

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

Bruno Lanson, Pierre Mignon, Mélusine Velde, Andreas Bauer, Martine

Lanson, Nathaniel Findling, Carlos Perez del Valle

## ▶ To cite this version:

Bruno Lanson, Pierre Mignon, Mélusine Velde, Andreas Bauer, Martine Lanson, et al.. Determination of layer charge density in expandable phyllosilicates with alkylammonium ions: A combined experimental and theoretical assessment of the method. Applied Clay Science, 2022, 229, pp.106665. 10.1016/j.clay.2022.106665. insu-03833511

## HAL Id: insu-03833511 https://insu.hal.science/insu-03833511

Submitted on 28 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1	Determination of layer charge density in expandable phyllosilicates with alkylammonium ions:				
2	A combined experimental and theoretical assessment of the method				
3					
4	Bruno Lanson <sup>a,*</sup> , Pierre Mignon <sup>b</sup> , Mélusine Velde <sup>a,c,d</sup> , Andreas Bauer <sup>c</sup> ,				
5	Martine Lanson <sup>a</sup> , Nathaniel Findling <sup>a</sup> , Carlos Perez del Valle <sup>e</sup>				
6					
7					
8	<sup>a</sup> Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTerre, F-				
9	38000 Grenoble, France				
10	<sup>b</sup> Univ. Lyon, Univ. Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622,				
11	Villeurbanne, France				
12	<sup>c</sup> Friedrich-Schiller-University Jena (FSU), Institute of Geosciences, Applied Geology, Burgweg				
13	11, 07749, Jena, Germany				
14	<sup>d</sup> Department of Biological Sciences, University of Chicago, USA				
15	<sup>e</sup> Univ. Grenoble Alpes, CNRS, DCM, F-38000 Grenoble, France				
16					
17	* Corresponding author: bruno.lanson@univ-grenoble-alpes.fr				
18					

#### 19 ABSTRACT

Layer charge deficit is a key crystal-chemical parameter for the classification and nomenclature of 20 2:1 phyllosilicates that also controls some of their fundamental properties such as cation exchange 21 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 composition (the structural formula method) or experimentally using the alkylammonium method, 24 25 that theoretically allows the determination of the mean layer charge density and of its distribution. In the present study density functional theory (DFT) and molecular dynamics (MD) simulations are 26 27 compared to experimental X-ray diffraction data for a series of synthetic saponites with layer charge ranging from medium-charge smectite to medium-charge vermiculite. Consistency of computed and 28 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 configurations such as the electrostatically-favored location of ammonium heads above/below Al-32 substituted tetrahedra. X-ray diffraction results showed that layer-to-layer distances intermediate 33 between those corresponding to the stable h1, h2, etc interlayer configurations described in the 34 literature result from the interstratification of different stable configurations. The overall 35 consistency of computational and experimental results confirms also the ability of the 36 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). The validity of the method appears however limited to smectite-group minerals [layer charge 39 density ranging from ~0.5 to  $\leq 1.2$  per O<sub>20</sub>(OH)<sub>4</sub>] most likely owing to the coexistence of both stable 40 "layered" and paraffin-like interlayer configurations for higher values of layer charge. In addition, 41 this consistency challenges the ability of the method to quantitatively describe distributions of layer 42 43 charge in expandable phyllosilicates even when using the complete series of alkylammonium cations. 44

#### 46 **1. Introduction**

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

60 The pivotal influence of layer charge density on properties of expandable phyllosilicates has induced significant efforts from the clay community to determine theoretically this crystal chemical 61 parameter from the smectite/vermiculite chemical composition (the so-called structural formula 62 method, SFM – Newman and Brown, 1987; Cicel and Komadel, 1994; Laird, 1994) or experimentally. 63 In this context, the so-called alkylammonium method (AAM) initially developed by Lagaly, Weiss, 64 and co-workers (Lagaly and Weiss, 1969, 1971; Lagaly, 1994) appears especially well suited, allowing 65 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 alkylammonium cations of increasing chain lengths (Lagaly, 1994). As the original method is time 68 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 the mean layer charge density. Considerable efforts have also been devoted to reconcile the results 71 72 obtained from SFM and AAM (Laird, 1994; Kaufhold, 2006; Kaufhold et al., 2011).

In parallel to the experimental AAM, molecular dynamics (MD) has been used to provide insights into the molecular-level interactions responsible for the experimentally observed changes in layer-to-layer distances as a function of alkyl chain length (Heinz et al., 2007; Liu et al., 2007). In 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 to describe the organization of large organic molecules in smectite interlayers although some 80 81 specific aspects remained unclear. The first issue is related to the underestimation of layer charge densities derived from the strict application of the AAM compared to those resulting from the SFM, 82 83 this AAM known bias challenging the consistency between computed and experimental results. A second issue is related to smectite interlayer structure in transition zones between the well-defined 84 85 configurations described by Lagaly and coworkers (Lagaly and Weiss, 1969, 1971; Lagaly, 1994). In the method description (Lagaly, 1994), layer-to-layer distances intermediate between those of the 86 87 well-defined configurations correspond to their coexistence/interstratification whereas they correspond to a unique "stable" configuration in the simulations (Heinz et al., 2007; Liu et al., 2007). 88

