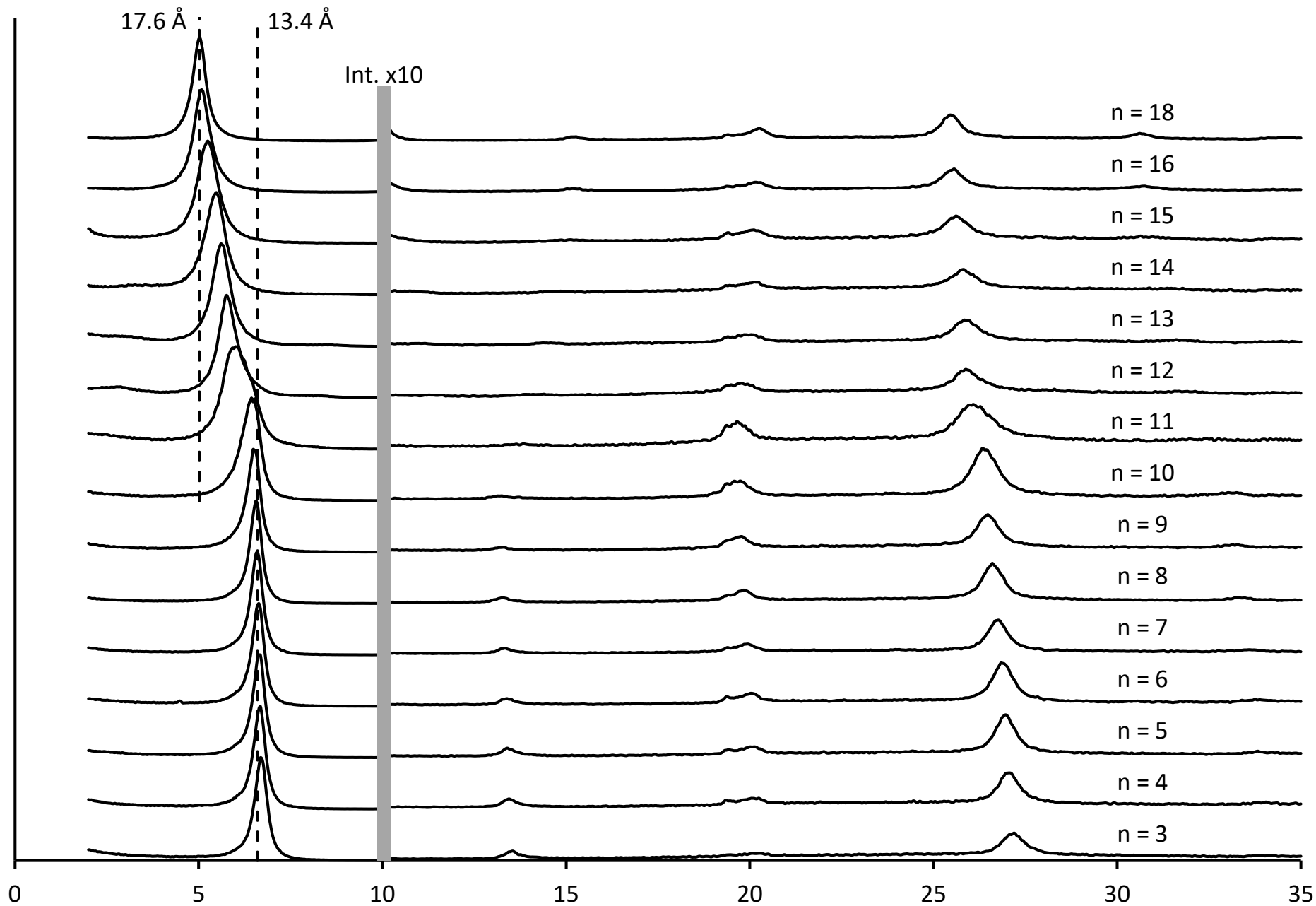
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697 Materials studio.

698 **Fig. 7** Representative MD snapshots of saponite interlayer hosting a pseudotrilinear of interlayer
699 alkylammonium cations. Layer charge: $x = 1.4$, alkyl chain length of the interlayer alkylammonium
700 cation: 12 carbons. View along the b axis.

701 **Fig. 8** DFT optimized configuration of saponite interlayer hosting alkylammonium cations in a
702 paraffin-like configuration. Layer charge: $x = 1.5$, alkyl chain length of the interlayer alkylammonium
703 cations: 4 and 5 carbons (left and right, respectively). View along the a axis. Snapshots generated
704 using Materials studio.

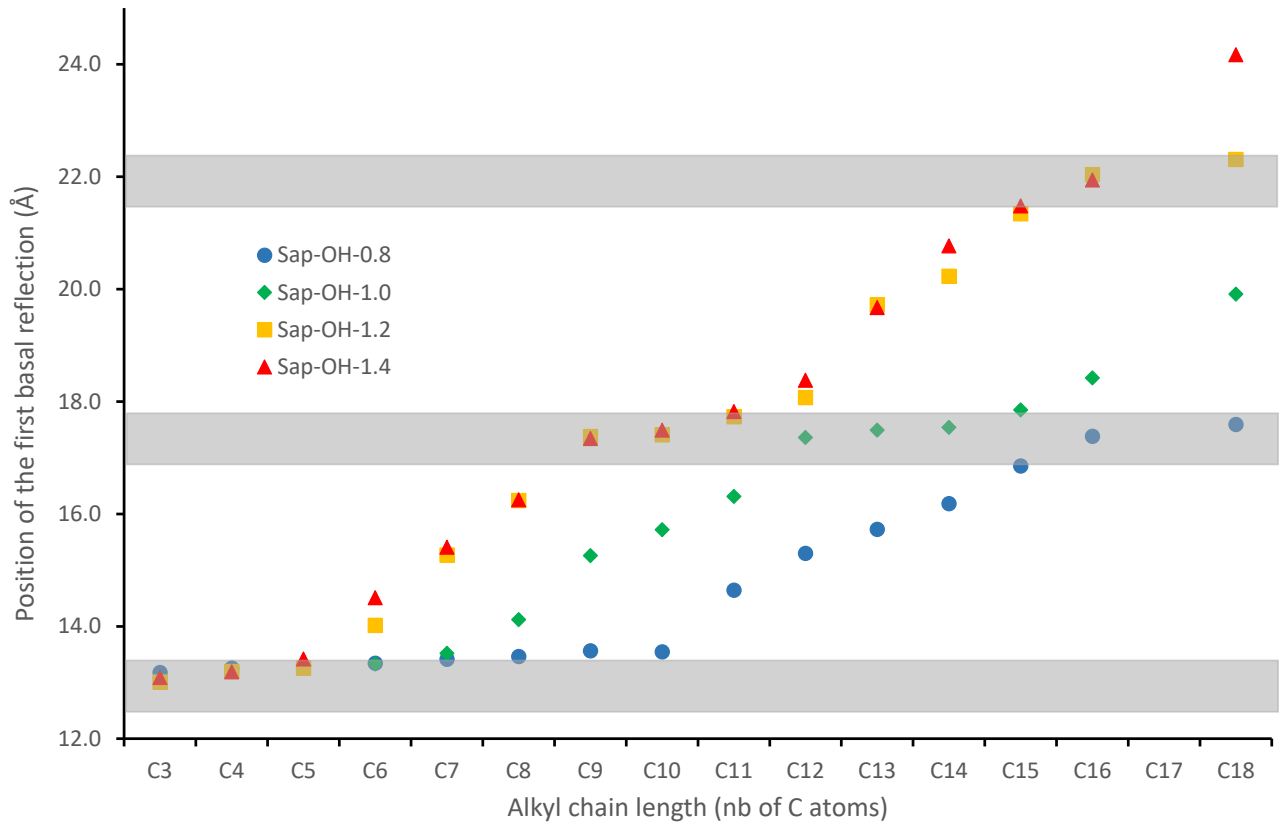
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708 monolayers and bilayers of interlayer alkylammonium cations [h1 and h2 configurations of Lagaly (1994), respectively].



