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Research paper

# Influence of layer charge on hydration properties of synthetic octahedrallycharged Na-saturated trioctahedral swelling phyllosilicates

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#### ABSTRACT

Smectite hydration impacts dynamical properties of interlayer cations and thus the transfer and fate of H<sub>2</sub>O. contaminants, and nutriments in surficial environments where this ubiquitous clay mineral is often one of the main mineral components. The influence of key crystal-chemical parameters, such as the amount of charge or the presence of fluorine, rather than hydroxyl groups, in smectite anionic framework, on hydration, organization of interlayer species, and related properties has been described for tetrahedrally substituted trioctahedral smectites (saponites). Despite the ubiquitous character of octahedrally substituted smectites, that make most of the world bentonite deposits, the influence of charge location on smectite hydration properties has not received similar attention. A set of octahedrally substituted trioctahedral smectites (hectorites) with a common structural formula  $Na_xMg_{6-x}Li_xSi_{8.0}O_{20}(OH)_4$  and a layer charge (x) varying from 0.8 to 1.6 was thus synthesized hydrothermally. The distribution of charge-compensating Na<sup>+</sup> cations and of associated H<sub>2</sub>O molecules was determined experimentally from the modeling of X-ray diffraction data obtained along water vapor desorption isotherms. Consistent distributions of charge-compensating cations and of associated H<sub>2</sub>O molecules were also computed from GCMC simulations as a function of layer charge. Interlayer H<sub>2</sub>O contents [2.5-5.5 and 8.0-10.0 H<sub>2</sub>O molecules per O<sub>20</sub>(OH)<sub>4</sub> for 1W and 2W hydrates, respectively] are similar in all Na-saturated smectite samples, independent of the location and amount of their layer charge. In contrast to synthetic saponite, for which stability of most hydrated layers was increased by increasing layer charge, the stability of synthetic hectorite hydrates is only marginally affected by layer charge. Consistently, the layer-to-layer distance of Nasaturated hectorite 2W (and 1W) layers is independent of layer charge (15.10-15.65 Å and 12.0-12.6 Å, respectively). The contrasting hydration behavior of synthetic Na-saturated saponite and hectorite is likely due to different electrostatic attraction between the 2:1 layer and interlayer cation, the charge undersaturation of O atoms at the surface of hectorite 2:1 layer being more diffuse compared to saponite. Combined with previous results on saponites, the present data and sample set provides key constraints to assess the validity of force fields simulating clay-water interactions for an unmatched variety of smectite with contrasting locations and amounts of layer charge deficits.

# 1. Introduction

Smectites are clay minerals ubiquitous in both terrestrial and marine surface environments and in sedimentary rocks where they are often one of the main mineral components. Smectite, whose TOT or 2:1 layers include two tetrahedral sheets sandwiching an octahedral one, represents the most hydrated pole of phyllosilicates and is a family name for all expandable varieties thereof. Vermiculites have a similar layer structure and differ from smectites by their higher layer charge deficit [1.2–1.8 and  $\approx 0.4–1.2$  e<sup>-</sup> per O<sub>20</sub>(OH)<sub>4</sub> in vermiculites and smectites, respectively – Guggenheim et al., 2006]. This charge contrast does not appear to induce significant modification of hydration behavior or of interlayer species distribution (Dazas et al., 2015). Both families of swelling phyllosilicates are thus hereafter jointly referred to as "smectite". Isomorphic substitutions by lower-valence cations occur in either tetrahedral or octahedral sheets and induce a permanent negative charge of the 2:1 layer, which is compensated for by the presence of hydrated cations in the interlayer space. Hydration of interlayer cations

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controls in turn smectite colloidal behavior and crystalline swelling (Mooney et al., 1952; Sato et al., 1992; Bérend et al., 1995; Boek et al., 1995; Cases et al., 1997; Young and Smith, 2000; Marry and Turq, 2003), and plays a pivotal role in the physical and chemical behaviors of surface environments and sedimentary rocks where smectite is abundant (Burst, 1969; Bouma et al., 1977; Matsuda et al., 2004; Takahashi et al., 2005; Bittelli et al., 2012). More specifically, smectite hydration strongly impacts dynamical properties of interlayer cations and thus the transfer and fate of H<sub>2</sub>O, contaminants, and nutriments (Malikova et al., 2006, 2007, 2010; Marry et al., 2011; Tertre et al., 2011a, 2011b; Michot et al., 2012), but also smectite ability to produce nanocomposites for a variety of applications (Fowden et al., 1983; Sinha Ray and Okamoto, 2003; Pavlidou and Papaspyrides, 2008; Guo et al., 2018).