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  $[0.8 \text{ to } 1.4 \text{ per } O_{20}(OH)_4]$ . 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; Stanjek et al., 1992; Mermut, 1994). Simulations were performed with both density functional 94 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 set of expandable phyllosilicates with formula А а common structural  $inter[Na_x]^{oct}[Mg_6]^{tet}[S_{i8.0-x}Al_x]O_{20}(OH)_4$  and a layer charge (x) varying from 0.8 to 1.4 per O\_{20}(OH)\_4 were 101 synthesized hydrothermally from gel precursors in an externally heated Morey-type pressure vessel 102 103 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 kbar, and a duration of 4 weeks were used for synthesis. After synthesis, all samples were Na-105 saturated at room temperature by contact with 1 mol·L<sup>-1</sup> aqueous solutions of NaCl. Excess NaCl 106

was removed by rinsing the solid by immersion for 24 h in deionized water (Siemens UltraClear, 18.2
 MΩ.cm) and separation of the solid fraction by centrifugation. Resulting monomineralic synthetic
 saponites are hereafter referred to as Sap-OH-x. Previous studies of samples prepared using the
 same experimental protocols for gel preparation and synthesis supported, from nuclear magnetic
 resonance and Ar adsorption data, an homogeneous distribution of Al substitutions in saponites,
 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

Homoionic saturation of saponites with alkylammonium cations having different carbon chain 115 116 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). In brief, the required amount of alkylamine (Table S2) was weighted and stirred and dissolved in 118 119 100mL of ethanol in a 1000 mL beaker. Next, 400 mL of ultrapure water were added to the solution while maintaining the stirring, commonly leading to the formation of a precipitate. Suspension was 120 then titrated with hydrochloric acid to pH 7.0. Concentrations and approximate volumes of 121 hydrochloric acid solutions required for the titration are reported in Table S2. For short chain 122 123 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 was added; ethanol (approximate volumes listed in Table S2) was then added to the stirred 125 126 suspension to allow for a complete dissolution of the precipitate. If necessary, precipitate dissolution was enhanced by heating the suspension to ~50 °C using a water bath. When clear and 127 128 pH neutral solutions were obtained, ultrapure water was added to a final volume of 1000 mL of appropriate alkylammonium cation concentrations (Table S2). 129

#### 130 2.2.2. Smectite saturation with alkylammonium cations

Homoionic saturation of saponites with alkylammonium cations having different carbon chain lengths was performed in 10 mL Teflon tubes using ~100 mg of synthetic saponite. After addition of 2 mL of the appropriate alkylammonium solution (4 mL for chains longer than 13 C atoms), the suspension was shaken vigorously. Tubes were shaken until foam, that may contain clay particles, disappeared. Tubes were then heated to 65 °C in an oven for 24 hrs, tube caps remaining slightly open. The cation-exchanged smectites were then centrifuged and rinsed with ethanol (2 mL per rinsing step). Rinsing steps were repeated 8-10 times until the ethanol supernatant did not leave white traces when dried on a glass slide. Alkylammonium-exchanged smectites were then finally airdried 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 suspension in ethanol on glass slides. XRD patterns were then recorded using a Bruker D8 142 diffractometer equipped with a MHG Messtechnik humidity controller coupled to an Anton Paar 143 144 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 two Soller slits, the antiscatter, and resolution slits were 0.3°, 2.3°, 0.3°, and 0.1°, respectively. 146 147 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) to minimize hydration of smectite interlayers. RH was continuously monitored with a hygrometer 149 (uncertainty of  $\sim 2\%$  RH) located close to the sample. 150

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

#### 162 2.4 Density functional theory (DFT) simulations

163 Crystal models defined with general structural formula  $Mg_6S_{i8.0-x}Al_xO_{20}(OH)_4.NH_3(CH_2)_nCH_3$ , 164 x = 1.0 and 1.5, and n = 1, 2, etc were used for DFT simulations. Simulations were performed using 165 a 2a × 1b × 1c super-cell for x =1.0, and a 2a × 2b × 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 AI substitutions in saponites reported in the literature (Sanz and Robert, 1992; Michot and Villieras, 2002; Sanz et al., 2006). Periodic DFT calculations were 170 performed with the Siesta 4.0b-485 code (Soler et al., 2002) using a generalized gradient 171 172 approximation and a Perdew-Burke-Emzerhof correlation-exchange functional with a mesh cut-off of 500Ry and 6 and 9 k-points in the Monkhorst Pack grid (Hernández-Haro et al., 2016). Troullier-173 174 Martins norm-conserving pseudopotentials (Troullier and Martins, 1991) and numerical atomic orbital and double  $\xi$  plus polarization basis sets were also used for calculations. DFT methods are 175 well suited to described systems containing cations as interlayer species as the present ones 176 177 (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 O<sub>20</sub>(OH)<sub>4</sub>. Initial atomic positions for both the clay layer and interlayer were derived by replicating the DFT optimized configurations in a  $6a \times 4b \times 10^{-1}$ 181 1c super-cell, and using the DFT-optimized layer displacement. For x = 0.8 and x = 1.0, initial 182 positions were obtained from DFT configurations optimized for x = 1.0; and for x = 1.2 and x = 1.4, 183 184 DFT configurations optimized for x = 1.5 were used. Owing to the replication of DFT optimized cells, substitutions are regularly distributed in the super-cells used for MD simulations. When necessary, 185 186 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 adjustments were performed to maintain the distribution of Al-substituted tetrahedra as regular as 188 possible. 189

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

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

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

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

x = 1.0, 1.2, and 1.4, h1 and h2 configurations were observed for decreasing chain lengths (Figs. 2,1, S1-S3), consistent with the basics of the method (Lagaly, 1994). A third plateau at ~22 Å, typicalfor the pseudotrimolecular layers of alkylammonium cations (h3 interlayer configuration – Lagaly,1994) was observed for high-charge samples and long alkylammonium chains (x = 1.2-1.4 and n =16-18 – Figs. 2, S2-S3).