710 **Fig. 2.** Evolution of the position of the first experimental basal reflection as a function of the alkyl
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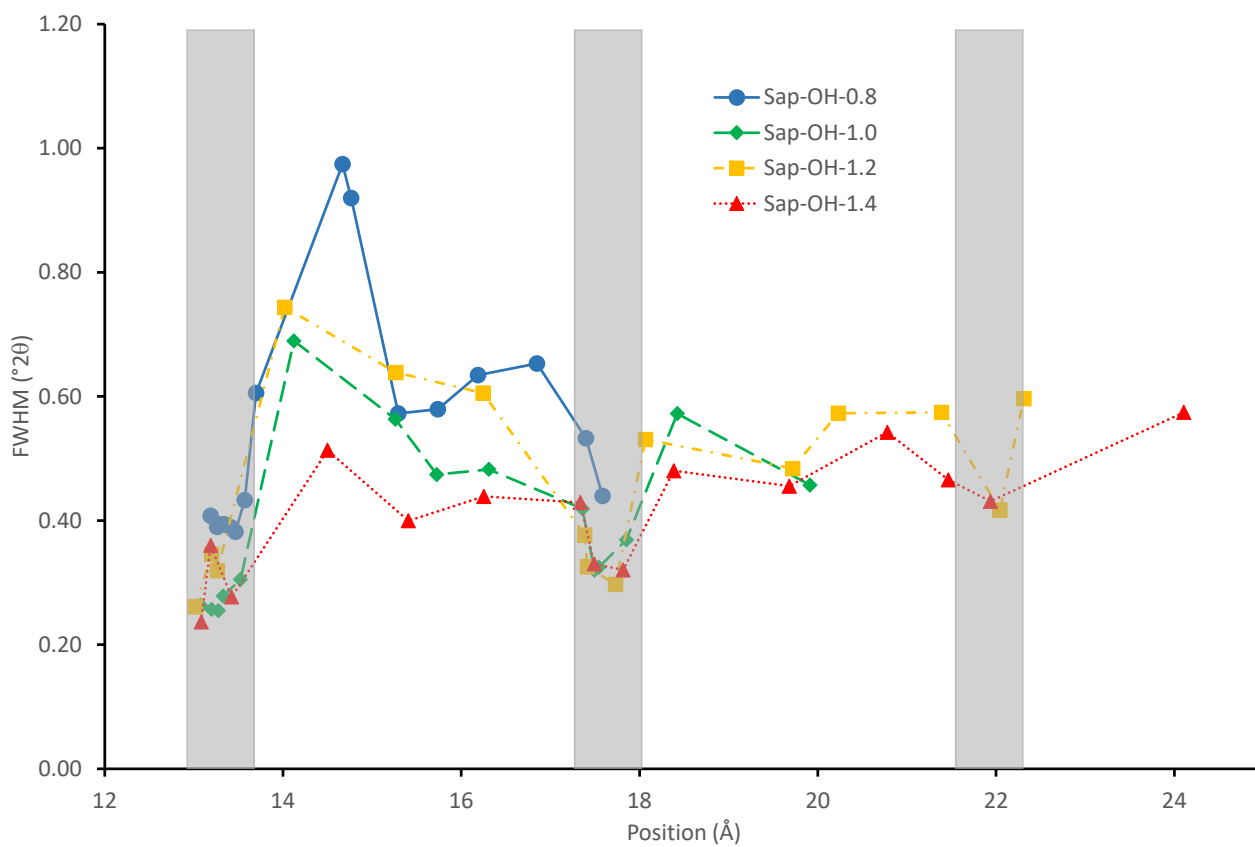
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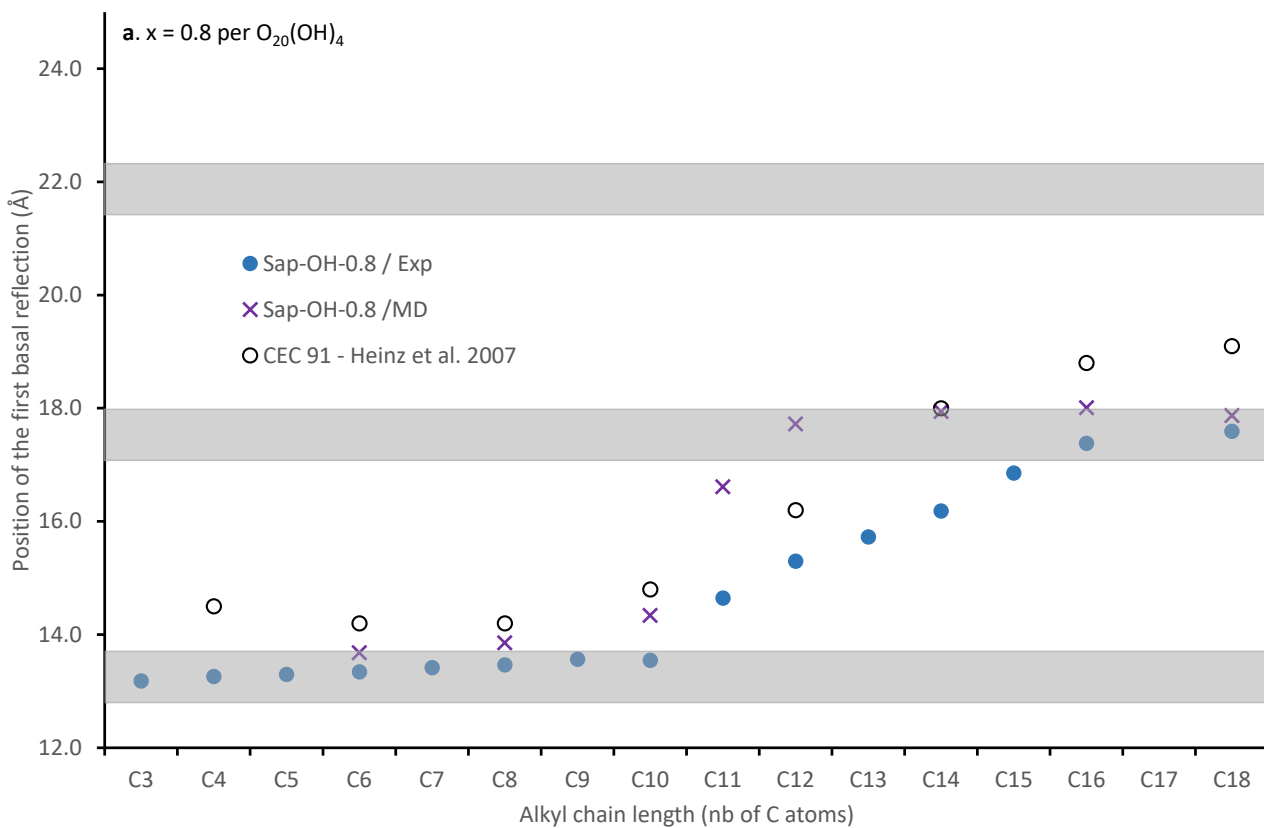
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718 reflection as a function of its position. Greyed zones as in **Fig. 2.**