The stepwise expansion of the layer-to-layer distance with increasing water activity has long been reported in the literature as the intercalation of 1, 2, and, less frequently, 3 planes of H<sub>2</sub>O molecules in smectite interlayers, leading to the well-known 1W  $(d_{001} = 11.6-12.9 \text{ Å}), 2W (d_{001} = 14.9-15.7 \text{ Å}), and$ 3W  $(d_{001} = 18-19 \text{ Å})$  hydration states, in addition to the dehydrated one (0W, d<sub>001</sub> = 9.6–10.2 Å – Nagelschmidt, 1936; Bradley et al., 1937; Mooney et al., 1952; Norrish, 1954; Walker, 1956) As reported in the early work of Hendricks, the continuous change of the apparent layerto-layer distance actually arises from the random occurrence of these different hydration states interstratified in smectite crystallites (Hendricks, 1938). XRD profile modeling procedures were thus developed to quantify smectite hydration heterogeneity as a function of relative humidity (Cases et al., 1992, 1997; Bérend et al., 1995). By fitting positions and profiles of 00l reflections over a large angular range, relative proportions of the different layer types can be determined together with the basal distance and water content of the different layer types (Ferrage et al., 2005b; Ferrage, 2016). This approach was used to determine the influence of the amount of charge, a key crystal-chemical parameter, in tetrahedrally substituted trioctahedral smectites (saponites) on their hydration behavior, the organization of their interlayer species, and related properties (Ferrage et al., 2010, 2011; Jimenez-Ruiz et al., 2012; Michot et al., 2012; Dazas et al., 2015). The presence of fluorine, rather than hydroxyl groups, in smectite anionic framework and its influence on hydration was also studied in both synthetic saponite and hectorite (Dazas et al., 2013). The much lower contents of interlayer H<sub>2</sub>O molecules in the latter varieties reported in these studies challenged the analogy between hydroxylated and fluorinated varieties. The contrast is enhanced for 2W hydrates [2.8–6.8 H<sub>2</sub>O molecules per O<sub>20</sub>(OH)<sub>4</sub> in fluorinated varieties compared to 8.0-10.0 in hydroxylated ones - Dazas et al., 2013, 2015] thus limiting the presence of interlayer H<sub>2</sub>O molecules to the cation hydration sphere.

Location of the layer charge deficit in the tetrahedral or octahedral sheets of the 2:1 layer is another key structural parameter whose influence on smectite hydration has been insufficiently described despite the ubiquitous character of octahedrally substituted smectites, that make most of the world bentonite deposits (Kaufhold et al., 2002; Christidis and Huff, 2009). Natural tetrahedrally and octahedrally charged smectites display indeed contrasting hydration behavior, the former exhibiting higher hydration heterogeneity (Ferrage et al., 2005b, 2007). To avoid a possible bias linked to the formation conditions of natural samples, the present study aimed at characterizing the hydration of hectorite, an octahedrally substituted trioctahedral smectite, using synthetic compounds obtained under the same conditions as previously studied saponites (Ferrage et al., 2010; Dazas et al., 2015). Specifically, interlayer H<sub>2</sub>O contents were determined for a set of four synthetic Na-saturated smectites with layer charges ranging from  $\approx 0.8-1.6 \text{ e}^-$  per O<sub>20</sub>(OH)<sub>4</sub> using H<sub>2</sub>O vapor (de)sorption isotherms. The relative proportions of the different smectite hydrates and the distribution of H<sub>2</sub>O molecules and charge-compensating Na<sup>+</sup> cations

within smectite interlayers were then determined from X-ray diffraction profile modeling for all smectites along the H<sub>2</sub>O vapor desorption isotherm. Hectorite hydration was determined as a function of the octahedral layer charge and compared to that of saponite samples having similar amounts of layer charge, and similar interlayer cation. Finally, Monte Carlo simulations were performed in the Grand Canonical ensemble to account for the respective distributions of interlayer species in both octahedrally and tetrahedrally substituted Na-saturated smectites (hectorites and saponites, respectively) over a wide compositional range.