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

Layer charge densities deduced from the evolution of XRD peak position with alkylammonium 246 247 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 equation proposed by Laird et al. (1989), layer charge densities determined using the modified 253 254 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 stoichiometry, consistent with the conclusions of Laird et al. (1989). No significant difference was 256 observed between Sap-OH-1.2 and Sap-OH-1.4, however, possibly indicating a limited sensitivity of 257 258 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 configurations after thermalization at 300 K. As a result, layer-to-layer distances computed from 263 264 both DFT and MD simulations were essentially similar for a given layer charge and alkyl chain length (Fig. 4b,d), although thermal expansion was noticeable. Specifically, the two computational 265 266 approaches used in the present study allowed describing the three stable configurations initially proposed by Lagaly (h1, h2, h3 – 1994), consistent with previous computational studies (Heinz et 267 268 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 surface O atoms. In addition, the starting model used in the present study for MD simulations was 278 279 derived from DFT simulations optimized at 0 K and thus corresponding to minimal LLD. In their study Heinz et al. (2007) compared their results with LLDs from the literature that are systematically higher 280 281 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 the improved crystallinity of the synthetic smectite used in the present study that allowed 284 285 minimizing positional shifts of diffraction peaks related to size-broadening (Stanjek and Friedrich, 1986; Stanjek et al., 1992; Mermut, 1994). 286

Alkylammonium cations located in saponite interlayers were distributed with the ammonium heads pointing towards layer surfaces to compensate efficiently for the layer charge deficit through H-bonding (Figs. 5a, 6a, 7a, S4a, S5a). In DFT-optimized structures, ammonium  $NH_3^+$  heads were located essentially above/below the ditrigonal cavity and bound to the layer through N-H••O-H and N-H••O-(Si,Al) H-bonds (see inset in Fig. 5b). Location of R-NH<sub>3</sub><sup>+</sup> 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.

DFT-computed N-H••O-(Si,Al) bond lengths between H atoms of the ammonium head and 294 surface O atoms from (Si,Al)O<sub>4</sub> tetrahedra scattered from 1.7-1.8 Å to 1.85-1.95 Å for Al and Si 295 tetrahedra, respectively. These distances were consistent with the long N••Al distances (3.45-296 3.55 Å) obtained from thermalized MD simulations(Fig. S6) but significantly larger than the 1.5 Å 297 reported by Heinz et al. (2007) for O••H distances, despite the shorter LLDs obtained in the present 298 study, consistent with XRD data. In the model used by Heinz et al. (2007), only octahedral 299 300 substitutions were considered and electrostatic forces may be over-estimated. Indeed, ammonium head charges were adjusted arbitrarily to +0.7 e<sup>-</sup> charge per ammonium head for all alkyl chains 301 302 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 with experimental LLDs (Fig. 4). In addition to the position above/below the ditrigonal cavity, MD 305 simulations performed in the present study indicated that in thermalized systems ammonium heads 306 307 may also be located above/below Al-substituted tetrahedra leading to shorter N••O-(Si,Al) distances (2.85-2.95 Å – Fig. S6), consistent with previous reports (Chen et al., 2017). This alternative 308 309 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 shown) owing to the presence of localized tetrahedral charges and to minimum steric constraints. 313 314 Increasing layer charge density results in a layer charge distribution that is more homogeneous and in the sole location of ammonium heads above/below ditrigonal cavities thus allowing a stronger 315 316 steric compression in the interlayers of higher charge saponites. Although no specific simulations were performed, location of ammonium heads above/below the ditrigonal cavity is thus most likely 317 favored by the presence of multiple Al-substituted tetrahedra among those defining this cavity. As 318 319 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, the alternative configuration of ammonium heads above/below Al-substituted tetrahedra was 322 323 absent from the simulations performed by Heinz et al. (2007) whatever the layer charge considered,

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

332 Alkyl chains forming the tails of the alkylammonium cations were essentially parallel to the basal surface of the 2:1 layers to optimize steric constraints. Consequently, h1 and h2 configurations 333 334 essentially correspond to 1 and 2 planes of C atoms from the alkyl chains bound to adjacent layers as initially proposed by Lagaly (1994 – Figs. S4b, S5b). These interlayer configurations were also 335 consistent with the ones reported by Heinz et al. (2007) for stable h1 and h2 configurations 336 computed for C10 and C22 chain lengths (NH<sub>3</sub> head groups) and a CEC 91meq/100g (see Fig. 1a in 337 Heinz et al., 2007). Finally, MD calculations suggested that the h3 configuration proposed by Lagaly 338 (1994 – Fig. 7), included two major planes of C atoms similar to those observed for the h2 339 configuration. An intermediate and apparently less organized zone sandwiched in between these 340 341 two planes hosted sections of the alkyl chains that were not accommodated in the two main planes, 342 similar to the organization of interlayer H<sub>2</sub>O 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 determined ones, the number of carbon atoms in the alkyl chains corresponding to the experimental 346 347 transition from one stability domain to another also corresponded nicely to simulation results (Fig. 4). For example, the stability domain of the h1 configuration (apparent LLD within the 12.8-13.7 Å 348 range) extended experimentally from short chain lengths to C10, C7, C5, and C5 for x = 0.8, 1.0, 1.2, 349 and 1.4, respectively. Similar LLD values (12.8-13.7 Å – Fig. 4) were computed for the h1 350 configuration from both DFT and classical MD simulations. The decrease of the maximum (critical) 351 chain length allowing this h1 configuration with increasing layer charge density was consistent with 352 353 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, 1.0, 1.2, and 1.4, respectively (Fig. 4). These chain lengths were consistent with those determined 357 using computational approaches and leading to LLDs typical for the h2 configuration. For MD 358 simulations, the LLD typical of the h2 configuration was slightly higher (18.0-18.7 Å – Fig. 4b) than 359 the distance usually reported experimentally for the h2 configuration. Similar LLDs exceeding 18.0 Å 360 were also reported by Heinz et al. (2007) for the h2 configuration. Compared to the maximum chain 361 length leading experimentally to a stable h2 configuration (18, 15, 11, and 11 C atoms for x = 0.8, 362 1.0, 1.2, and 1.4, respectively), the stability domain computed for the h2 configuration was extended 363 364 slightly towards longer alkyl chain lengths (e.g., 16-17 C atoms for x = 1.0), possibly as the result of the larger LLD computed for this h2 configuration. The stability domain of the h2 configuration 365 computed for lower charge density extended also towards shorter alkyl chain lengths however, as 366 a LLD of 17.7 Å, consistent with this interlayer configuration was computed for x = 0.8 and C12 (Fig. 367 <mark>4a</mark>). 368