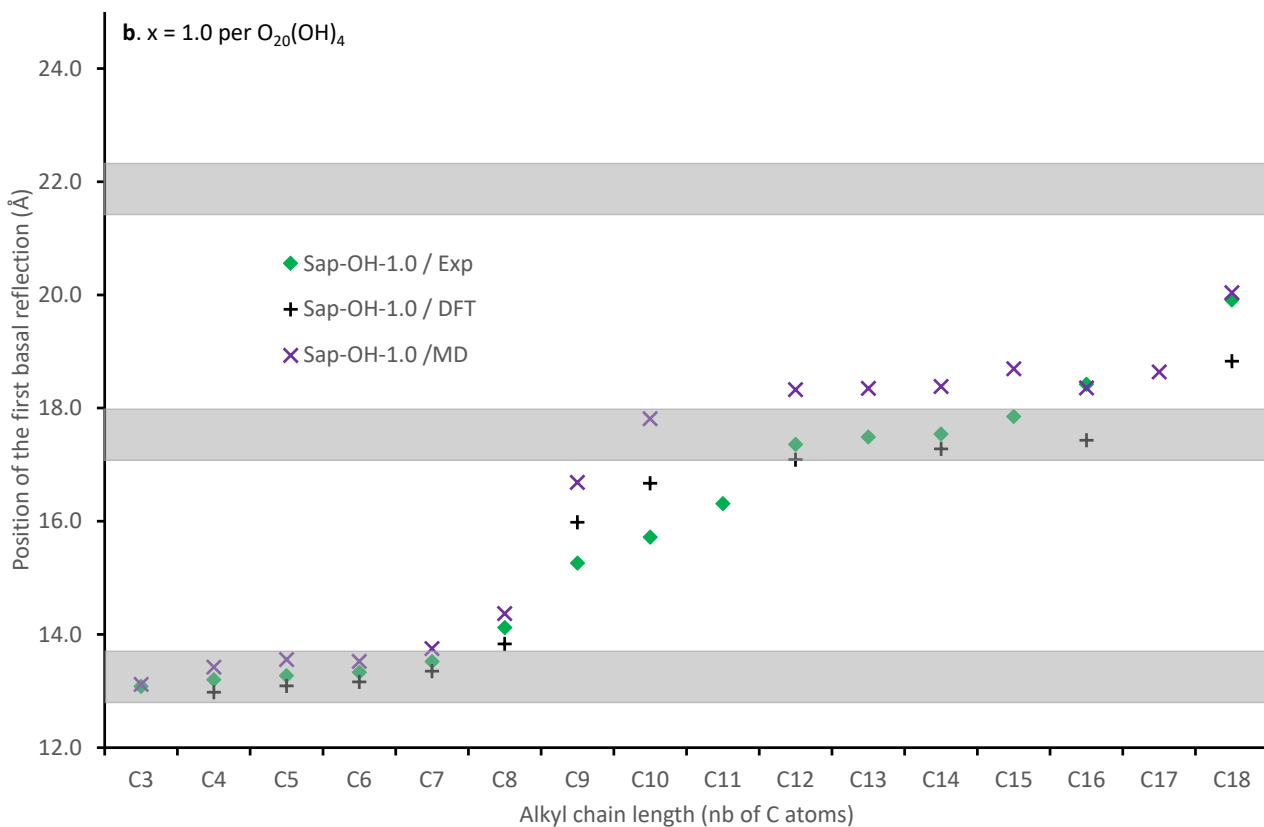
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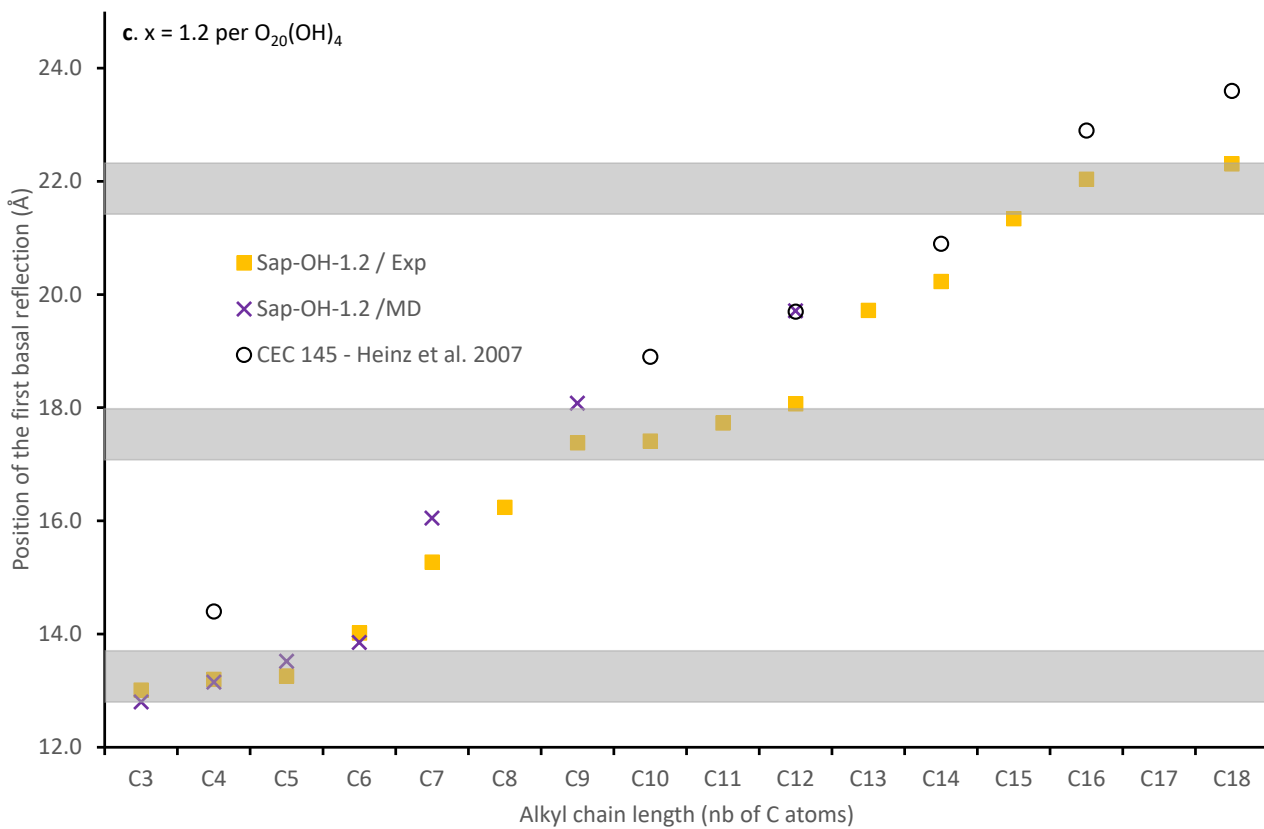
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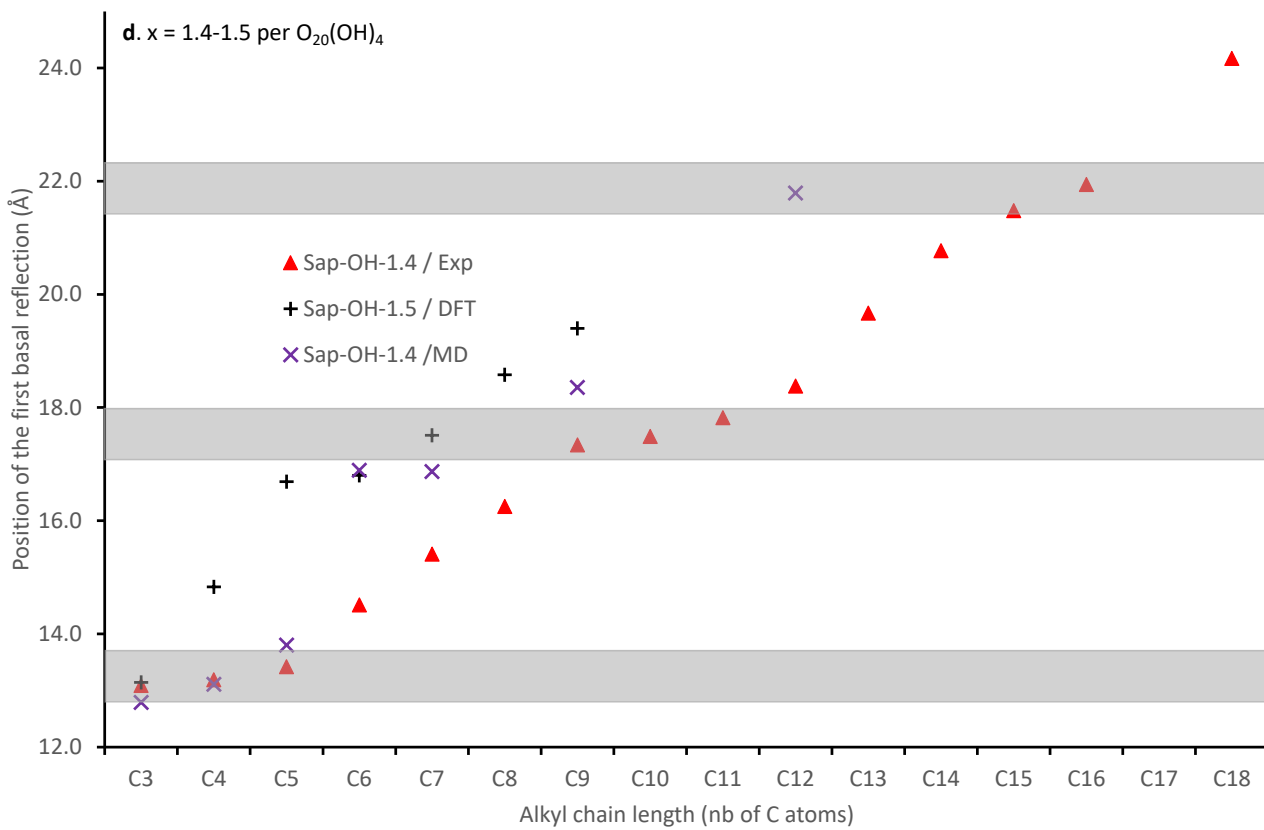
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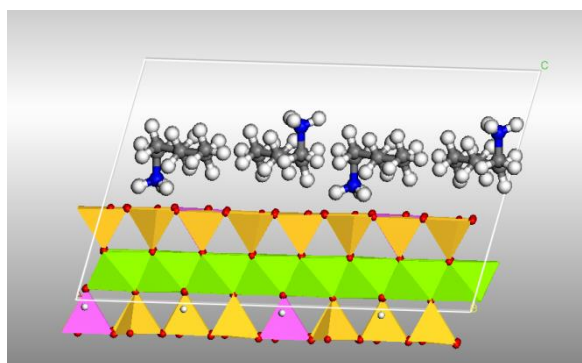
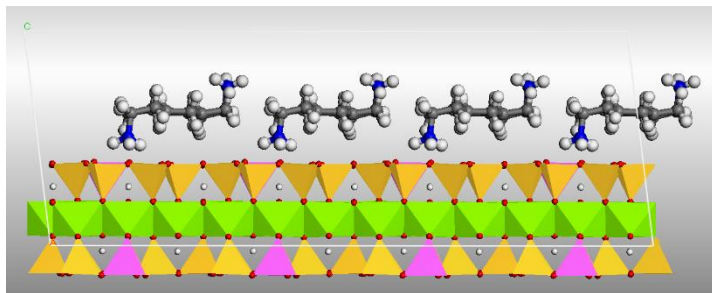
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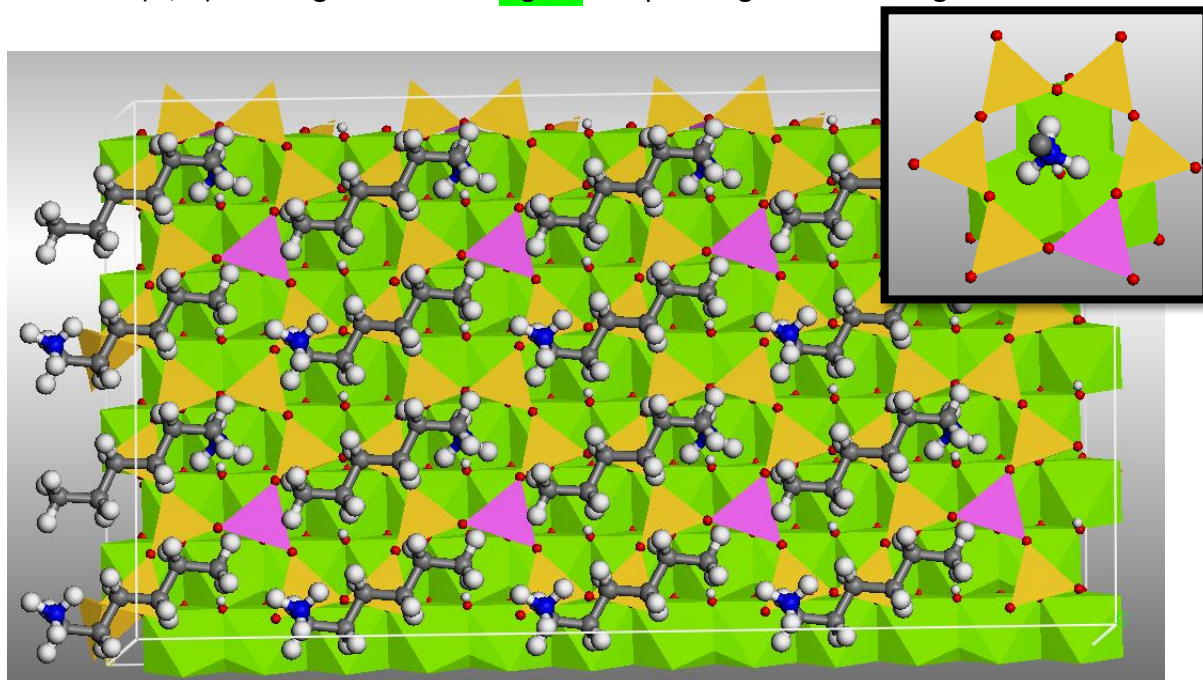
729 **Fig. 5a** DFT optimized configuration of saponite interlayer hosting a monolayer of
730 alkylammonium cations [interlayer h1 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl
731 chain length of the interlayer alkylammonium cation: 6 carbons. Left and right, views along a and b
732 axes, respectively. Si, Al, and Mg polyhedra are shown in orange, magenta, and green, respectively.
733 O, N, C, and H atoms are shown as red, blue, and dark and light grey balls, respectively. Snapshots
734 generated using Materials studio.