# 2. Materials and methods

# 2.1. Sample preparation

Hectorites with a common structural formula NaxMg6-<sub>x</sub>Li<sub>x</sub>Si<sub>8.0</sub>O<sub>20</sub>(OH)<sub>4</sub> and a layer charge (x) varying from 0.8 to 1.6 were synthesized hydrothermally from gel precursors prepared from solid Na<sub>2</sub>NO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> carbonates, MgNO<sub>3</sub> solution, and TEOS as sources of Na, Li, Mg, and Si, respectively (Hamilton and Henderson, 1968). Syntheses were performed for 4 weeks at a temperature of 400 °C and a water pressure of 1 kbar in an externally heated Morey-type pressure vessel with an internal silver tubing, starting from  $\approx 2.5$  g of gel and  $\approx$  33 mL H<sub>2</sub>O to reach the required pressure. Synthesized hectorites are hereafter referred to as Hect-OH-x, x being the amount of layer charge deficit per O<sub>20</sub>(OH)<sub>4</sub>. Layer charge of synthesized smectites was assessed from the stoichiometry of gel precursors, after verifying the absence of impurity in the reaction products by X-ray diffraction (XRD). After synthesis, all samples were Na-saturated by being shaken mechanically in a 1 mol  $L^{-1}$  aqueous solution of NaCl ( $\approx 3.0$  g of synthesized smectite in  $\approx 250$  mL of solution) for 24 h before separation of the solid fraction by centrifugation ( $\approx 15,000 \times g$  for 20 min). NaCl remaining in excess was then removed by rinsing the solid three times for 24 h in deionized water (Siemens UltraClear, 18.2 M $\Omega$  cm<sup>-1</sup>). Finally, the solid fraction was recovered by centrifugation.

# 2.2. Experimental sample characterization

Water vapor sorption isotherms were collected volumetrically at 25 °C on hectorite powders using a BELSORP-max instrument from BEL Japan. Lyophilized hectorite aliquots (≈100 mg) were initially outgassed at 150 °C for 24 h under a residual pressure of  $10^{-5}$ – $10^{-4}$  Pa. Specific surface area was determined for all Na-saturated samples using the same instrument and the BET method (Table S1). For all samples, oriented slides were prepared by pipetting an aqueous clay suspension on glass slides and drying it at room temperature. The amount of deposited material was systematically weighed ( $\approx$ 4.0–10.0 mg cm<sup>-2</sup>). XRD patterns were then recorded using a Bruker D8 diffractometer operated at 40 kV and 40 mA and equipped with a MHG Messtechnik humidity controller coupled to an Anton Paar CHC+ chamber. Intensities were measured with a SolXE Si(Li) solid-state detector (Baltic Scientific Instruments) for 6 s per  $0.04^{\circ}2\theta$  step over the 2–50°2 $\theta$ Cu Ka angular range. Divergence slit, the two Soller slits, the antiscatter, and resolution slits were 0.3°, 2.3°, 0.3°, and 0.1°, respectively. Samples were kept at 23 °C in the CHC+ chamber during data collection, whereas the desired relative humidity (RH) value was maintained by using a constant flow of mixed dry/saturated air. RH was continuously monitored with a hygrometer (uncertainty of  $\approx 2\%$  RH) located close to the sample along the whole isotherm. Samples were first equilibrated at  $\approx$  95% RH for 6–12 h before starting data collection. Along the desorption isotherm, samples were then equilibrated for 2 h at each new RH value before collecting XRD data, hydration stability being systematically checked by recording again the low-angle reflection after collection of a complete XRD pattern.