#### 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 Lagaly and coworkers (Lagaly and Weiss, 1971; Lagaly, 1994) and of the transition zones were 371 372 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 values increased steadily from those corresponding to one stability domain to the next one, 374 375 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 broadening of XRD maxima located between these LLDs (Fig. 3) supports such interstratification. 378 Lagaly and coworkers (Lagaly and Weiss, 1971; Lagaly, 1994) related the coexistence of different 379 interlayer configurations within a given crystal to the heterogeneity of layer charge density. The use 380 of synthetic smectites for the experimental section of the present study was expected to reduce 381 significantly this heterogeneity but no specific decrease of the extent of these intermediate domains 382 was observed compared to natural smectites (Lagaly and Weiss, 1970, 1971; Laird et al., 1989; 383 Lagaly, 1994). 384

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

#### 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 of alkyl chain length) calculated for h1 and h2 configurations using computational approaches and 401 402 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 consistent with those derived from smectite structural formula was strongly improved however by 405 406 using the revised equation proposed by Laird et al. (1989). In the present case, layer charge densities deduced from the alkylammonium method and this revised equation were 0.72, 0.99, 1.28, and 1.31 407 408 for Sap-OH-x with x = 0.8, 1.0, 1.2, and 1.4, respectively. Note that layer charge density values obtained using the alkylammonium method may provide a more realistic description of smectite 409 properties, and in particular of their cation exchange capacity however (Kaufhold, 2006; Kaufhold 410 et al., 2011). Adequate corrections to measured cation exchange capacity values may however allow 411 412 improving the agreement with layer charge densities obtained using the structural formula method (Środoń and McCarty, 2008). 413

The similar layer charge density values obtained for Sap\_OH\_1.2 and Sap\_OH\_1.4 challenge however the ability of the alkylammonium method to accurately determine the layer charge density of high-charge expandable phyllosilicates (vermiculites). For the two samples investigated, the 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<sub>20</sub>(OH)<sub>4</sub>), with stepwise, or wave-like, changes 419 of the apparent basal distance with alkyl chain length (Lagaly, 1994). The reduced extension of the domains corresponding to stable h1 and h2 configurations possibly limits the applicability of the 420 421 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, 1994). Consistently, the  $\alpha$  angle determined from a linear fit to the data (pos. = 10.172 + 0.744 × n, 423  $R^2 = 0.9865$ ) was unrealistically low (36.2°) to allow layer-charge determination using the various 424 425 empirical curves proposed for high-charge vermiculites (Lagaly and Weiss, 1969; Ghabru et al., 1989; Mermut, 1994). For these low-to-medium charge vermiculites  $(1.2 \le x \le 1.5 \text{ per } O_{20}(OH)_4)$ , 426 427 interstratification of interlayers exhibiting stable h1/h2 configurations and paraffin-like configuration of alkylammonium cations thus appears as a possible alternative hypothesis for the 428 429 inefficiency of both methods, thus hampering the use of the alkylammonium method for such expandable phyllosilicates. The stability of paraffin-like configurations for a layer charge x = 1.5 (per 430 O<sub>20</sub>(OH)<sub>4</sub>) and short alkyl chain lengths (4-5 carbons – Fig. 8) evidenced by DFT calculations supports 431 432 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, respectively) or to the contrasting layer charge densities. The alkylammonium method does not 435 436 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 that of interlayer cations. 438

Finally, both DFT and MD simulations showed that even for highly homogeneous layer charge 439 440 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 show that intermediate distances, and thus interstratification of different stable configurations, 444 occur also for homogeneous layer charge distributions, thus challenging the ability of the 445 alkylammonium method to describe quantitatively layer charge distributions. Similarity of peak 446 447 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

Layer-to-layer distances computed from DFT and MD simulations are consistent with those 455 determined experimentally on a series of synthetic saponites with layer charge ranging from 456 457 medium-charge smectite to medium-charge vermiculite over the whole range of alkyl chain length considered in the present study. Despite minor differences, this consistency confirms the ability of 458 459 computational methods to accurately predict the organization of large organic molecules in smectite interlayers and to unravel the molecular interactions ruling this organization. DFT 460 simulations allow high-precision predictions of structure models but computational costs do no 461 462 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 alternative configurations allowed by thermal expansion of DFT-optimized models. For example, 465 466 location of ammonium heads above/below Al-substituted tetrahedra is not observed in DFT simulations owing to the limited interlayer space, whereas the slight increase of LLD values upon 467 thermalization allow these electrostatically-favored configurations. In addition, although LLD values 468 469 intermediate between those corresponding to the stable h1, h2, etc configurations described by Lagaly (1994) may be computed, experimentally determined intermediate distances rather result 470 471 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 structural formula when using the revised equations proposed by Laird et al. (1989). The validity of 474 475 AAM appears however limited to smectite-group minerals, that is to 2:1 phyllosilicates with layer charge density ranging from ~0.5 to  $\leq$ 1.2 per O<sub>20</sub>(OH)<sub>4</sub>. For high-charge smectite to medium-charge 476 vermiculites  $(1.2 \le x \le 1.5 \text{ per } O_{20}(OH)_4)$ , the coexistence of both stable "layered" and paraffin-like 477 configurations in phyllosilicate interlayers most likely hampers a proper use of the method. Finally, 478 479 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

interest of the original method compared to simplified methods involving the use of a reducednumber 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