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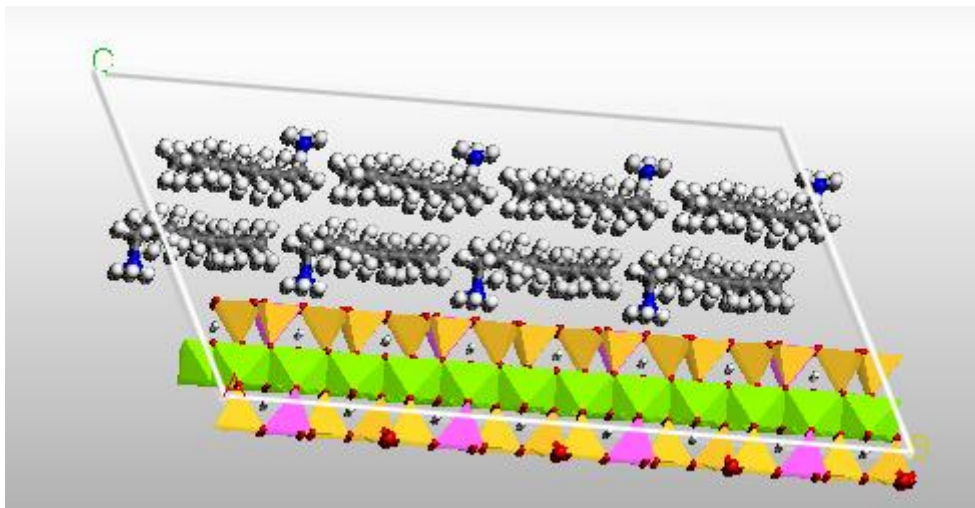
737 **Fig. 5b** DFT optimized configuration of saponite interlayer hosting a monolayer of
738 alkylammonium cations [interlayer h1 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl
739 chain length of the interlayer alkylammonium cation: 6 carbons. View along the c^* axis. Inset: Close-
740 up on N-H...O-(Si,Al) bonding. Colors as in **Fig. 5a**. Snapshots generated using Materials studio.



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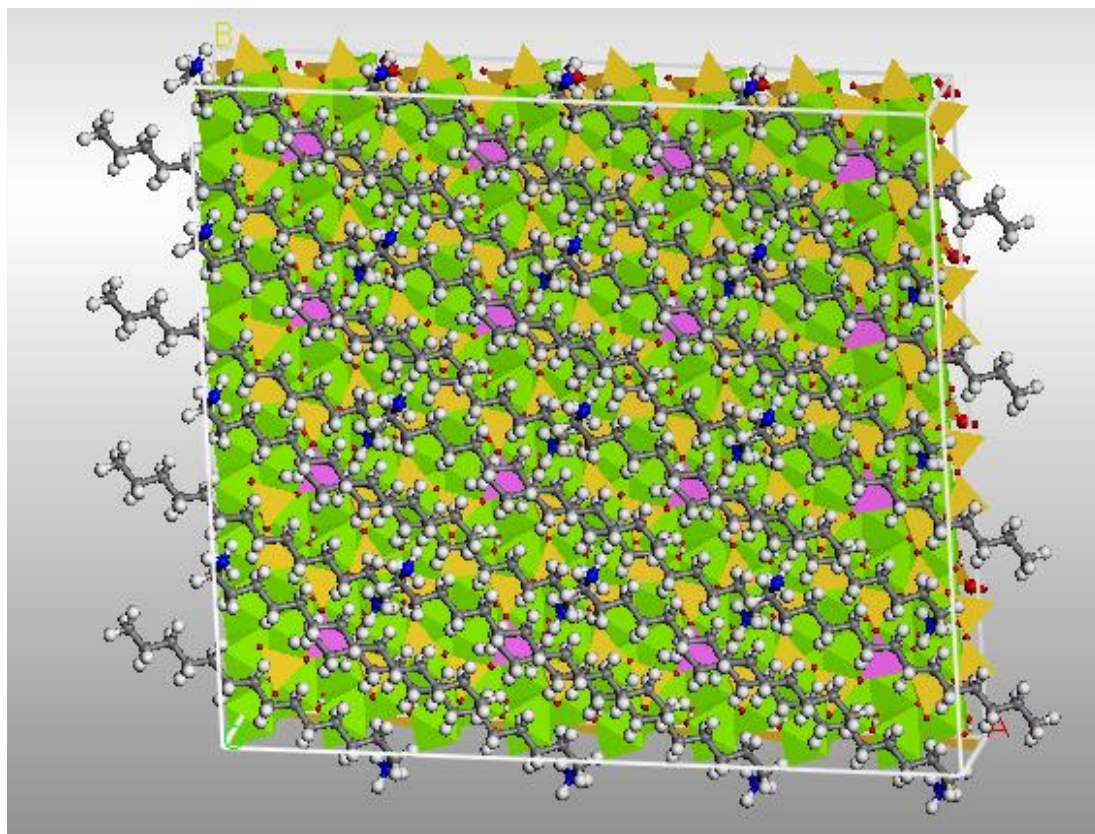
743 **Fig. 6a** DFT optimized configuration of saponite interlayer hosting a bilayer of alkylammonium
744 cations [interlayer h2 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl chain length of the
745 interlayer alkylammonium cation: 14 carbons. From top to bottom, view along the a axis. Colors as
746 in **Fig. 5a**. Snapshots generated using Materials studio.