#### 2.3. XRD profile modeling

The algorithms developed initially by Drits, Sakharov, and coworkers (Drits and Sakharov, 1976; Drits and Tchoubar, 1990; Sakharov and Lanson, 2013) were used to fit experimental XRD profiles using a trial-and-error approach. This approach relies on a user-driven optimization of a structure model to fit XRD data. Although it precludes taking into account correlations between parameters, owing to the lack of covariance matrix calculation, this approach has proven successful for the structural characterization of defective and interstratified lamellar structures (Drits and Tchoubar, 1990; Lanson, 2011). Instrumental and experimental factors such as horizontal and vertical beam divergences, goniometer radius, and length and thickness of the oriented slides were measured and introduced in the calculations without further adjustment. The mass absorption coefficient ( $\mu^*$ ) was set to  $45 \text{ cm}^2 \text{g}^{-1}$  (Moore and Reynolds Jr, 1997). The lognormal distribution of coherent scattering domain (CSD) sizes along the c\* axis was characterized by a maximum value, set to 80 layers and by a mean value (N - Drits et al., 1997). The z-coordinates of atoms constituting the 2:1 (or TOT) smectite layer were adjusted from those of phlogopite (ICSD #95346). The interlayer configuration for trihydrated smectite layers  $(3W - d_{001} = 18-19 \text{ Å})$  includes planes of interlayer H<sub>2</sub>O molecules located at  $\approx 1.25$  and  $\approx 3.5$  Å from the interlayer midplane which is hosting interlayer cations (Dazas et al., 2014). Debye-Waller parameters proposed by these authors for these two planes of H<sub>2</sub>O molecules (Bwat) were used (Dazas et al., 2014). For bihydrated layers (2W  $d_{001} = 14.9-15.7$  Å), the interlayer configuration used includes one plane of H<sub>2</sub>O molecules on each side of the interlayer midplane hosting cations (Ferrage et al., 2005a). This model is characterized by the distance ( $\Delta d2W$ ) between the interlayer midplane and each of the planes of H<sub>2</sub>O molecules. Debye-Waller parameter was refined for these H<sub>2</sub>O molecules to account for their positional disorder (Ferrage et al., 2005a). For monohydrated layers  $(1W - d_{001} = 11.6-12.9 \text{ Å})$  both cations and H<sub>2</sub>O molecules were located at the interlayer midplane. A similar configuration, devoid of interlayer H2O molecules, was used for dehydrated layers (0W –  $d_{001} = 9.6-10.2$  Å). The overall interlayer water content at a given RH was constrained by water vapor (de) sorption isotherms and not refined, although the distribution of this global content between the different types of hydrated layers was refined. Layer-to-layer distance, preferred orientation of the particles in the sample ( $\sigma^*$ ), N, and  $\Delta d2W$  were considered as variable parameters. In addition, because of the weak bonds between adjacent smectite layers, layer thickness was allowed to deviate from the average  $d_{001}$ value. This cumulative deviation from the periodicity is described as a "disorder of second type" (Guinier, 1964; Drits and Tchoubar, 1990), and accounted for by introducing a variance parameter  $\sigma_z$  (Ferrage et al., 2005a).

The fitting procedure is described in detail elsewhere (Ferrage et al., 2005a, 2005b, 2010). Briefly, a main structure, periodic (that is with only one layer type) if possible, was used to reproduce as much as possible of the data. If necessary, additional contributions to the diffracted intensity were introduced to account for the misfit. Up to four interstratified structures, each with a different composition (relative proportion of the different layer types), were necessary to reproduce some of the XRD patterns because of the observed hydration heterogeneity. Interstratification of the different types of hydrated layers was systematically random in all contributions to the diffracted intensity. The use of several interstratified structures to fit the data does not reflect the actual presence of different populations of particles in the sample, and layers with a given hydration state were thus assumed to have identical parameters (layer thickness and interlayer configuration) in all interstratified structures to reduce the number of variable parameters. Similarly, N and  $\sigma_z$  parameters were considered identical for all interstratified structures used to fit a given pattern, although these parameters were varied as a function of RH. The relative proportions of the different interstratified structures and their compositions were also

# Table 1

 $d_{001}$  layer-to-layer distances used for GCMC calculations of hectorite interlayer species distributions.