### 488 Acknowledgments

Part of the simulations presented in this article were performed using the Froggy platform of
the GRICAD infrastructure (https://gricad.univ-grenoble-alpes.fr), which is supported by the RhôneAlpes region (GRANT CPER07\_13 CIRA) and the Equip@Meso project (reference ANR-10-EQPX-2901) of the "Investissements d'Avenir" program supervised by the Agence Nationale pour la
Recherche. ISTerre is part of Labex OSUG@2020 (ANR10-LABX56).
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this article.

#### 499 References

- Aristilde, L., Lanson, B., Charlet, L., 2013. Interstratification Patterns from the pH-Dependent Intercalation of
   a Tetracycline Antibiotic within Montmorillonite Layers. Langmuir 29, 4492-4501.
- Bergaoui, L., Lambert, J.-F., Franck, R., Suquet, H., Robert, J.-L., 1995. Al-pillared saponites. Part 3.—Effect of
   parent clay layer charge on the intercalation—pillaring mechanism and structural properties. Journal of
   the Chemical Society, Faraday Transactions 91, 2229-2239.
- 505 Chen, C., Liu, X., Zhang, Y., Zhang, C., Lu, X., 2017. Molecular dynamics simulation of Alkylammonium-506 intercalated vermiculites. Clay Clay Miner. 65, 378-386.
- 507 Christidis, G.E., Blum, A.E., Eberl, D.D., 2006. Influence of layer charge and charge distribution of smectites 508 on the flow behaviour and swelling of bentonites. Appl. Clay Sci. 34, 125-138.
- Cicel, B., Komadel, P., 1994. Structural formulae of layer silicates, in: Amonette, J.E., Zelazny, L.W. (Eds.),
   Quantitative Methods in Soil Mineralogy. Soil Science Society of America, Madison, Wisconsin, USA.,
   pp. 114-136.
- 512 Corbin, G., Vulliet, E., Lanson, B., Rimola, A., Mignon, P., 2021. Adsorption of pharmaceuticals onto smectite 513 clay minerals: A combined experimental and theoretical study. Minerals 11, 62.
- Cygan, R.T., Liang, J.-J., Kalinichev, A.G., 2004. Molecular models of hydroxide, oxyhydroxide, and clay phases
   and the development of a general force field. J. Phys. Chem. B 108, 1255-1266.
- 516 Dazas, B., Ferrage, E., Delville, A., Lanson, B., 2014. Interlayer structure model of tri-hydrated low-charge
   517 smectite by X-ray diffraction and Monte Carlo modeling in the Grand Canonical ensemble. Amer.
   518 Mineral. 99, 1724-1735.
- Dazas, B., Lanson, B., Delville, A., Robert, J.-L., Komarneni, S., Michot, L.J., Ferrage, E., 2015. Influence of
   Tetrahedral Layer Charge on the Organization of Interlayer Water and Ions in Synthetic Na-Saturated
   Smectites. J. Phys. Chem. C 119, 4158-4172.
- 522 Dohrmann, R., 2006. Cation exchange capacity methodology I: An efficient model for the detection of 523 incorrect cation exchange capacity and exchangeable cation results. Appl. Clay Sci. 34, 31-37.
- Dohrmann, R., Kaufhold, S., Echle, W., Meyer, F.M., 1999. Beyond the methylene blue test: Introduction of
   the Cu(II)-triethylene tetramine method for smectite estimation in bentonite, Euroclay, Krakow,
   Poland, p. 76.
- Feng, Y., Williams, G.R., Leroux, F., Taviot-Guého, C., O' Hare, D., 2006. Selective anion-exchange properties
   of second-stage layered double hydroxide heterostructures. Chem. Mater. 18, 4312-4318.
- Ferrage, E., 2016. Investigation of the interlayer organization of water and ions in smectite from the
   combined use of diffraction experiments and molecular simulations: A review of methodology,
   applications, and perspectives. Clay Clay Miner. 64, 348-373.
- Ferrage, E., Lanson, B., Michot, L.J., Robert, J.L., 2010. Hydration properties and interlayer organization of
   water and ions in synthetic Na-smectite with tetrahedral layer charge. Part 1. Results from X-ray
   diffraction profile modeling. J. Phys. Chem. C 114, 4515-4526.
- Ferrage, E., Lanson, B., Sakharov, B.A., Drits, V.A., 2005. Investigation of smectite hydration properties by
   modeling experimental X-ray diffraction patterns: Part I. Montmorillonite hydration properties. Amer.
   Mineral. 90, 1358-1374.
- Ferrage, E., Lanson, B., Sakharov, B.A., Geoffroy, N., Jacquot, E., Drits, V.A., 2007. Investigation of
  dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles: Influence of layer
  charge and charge location. Amer. Mineral. 92, 1731-1743.
- 541 Ferrage, E., Sakharov, B.A., Michot, L.J., Delville, A., Bauer, A., Lanson, B., Grangeon, S., Frapper, G., Jimenez-542 Ruiz, M., Cuello, G.J., 2011. Hydration properties and interlayer organization of water and ions in