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749 **Fig. 6b** DFT optimized configuration of saponite interlayer hosting a bilayer of alkylammonium
750 cations [interlayer h2 configuration – Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl chain length of the
751 interlayer alkylammonium cation: 14 carbons. View along the c^* axis. Colors as in **Fig. 5a**. Snapshots
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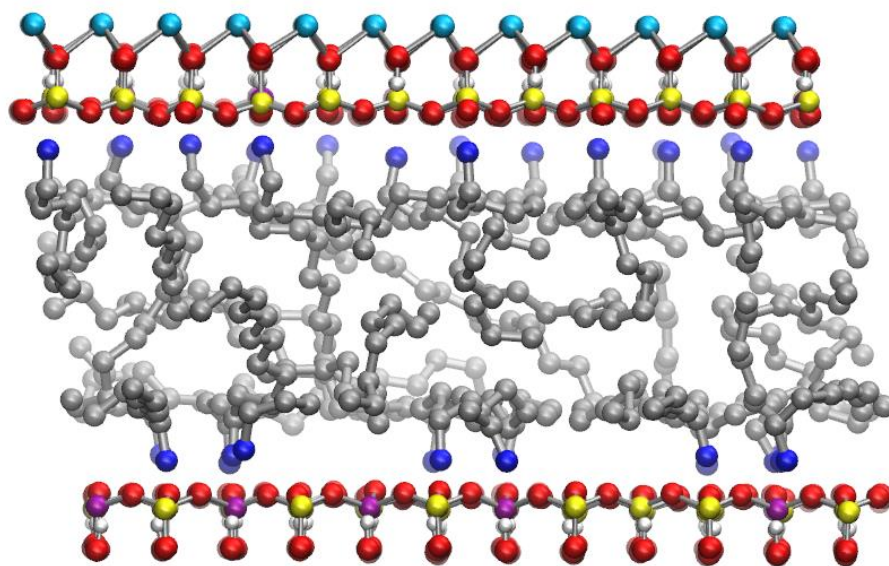


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755 **Fig. 7** Representative MD snapshots of saponite interlayer hosting a pseudotrimer of interlayer
756 alkylammonium cations. Layer charge: $x = 1.4$, alkyl chain length of the interlayer alkylammonium
757 cation: 12 carbons. View along the b axis. Si, Al, Mg, O, N, C, and H atoms are shown as yellow,
758 magenta, light blue, dark blue, dark grey, and white balls, respectively. H atoms from the
759 alkylammonium cations are not shown.

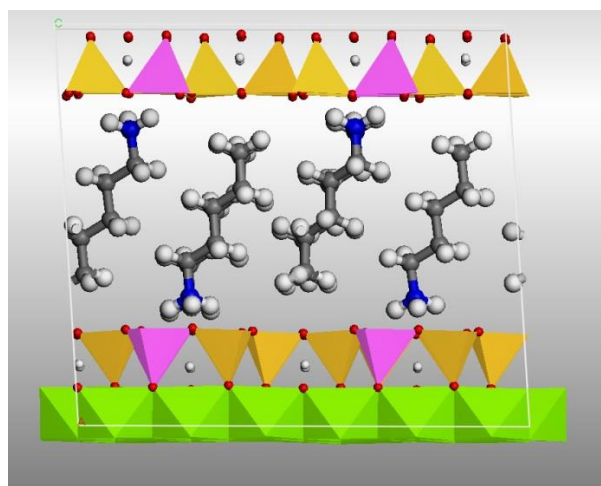
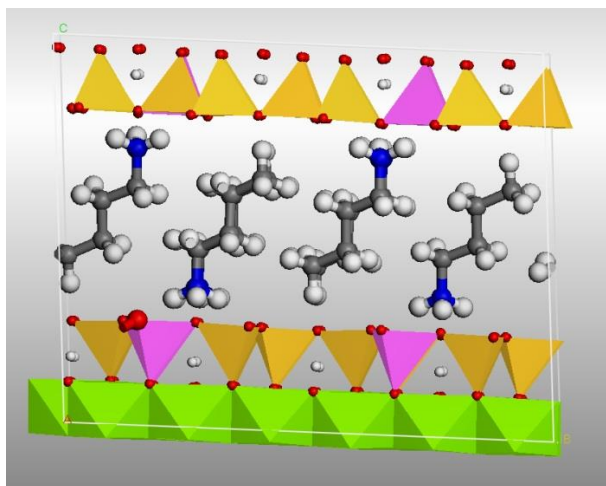
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763 **Fig. 8** DFT optimized configuration of saponite interlayer hosting alkylammonium cations in a
764 paraffin-like configuration. Layer charge: $x = 1.5$, alkyl chain length of the interlayer alkylammonium
765 cations: 4 and 5 carbons (left and right, respectively). View along the a axis. Colors as in **Fig. 5a**.
766 Snapshots generated using Materials studio.



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1 **Determination of layer charge density in expandable phyllosilicates with alkylammonium ions:**
2 **A combined experimental and theoretical assessment of the method**

3
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5 Martine Lanson^a, Nathaniel Findling^a, Carlos Perez del Valle^e

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8 Supplementary information

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22 **Table S1** Alkylamines used for the preparation of alkyl chains

Alkyl chain name	Chain length	CAS number
propylamine	3	107-10-8
butylamine	4	109-73-9
amylamine (pentylamine)	5	110-58-7
hexylamine	6	111-26-2
heptylamine	7	111-68-2
octylamine	8	111-86-4
nonylamine	9	112-20-9
decylamine	10	2016-57-1
undecylamine	11	7307-55-3
dodecylamine	12	124-22-1
tridecylamine	13	2869-34-3
tetradecylamine	14	2016-42-4
pentadecylamine	15	2570-26-5
hexadecylamine	16	143-27-1
heptadecylamine	17	-
octadecylamine	18	124-30-1

24 **Table S2** Amounts of the different chemicals used for the preparation of alkyl chains [modified and extended from Lagaly (1994)].

Length of the alkylamine chain	Mass of alkylamine (g)	Approx. volume of HCl to neutralize the solution (mL)	[HCl] used to neutralize the solution (mol/L)	Approx. Vol. of additional ethanol (mL)	Expected alkylamine final concentration (mol/L)
3	118.2	130	10.27		2.0
4	146.3	185	10.27		2.0
5	174.3	200	10.27		2.0
6	202.4	210	10.27		2.0
7	57.6	250	2		0.5
8	64.6	260	2		0.5
9	71.6	250	2		0.5
10	78.6	250	2		0.5
11	17.1	52	2		0.1
12	18.5	60	2		0.1
13	19.9		2		0.1
14	21.3	50	2	112	0.1
15	22.7	50	2	100	0.1
16	12.1	20	2	250	0.05
17	-	-	-	-	-
18	13.5	25	2	350	0.05