Hectorite layer charge deficit [per O20(OH)4]	Layer-to-layer distance of 1W hydrate (d <sub>001</sub> in Å)	Layer-to-layer distance of 2W hydrate ( $d_{001}$ in Å)
0.8	12.47	15.51
1.0	12.45	15.43
1.3	12.49	15.44
1.6	12.49	15.49

adjusted.

#### 2.4. Grand canonical Monte Carlo simulations

Monte Carlo simulations were performed in the grand canonical ensemble to assess the content of interlayer H<sub>2</sub>O and the equilibrium state of interlayer cations and H<sub>2</sub>O molecules (Adams, 1974, 1975; Allen and Tildesley, 2017). Simulations were performed at both 20 and 80% RH (1W and 2W hydration states, respectively) and 300 K using a homemade program (Delville, 1991; Rinnert et al., 2005; Michot et al., 2007, 2012; Porion et al., 2008; Jimenez-Ruiz et al., 2012). The rigid simulation box included three interlayers and related 2:1 layers that encompassed six and four unit cells along the a and b directions, respectively. The chosen -a/3 layer displacement led to a face to face configuration for ditrigonal cavities and allowed matching closely experimentally determined H<sub>2</sub>O contents, whereas the actual value of this displacement did not influence significantly the distribution of interlayer species along the c\* axis. The layer-to-layer distance was set from experimental d<sub>001</sub> values (Table 1) for Na<sub>x</sub>Mg<sub>6-x</sub>Li<sub>x</sub>Si<sub>8.0</sub>O<sub>20</sub>(OH)<sub>4</sub> compositions with x = 0.8, 1.0, 1.3, and 1.6.

The SPC/E water model and a version of the ClavFF force field slightly modified by a cross-validation of atomic density profiles derived from GCMC simulations and X-ray diffraction pattern modeling were used to simulate clay-water interactions (Cygan et al., 2009; Ferrage et al., 2011). GCMC simulations encompassed 5000 blocks, each with 10,000 elementary steps allowing stabilization of interlayer H<sub>2</sub>O molecule content. At each step, one of the smectite interlayers was selected randomly, and with an equal probability an attempt was made (i) to remove a randomly chosen  $H_2O$  molecule, (ii) to add an additional H<sub>2</sub>O molecule in a random configuration, or (iii) to move a randomly chosen cation or H<sub>2</sub>O molecule. During calculations, an Ewald summation was used in addition to the three-dimensional minimum image convention to ensure the convergence of the electrostatic energy (Heyes, 1994). A final run including 5000 blocks of 5000 steps was performed to generate the equilibrium properties of interlayer species and to derive three-dimensional radial cation - H<sub>2</sub>O distribution functions.

# 3. Results and discussion

#### 3.1. Water vapor desorption isotherms

Experimental isotherms are typical for sorption of polar molecules on swelling phyllosilicates (Rouquerol et al., 2013), the two main plateaus at  $\approx 6$  and  $\approx 12$  mmol of H<sub>2</sub>O molecules per gram of dry smectite corresponding to domains dominated by 1W and 2W smectite layers (Sing et al., 2008), respectively, similar to saponite (Michot et al., 2005). Hectorite water vapor desorption isotherms are essentially independent of the layer charge deficit. Capillary sorption of H<sub>2</sub>O molecules when approaching water vapor saturation prevents determining the upper end of the 2W stability domain. On the other end, this domain extends down to  $\approx 60\%$  RH for all samples. In all cases, H<sub>2</sub>O content ranges from  $\approx 15.0$  to  $\approx 11.0$  mmol/g over this domain (Fig. 1), and the 2W-to-1W transition spreads over  $\approx 20\%$  RH. 1W stability domain thus extends from  $\approx 40\%$  RH to  $\approx 5\%$  RH, with H<sub>2</sub>O contents ranging from