- 543 synthetic Na-smectite with tetrahedral layer charge. Part 2. Towards a precise coupling between 544 molecular simulations and diffraction data. J. Phys. Chem. C 115, 1867-1881.
- 545 Gates, W.P., Bouazza, A., Churchman, G.J., 2009. Bentonite clay keeps pollutants at bay. Elements 5, 105-546 110.
- Ghabru, S.K., Mermut, A.R., Arnaud, R.J.S., 1989. Layer-charge and cation-exchange characteristics of
   vermiculite (Weathered biotite) isolated from a gray lusivol in northeastern saskatchewan. Clay Clay
   Miner. 37, 164-172.
- 550 Glaeser, R., Méring, J., 1954. Isothermes d'hydratation des montmorillonites bi-ioniques (Ca, Na). Clay 551 Mineral Bulletin 2, 188-193.
- Guggenheim, S., Adams, J.M., Bain, D.C., Bergaya, F., Brigatti, M.F., Drits, V.A., Formoso, M.L.L., Galan, E.,
   Kogure, T., Stanjek, H., 2006. Summary of recommendations of nomenclature committees relevant to
   clay mineralogy: report of the Association Internationale pour l'Etude des Argiles (AIPEA)
   Nomenclature Committee for 2006. Clay Miner. 41, 863-877.
- Hamilton, D.L., Henderson, C.M.B., 1968. The preparation of silicate compositions by a gelling method.
   Mineral. Mag. 36, 832-838.
- Heinz, H., Vaia, R.A., Krishnamoorti, R., Farmer, B.L., 2007. Self-Assembly of Alkylammonium Chains on
   Montmorillonite: Effect of Chain Length, Head Group Structure, and Cation Exchange Capacity. Chem.
   Mater. 19, 59-68.
- Hernández-Haro, N., Muñoz-Santiburcio, D., Del Valle, C.P., Ortega-Castro, J., Sainz-Díaz, C.I., Garrido, C.J.,
   Hernández-Laguna, A., 2016. Compressibility of 2*M*<sub>1</sub> muscovite-paragonite series minerals: A
   computational study to 6 GPa. Amer. Mineral. 101, 1207-1216.
- Hobza, P., Kabeláč, M., Šponer, J., Mejzlík, P., Vondrášek, J., 1997. Performance of empirical potentials
   (AMBER, CFF95, CVFF, CHARMM, OPLS, POLTEV), semiempirical quantum chemical methods (AM1,
   MNDO/M, PM3), and ab initio Hartree–Fock method for interaction of DNA bases: Comparison with
   nonempirical beyond Hartree–Fock results. J. Comput. Chem. 18, 1136-1150.
- Jackson, M.L., 2005. Soil chemical analysis Advanced course, Revision of 2nd Edition 11th printing ed.
   Parallel Press, Univ. Wisconsin-Madison Libraries, Madison, Wi.
- Kaufhold, S., 2006. Comparison of methods for the determination of the layer charge density (LCD) of
   montmorillonites. Appl. Clay Sci. 34, 14-21.
- Kaufhold, S., Dohrmannn, R., Stucki, J.W., Anastácio, A.S., 2011. Layer charge density of smectites Closing
  the gap between the structural formula method and the alkyl ammonium method. Clay Clay Miner.
  59, 200-211.
- 575 Lagaly, G., 1981. Characterization of clays by organic compounds. Clay Miner. 16, 1-21.
- Lagaly, G., 1994. Layer charge determination by alkylammonium ions, in: Mermut, A.R. (Ed.), Layer charge
   characteristics of 2:1 silicate clay minerals. Clay Minerals Society, Aurora, Co, pp. 1-46.
- Lagaly, G., Weiss, A., 1969. Determination of the layer charge in mica type layer silicates, in: Heller, L. (Ed.),
   International Clay Conference. Israel University Press, Jerusalem, Tokyo, Japan, pp. 61-80.
- Lagaly, G., Weiss, A., 1970. Anordnung und Orientierung kationischer Tenside auf Silicatoberflächen. Kolloid Z. u. Z. Polymere 238, 485-493.
- Lagaly, G., Weiss, A., 1971. Anordnung und Orientierung kationischer Tenside auf Silicatoberflächen. Kolloid Z. u. Z. Polymere 243, 48-55.
- Laird, D.A., 1994. Evaluation of structural formulae and alkylammonium methods of determining layer
   charge, in: Mermut, A.R. (Ed.), Layer charge characteristics of 2:1 silicate clay minerals. Clay Minerals
   Society, Chantilly, Va, pp. 79-104.
- Laird, D.A., 2006. Influence of layer charge on swelling of smectites. Appl. Clay Sci. 34, 74-87.