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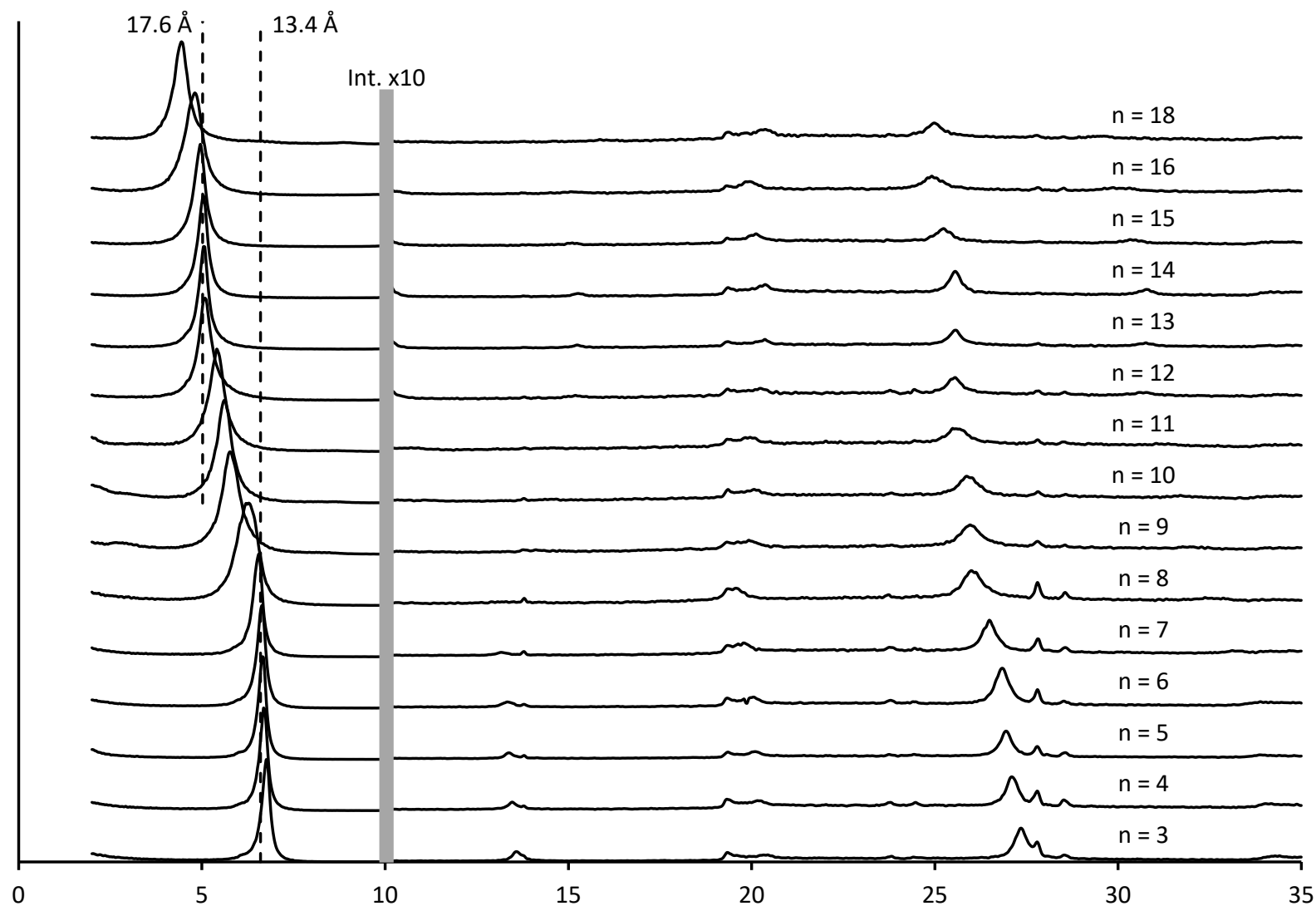
27 **TABLE S3** Details of the atomic models used for molecular dynamics simulations. Number of tetrahedral substitutions (Nb sub) in the 6a × 4b
28 super-cell used for the simulations, and resulting layer charge deficit.

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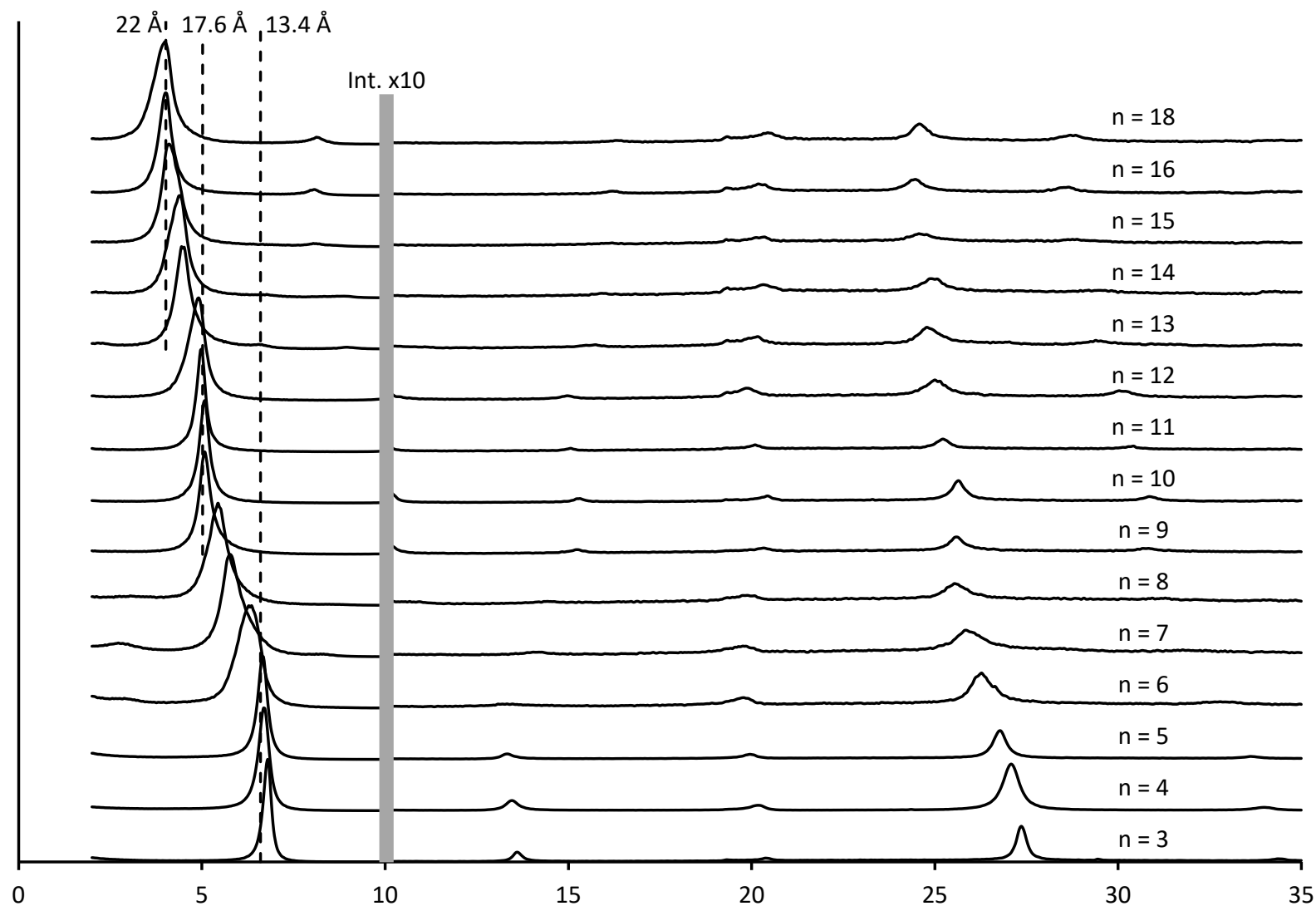
	x=0.8	x=1.0	x=1.2	x=1.4
Nb Sub	18	24	28	34
charge	0.75	1.00	1.17	1.42