Hect-1.0-OH

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Fig. 1. Water content as a function of relative humidity for hectorites (solid line) and saponite (dash line) samples along the water vapor desorption isotherm (A). The layer charge deficit is color-coded for both hectorites and saponites (see Figure). Isotherms for Hect-OH-0.8 and saponites from the literature (Ferrage et al., 2010; Dazas et al., 2013, 2015). Hectorite water content as a function of relative humidity (B). Solid lines were obtained from water vapor desorption isotherms, whereas dots represent H<sub>2</sub>O contents determined from XRD profile modeling. Black dashed lines indicate the range of H<sub>2</sub>O contents derived from GCMC calculations for both 2W and 1W layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 2.** Comparison between experimental and calculated XRD patterns as a function of RH for Hect-OH-1.0. Experimental and calculated XRD patterns are shown as solid red and black lines, respectively. Difference plots are shown at the bottom of the figure as grey lines. The vertical grey bars indicate a modified scale factor for high-angle regions compared to the  $4-10^{\circ}$  20 angular range. The goodness of fit parameter Rp is indicated for each pattern. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Comparison between experimental and calculated XRD patterns as a function of RH for Hect-OH-1.3. Patterns as for Fig. 2. Diffraction lines from halite (NaCl) impurity are indicated as Hal.

 $\approx$  7.0 to  $\approx$  4.5 mmol/g over this domain for all hectorites (Fig. 1).

# 3.2. XRD profile modeling

XRD data and corresponding optimum fits are shown for all samples as a function of RH in Figs. 2–4. The relative proportions of the different contributions to the calculated intensity and their compositions (proportions of the different layer types interstratified – See Fig. S1 for details) are reported in Tables 2–4. These Tables also include the main



**Fig. 4.** Comparison between experimental and calculated XRD patterns as a function of RH for Hect-OH-1.6. Patterns as for Fig. 2.

structural parameters of crystals (*N*), layers (layer-to-layer distance and its fluctuation –  $\sigma_z$ ), and interlayer H<sub>2</sub>O content and organization, with values of  $\Delta d2W$  and B<sub>wat</sub> parameters (Ferrage et al., 2011; Dazas et al., 2015).

# 3.2.1. Hect-1.0-OH

Four contributions are used to fit XRD data recorded at 95% RH (Fig. 2), the main one being an essentially periodic 2W smectite with  $d_{001} = 15.55$  Å. A second contribution (contribution #3 in Table 2)

Table 2 Structural parameters used to fit experime	ental XRD pa	tterns of	f Hect-O	H-1.0 as	a functi	on of rel	ative hu	nidity.												
Relative humidity %		95	06	85	80	75	70	65	60	55	50	45	40	55	80	25	20	15	10	2
Number of H <sub>2</sub> O molecules per [O <sub>20</sub> (OH) <sub>4</sub> ]	1W layers 2W layers	5.60 9.4	5.60 q 3	5.60 9.2	5.60 9.2	5.60 9.0	5.60 8 q	5.60 8 q	5.60 8.8	5.55 8.8	5.50 8.8	5.05 8.6	4.80 4	1.30 4	1.10	4.00	3.90	3.85	3.40	2.80
Debye–Waller factor of $\mathrm{H}_{2}\mathrm{O}$ molecules $(\mathrm{\AA}^{2})$	Bwat1W	50	202	202	20	50	50	50	45	42	40 10 10	40	- 60 L		ີ ທີ່ ເ	30	25	25	24	20
Laver-to-laver distances (Å)	bwat2W 0W	17	17	54	73	73	77	77	17	24 9.70	6.70	24 9.70	6.70	0.70	c. 0.70	9.70	9.70	9.70	9.70	9.70
	1W	13.47	13.46	13.45	13.45	13.3	13.1	12.6	12.585	12.58	12.575	12.57	12.56	2.55	2.525	12.465	12.45	12.35	12.25	12.135
	2W 3W	15.55 18.0	15.50 18.0	15.47 18.0	15.43 18.0	15.40 18.0	15.37 18.0	15.33 18.0	15.29 18.0	15.26	15.22	15.10	15.00	4.90	4.80					
<u>Ad</u> 2W (Å)		1.53	1.51	1.44	1.40	1.37	1.37	1.35	1.33	1.34	1.33	1.26	1.25	.24	.25					
$\sigma_{\rm z}$ (Å)		0.22	0.18	0.17	0.17	0.20	0.22	0.24	0.23	0.22	0.26	0.22	0.23 (	.25 (	0.28	0.30	0.30	0.24	0.24	0.20
o* (°)		5.0	4.4	3.8	3.8	3.8	4.0	4.3	4.4	4.0	4.2	4.4	4.6	.0	1.2	4.2	4.4	4.4	4.8	4.2
CSD (layers)		11.5	12.4	13.5	13.7	14.0	13.5	13.0	13.0	14.0	13.0	14.2	14.0	.0.9	6.5	17.0	17.0	15.3	16.0	16.0
Contribution #1	Ab (%)	78	88	88	06	89	88	81	67	41	25	4	e							
	3W																			
	2W	99.5	98.5	97.5	97	97	97	97	97	95	83	82	63							
	1W	0.5	1.5	2.5	°	3	3	3	3	3	11	11	30							
	0W									2	9	7	7							
Contribution #2	Ab (%)	3	6	6	7	9	4	15	25	34	41	11	10 8	~		19	17	18	14	15
	3W	65	40	35	33	31	16													
	2W	35	60	65	67	69	84	70	72	75	57	48	33	00	00					
	1W							30	28	23	38	52	67 7	0	55	89	80	79	75	30
	0W									2	5			,		11	20	21	25	20
Contribution #3	Ab (%)	5	e	°	°	5	8	5	8	15	27	27							22	36
	3W																			
	2W	65	63	60	59	57	60	47	46	50	25	18								
	1W	35	37	40	41	43	40	53	54	50	75	82							85	20
	0W																		15	30
Contribution #4	Ab (%)	14								10	7	58	87	10	4	81	83	82	65	49
	3W	30																		
	2W	70								19										
	1W									78	97	66	66	80	80	97.5	98.5	98.5	98	92
	0W									3	e	1	1			2.5	1.5	1.5	7	8