- Laird, D.A., Scott, A.D., Fenton, T.E., 1989. Evaluation of the alkylammonium method of determining layer
   charge. Clay Clay Miner. 37, 41-46.
- Lanson, B., 2011. Modelling of X-ray diffraction profiles: Investigation of defective lamellar structure crystal
   chemistry, in: Brigatti, M.F., Mottana, A. (Eds.), Layered Mineral Structures and Their Application in
   Advanced Technologies. Mineralogical Society Great Britain & Ireland, London, pp. 151-202.
- Liu, X., Lu, X., Wang, R., Zhou, H., Xu, S., 2007. Interlayer structure and dynamics of alkylammonium intercalated smectites with and without water: A molecular dynamics study. Clay Clay Miner. 55, 554 564.
- Méring, J., 1949. L'interférence des rayons-X dans les systèmes à stratification désordonnée. Acta Crystallogr.
   2, 371-377.
- Méring, J., Glaeser, R., 1954. Sur le rôle de la valence des cations échangeables dans la montomorillonite.
   Bull. Soc. Fr. Minér. Cristallogr. 77, 519-530.
- Mermut, A.R., 1994. Problems associated with layer charge characterization of phyllosilicates, in: Mermut,
   A.R. (Ed.), Layer charge characteristics of 2:1 silicate clay minerals. Clay Minerals Society, Chantilly, Va,
   pp. 106-122.
- Michot, L.J., Villieras, F., 2002. Assessment of surface energetic heterogeneity of synthetic Na-saponites. The
   role of layer charge. Clay Miner. 37, 39-57.
- Mignon, P., Corbin, G., Le Crom, S., Marry, V., Hao, J., Daniel, I., 2020. Adsorption of nucleotides on clay
   surfaces: Effects of mineral composition, pH and solution salts. Appl. Clay Sci. 190, 105544.
- Möller, M.W., Hirsemann, D., Haarmann, F., Senker, J., Breu, J., 2010. Facile Scalable Synthesis of Rectorites.
   Chem. Mater. 22, 186-196.
- Moore, D.M., Reynolds, R.C., Jr, 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals.
   Oxford University Press, Oxford.
- Newman, A.C.D., Brown, G., 1987. The chemical constitution of clays, in: Newman, A.C.D. (Ed.), Chemistry of
   Clays and Clay Minerals. kJohn Wiley and Sons, New York, NY, USA, pp. 1-128.
- Olis, A.C., Malla, P.B., Douglas, L.A., 1990. The rapid estimation of the layer charges of 2:1 expanding clays
   from a single alkylammonium ion expansion. Clay Miner. 25, 39-50.
- Paineau, E., Bihannic, I., Baravian, C., Philippe, A.-M., Davidson, P., Levitz, P., Funari, S.S., Rochas, C., Michot,
  L.J., 2011a. Aqueous Suspensions of Natural Swelling Clay Minerals. 1. Structure and Electrostatic
  Interactions. Langmuir 27, 5562-5573.
- Paineau, E., Michot, L.J., Bihannic, I., Baravian, C., 2011b. Aqueous Suspensions of Natural Swelling Clay
   Minerals. 2. Rheological Characterization. Langmuir 27, 7806-7819.
- Plimpton, S., 1995. Fast parallel algorithms for short-range molecular dynamics. Journal of Computational
   Physics 117, 1-19.
- Robert, J.L., Beny, J.M., Della Ventura, G., Hardy, M., 1993. Fluorine in micas: Crystal-chemical control of the
   OH-F distribution between trioctahedral and dioctahedral sites. Eur. J. Mineral. 5, 7-18.
- Sanz, J., Robert, J.-L., 1992. Influence of structural factors on <sup>29</sup>Si and <sup>27</sup>Al NMR chemical shifts of
   phyllosilicates 2:1. Phys. Chem. Miner. 19, 39-45.
- Sanz, J., Robert, J.-L., Diaz, M., Sobrados, I., 2006. Influence of charge location on <sup>29</sup>Si NMR chemical shift of
   2:1 phyllosilicates. Amer. Mineral. 91, 544-550.
- Sato, T., Watanabe, T., Otsuka, R., 1992. Effects of layer charge, charge location, and energy change on
   expansion properties of dioctahedral smectites. Clay Clay Miner. 40, 103-113.
- Soler, J.M., Artacho, E., Gale, J.D., García, A., Junquera, J., Ordejón, P., Sánchez-Portal, D., 2002. The SIESTA
   method forab initioorder-Nmaterials simulation. Journal of Physics: Condensed Matter 14, 2745-2779.

- Środoń, J., McCarty, D.K., 2008. Surface area and layer charge of smectite from CEC and EGME/H2O-retention
   measurements. Clay Clay Miner. 56, 155-174.
- 634 Stanjek, H., Friedrich, R., 1986. The determination of layer charge by curve-fitting of Lorentz- and 635 Polarization-corrected X-ray diagrams. Clay Miner. 21, 183-190.
- Stanjek, H., Niederbudde, E.A., Hausler, W., 1992. Improved evaluation of layer charge of n-alkylammonium treated fine soil clays by Lorentz- and polarization-correction and curve-fitting. Clay Miner. 27, 3-19.
- Swadling, J.B., Coveney, P.V., Greenwell, H.C., 2010. Clay minerals mediate folding and regioselective
   interactions of RNA: A large-scale atomistic simulation study. J. Am. Chem. Soc. 132, 13750-13764.
- Swadling, J.B., Suter, J.L., Greenwell, H.C., Coveney, P.V., 2013. Influence of surface chemistry and charge on
   mineral–RNA interactions. Langmuir 29, 1573-1583.
- Szczerba, M., Kalinichev, A.G., 2016. Intercalation of ethylene glycol in smectites: Several molecular
   simulation models verified by X-ray diffraction data. Clay Clay Miner. 64, 488-502.
- Szczerba, M., Kłapyta, Z., Kalinichev, A., 2014. Ethylene glycol intercalation in smectites. Molecular dynamics
   simulation studies. Appl. Clay Sci. 91–92, 87-97.
- Taviot-Guého, C., Feng, Y., Faour, A., Leroux, F., 2010. Intercalation chemistry in a LDH system: anion
   exchange process and staging phenomenon investigated by means of time-resolved, *in situ* X-ray
   diffraction. Dalton Transactions 39, 5994-6005.
- Thyveetil, M.-A., Coveney, P.V., Greenwell, H.C., Suter, J.L., 2008. Computer simulation study of the structural
   stability and materials properties of DNA-intercalated layered double hydroxides. J. Am. Chem. Soc.
   130, 4742-4756.
- Troullier, N., Martins, J.L., 1991. Efficient pseudopotentials for plane-wave calculations. II. Operators for fast
   iterative diagonalization. Phys. Rev. B 43, 8861-8869.
- Vaia, R.A., Teukolsky, R.K., Giannelis, E.P., 1994. Interlayer structure and molecular environment of alkylammonium layered silicates. Chem. Mater. 6, 1017-1022.
- Vinci, D., Dazas, B., Ferrage, E., Lanson, M., Magnin, V., Findling, N., Lanson, B., 2020. Influence of layer charge
   on hydration properties of synthetic octahedrally-charged Na-saturated trioctahedral swelling
   phyllosilicates. Appl. Clay Sci. 184, 105404.
- Wang, J., Wolf, R.M., Caldwell, J.W., Kollman, P.A., Case, D.A., 2004. Development and testing of a general
   Amber force field. J. Comput. Chem. 25, 1157-1174.
- Woods, R.J., Chappelle, R., 2000. Restrained electrostatic potential atomic partial charges for condensed phase simulations of carbohydrates. Journal of Molecular Structure: THEOCHEM 527, 149-156.
- Young, M.A., Jayaram, B., Beveridge, D.L., 1997. Intrusion of Counterions into the Spine of Hydration in the
   Minor Groove of B-DNA: Fractional Occupancy of Electronegative Pockets. J. Am. Chem. Soc. 119, 59 665
   69.