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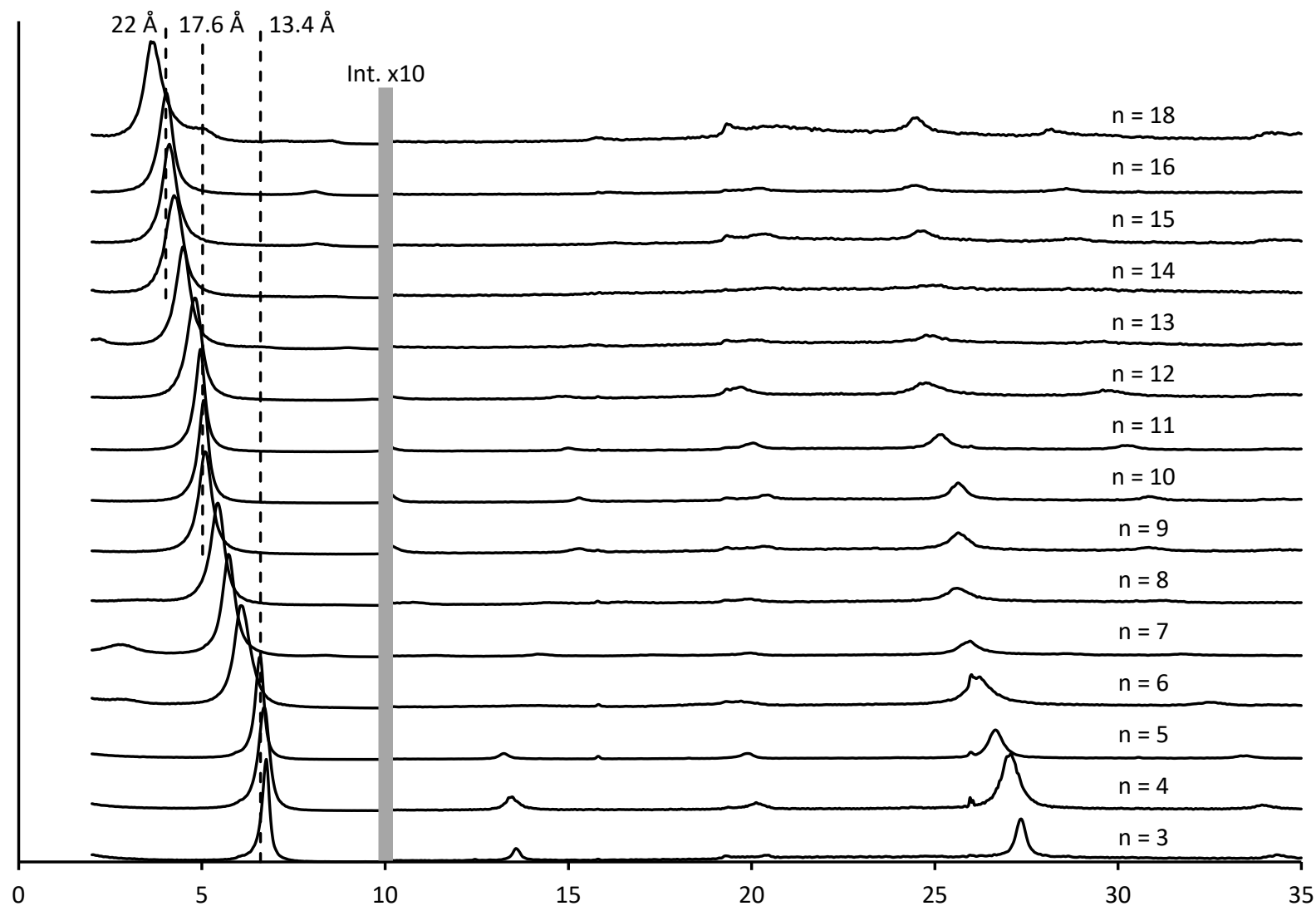
31 **Fig. S1.** X-ray diffraction patterns recorded on Sap-OH-1.0 as a function of the alkyl chain length of the interlayer alkylammonium cation (expressed
32 as the number n of carbon atoms in the alkyl chain). Data were collected at 5 %RH. Dashed lines indicate the layer-to-layer distances typical for
33 monolayers and bilayers of interlayer alkylammonium cations [h1 and h2 configurations of Lagaly (1994), respectively].



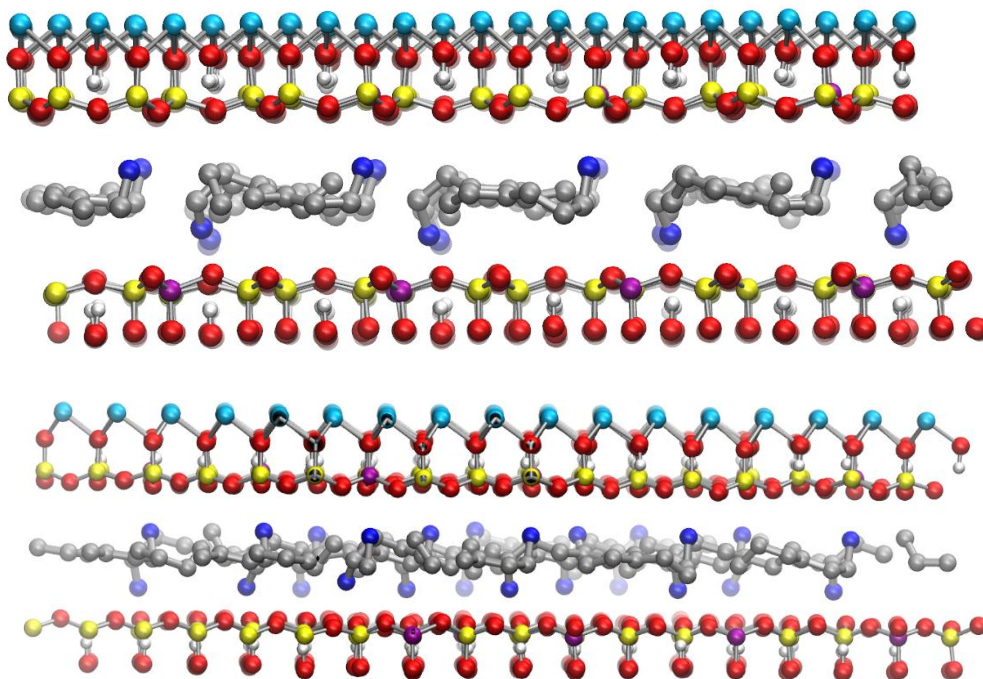
35 **Fig. S2.** X-ray diffraction patterns recorded on Sap-OH-1.2 as a function of the alkyl chain length of the interlayer alkylammonium cation (expressed
36 as the number n of carbon atoms in the alkyl chain). Data were collected at 5 %RH. Dashed lines indicate the layer-to-layer distances typical for
37 mono-, bi- and pseudo tri-layers of interlayer alkylammonium cations [h1, h2, and h3 configurations of Lagaly (1994), respectively].



39 **Fig. S3.** X-ray diffraction patterns recorded on Sap-OH-1.4 as a function of the alkyl chain length of the interlayer alkylammonium cation (expressed
40 as the number n of carbon atoms in the alkyl chain). Data were collected at 5 %RH. Dashed lines indicate the layer-to-layer distances typical for
41 mono-, bi- and pseudo tri-layers of interlayer alkylammonium cations [h1, h2, and h3 configurations of Lagaly (1994), respectively].



43 **Fig. S4a** Representative MD snapshots of alkylammonium saponite hosting a single plane of
44 interlayer alkylammonium cations [h1 configuration from Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl
45 chain length of the interlayer alkylammonium cation: 6 carbons. From top to bottom, views along a
46 and b axes, respectively. Si, Al, Mg, O, N, C, and H atoms are shown as yellow, magenta, light blue,
47 dark blue, dark grey, and white balls, respectively. H atoms from the alkylammonium cations are
48 not shown.

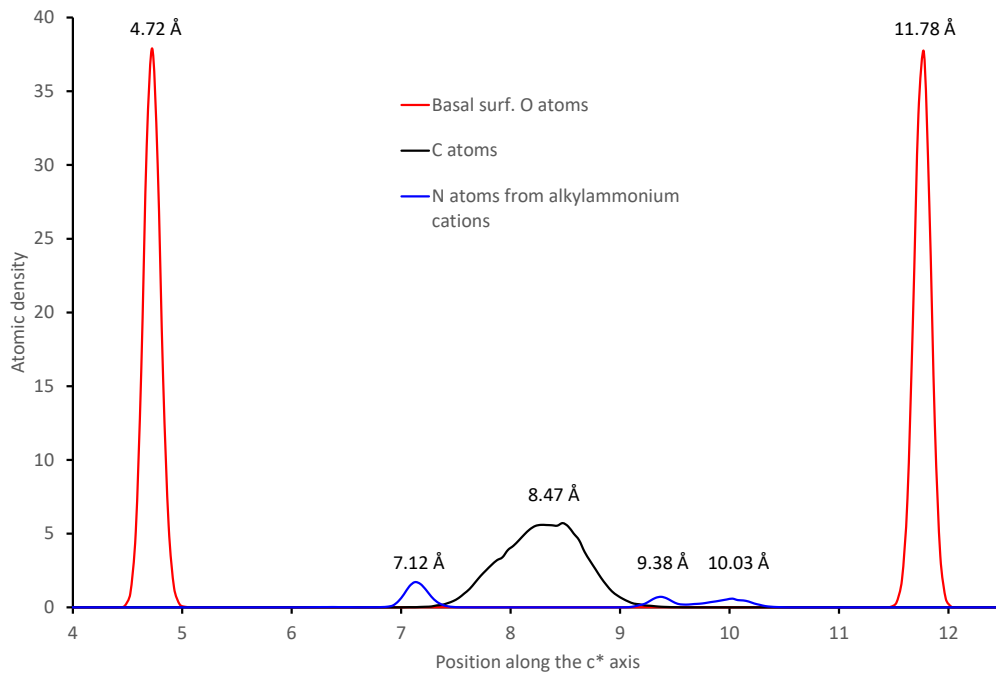


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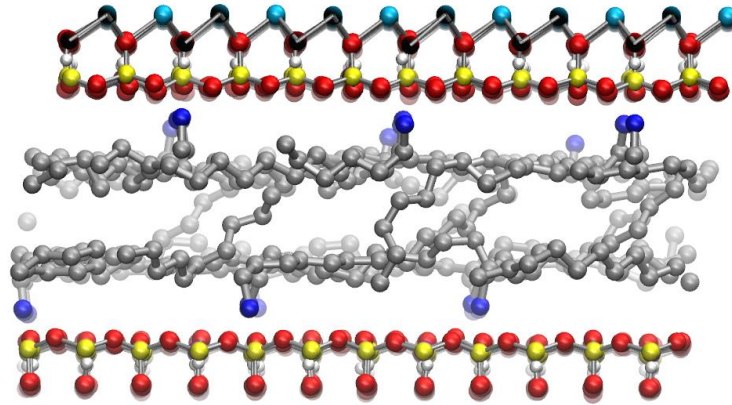
52 **Fig. S4b** Distribution of atomic density derived from MD calculations for alkylammonium saponite
53 hosting a single plane of interlayer alkylammonium cations [h1 configuration from Lagaly (1994)] in
54 projection along the c^* axis. Layer charge: $x = 0.8$, alkyl chain length : 6 carbons. Solid red, black, and
55 blue lines represent O atoms from the 2:1 layer surface and C and N atoms from the interlayer
56 alkylammonium cation, respectively.



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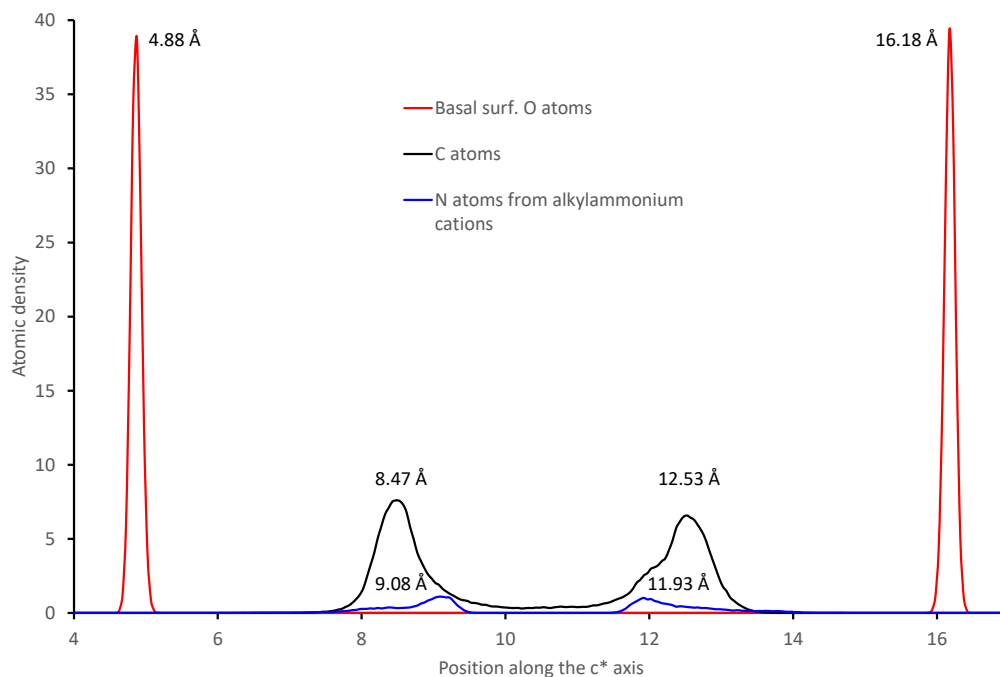
59 **Fig. S5a** Representative MD snapshots of alkylammonium saponite hosting two planes of interlayer
60 alkylammonium cations [h2 configuration from Lagaly (1994)]. Layer charge: $x = 1.0$, alkyl chain
61 length of the interlayer alkylammonium cation: 14 carbons. View along the b axis. Colors as in Fig.
62 S4a.



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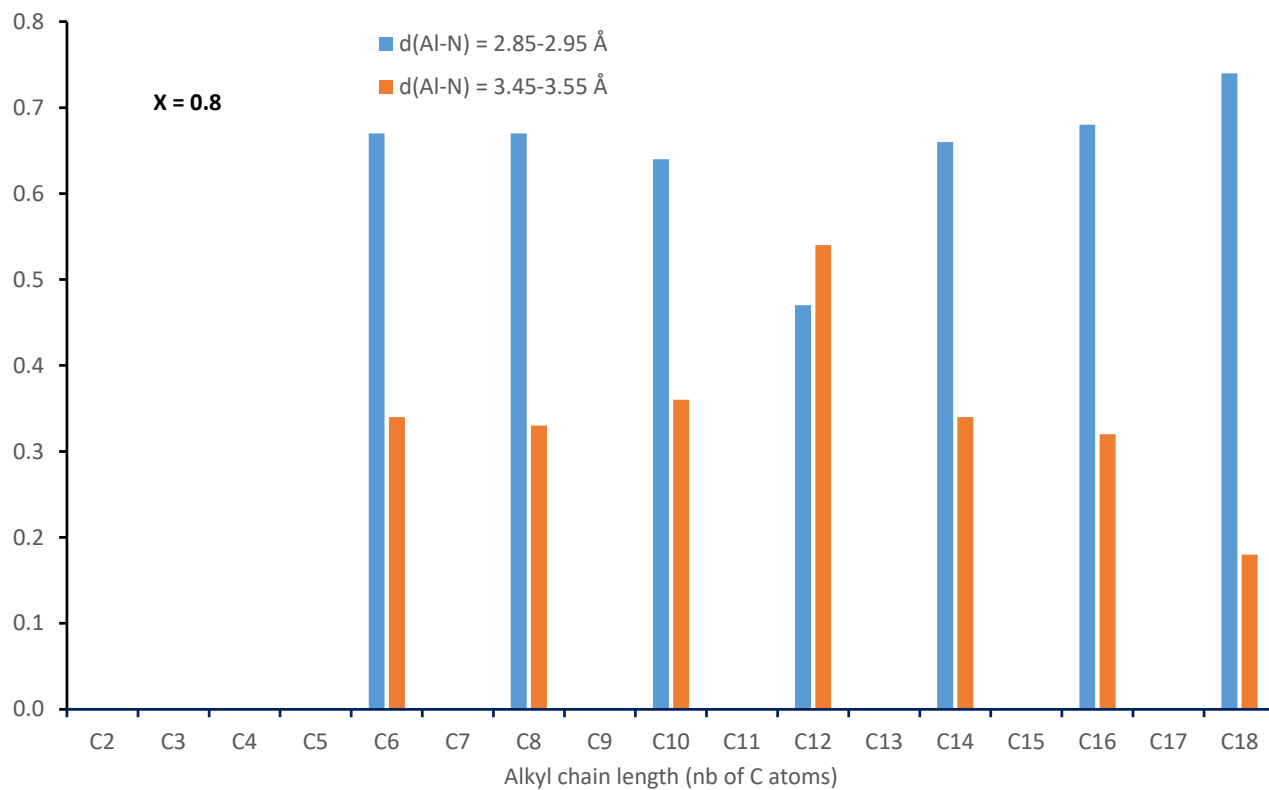
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66 hosting two planes of interlayer alkylammonium cations [h2 configuration from Lagaly (1994)] in
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68 and blue lines represent O atoms from the 2:1 layer surface and C and N atoms from the interlayer
69 alkylammonium cation, respectively.



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72 **Fig. S6** Relative proportions of ammonium heads located above Al-substituted tetrahedra and ditrigonal
73 cavities (blue and orange, respectively) determined from molecular dynamics simulations for different alkyl
74 chain lengths ($x = 0.8$).



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77 **References**

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79 characteristics of 2:1 silicate clay minerals. Clay Minerals Society, Aurora, Co, pp. 1-46.