#### 667 Figure captions

Fig. 1. X-ray diffraction patterns recorded on Sap-OH-08 as a function of the alkyl chain length of the
 interlayer alkylammonium cation (expressed 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 monolayers and bilayers of interlayer alkylammonium cations [h1 and h2 configurations of
 Lagaly (1994), respectively].

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

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

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

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

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

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

**Fig. 6b** DFT optimized configuration of saponite interlayer hosting a bilayer of alkylammonium cations [interlayer h2 configuration – Lagaly (1994)]. Layer charge: x = 1.0, alkyl chain length of the 696 interlayer alkylammonium cation: 14 carbons. View along the c\* axis. Snapshots generated using697 Materials studio.

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

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

Fig. 1. X-ray diffraction patterns recorded on Sap-OH-08 as a function of the alkyl chain length of the interlayer alkylammonium cation (expressed
 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
 monolayers and bilayers of interlayer alkylammonium cations [h1 and h2 configurations of Lagaly (1994), respectively].



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





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



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





C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 Alkyl chain length (nb of C atoms) C18

726

727

C4

C3

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



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



741

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



747

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



753

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

760



761

762

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





1	Determination of layer charge density in expandable phyllosilicates with alkylammonium ions:
2	A combined experimental and theoretical assessment of the method
3	
4	Bruno Lanson <sup>a,*</sup> , Pierre Mignon <sup>b</sup> , Mélusine Velde <sup>a,c,d</sup> , Andreas Bauer <sup>c</sup> ,
5	Martine Lanson <sup>a</sup> , Nathaniel Findling <sup>a</sup> , Carlos Perez del Valle <sup>e</sup>
6	
Ū	
7	
8	Supplementary information
-	
9	
10	
11	<sup>a</sup> Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTerre, F-
12	38000 Grenoble, France
13	<sup>b</sup> Univ. Lyon, Univ. Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622,
14	Villeurbanne, France
4 5	(Evidence Cabillan University Lana (ECU) Institute of Consciousors, Applied Conlegy, Duraway
15	"Friedrich-Schlier-University Jena (FSU), Institute of Geosciences, Applied Geology, Burgweg
16	11, 07749, Jena, Germany
17	<sup>d</sup> Department of Biological Sciences, University of Chicago, USA
18	Univ Grenoble Alnes CNRS DCM E-38000 Grenoble France
10	oniv. orchobic Alpes, enno, Dew, r 50000 orchobic, france
19	
20	* Corresponding author: bruno.lanson@univ-grenoble-alpes.fr
_•	
21	

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

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

Length of the alkylamine chain	Mass of alkylamine	Approx. volume of HCl to neutralize the solution	[HCl] used to neutralize the solution	Approx. Vol. of additional ethanol	Expected alkylamine final concentration
	(g)	(mL)	(mol/L)	(mL)	(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

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

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

	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	

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



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 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 mono-, bi- and pseudo tri-layers of interlayer alkylammonium cations [h1, h2, and h3 configurations of Lagaly (1994), respectively].



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
 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
 mono-, bi- and pseudo tri-layers of interlayer alkylammonium cations [h1, h2, and h3 configurations of Lagaly (1994), respectively].



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



49

50

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



57

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



Fig. S5b Distribution of atomic density derived from MD calculations for alkylammonium saponite
hosting two planes of interlayer alkylammonium cations [h2 configuration from Lagaly (1994)] in
projection along the c\* axis. Layer charge: x = 0.8, alkyl chain length: 14 carbons. Solid red, black,
and blue lines represent O atoms from the 2:1 layer surface and C and N atoms from the interlayer
alkylammonium cation, respectively.



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



## 77 References

Lagaly, G., 1994. Layer charge determination by alkylammonium ions, in: Mermut, A.R. (Ed.), Layer charge
 characteristics of 2:1 silicate clay minerals. Clay Minerals Society, Aurora, Co, pp. 1-46.