Table 3Structural parameters used to fit experime	ental XRD pa	tterns of	Hect-O	H-1.3 as	functio.	n of rela	tive hun	lidity.												
Relative humidity %		95	06	85	80	75	70	65	60	55	50	45	40	35	30 2	25	20	15	10	5
Number of $H_2O$ molecules per $[O_{20}(OH)_4]$	1W layers	6.0	6.0	5.9	5.9	5.9	5.9	5.9	5.9	5.8	5.0	4.9	4.2	4.1	3.9	3.85	3.7	3.6	3.0	2.5
( 0	2W layers	9.8	9.4	9.2	9.1	9.0	9.0	9.0	8.6	8.4	8.0	7.8	7.8	7.8	7.6	2.6	7.2	7.2	7.2	7.2
Debye–Waller factor of $H_2O$ molecules (Å <sup>2</sup> )	Bwat1W	50	50	50	50	50	50	50	50	50	48	48	43	42	42	40	38	39	35	35
	Bwat2W	23	21	20	19	19	20	21	20	18	18	18	16	15	15	15	15	15	15	15
Layer-to-layer distances (Å)	0W										9.70	9.70	9.70	9.70	9.70	9.70	9.70	9.70	9.70	9.70
	1W	13.25	13.20	13.20	13.10	13.00	13.00	12.90	12.64	12.62	12.60	12.555	12.55	12.54	12.53	12.52	12.49	12.42	12.35	12.245
	2W	15.54	15.50	15.47	15.44	15.40	15.39	15.35	15.33	15.29	15.24	15.20	15.10	15.00	14.95	14.90	14.90	14.80	14.80	14.80
	3W	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0										
Δd2W (Å)		1.47	1.45	1.43	1.39	1.38	1.37	1.36	1.35	1.34	1.34	1.33	1.30	1.28	1.28	1.28	1.27	1.27	1.27	1.27
$\sigma_{\rm z}$ (Å)		0.14	0.16	0.16	0.17	0.17	0.19	0.20	0.20	0.18	0.20	0.20	0.20	0.20	0.22 (	0.24	0.25	0.24	0.24	0.18
o* (°)		1.5	1.5	1.6	1.8	1.8	2.5	2.6	2.8	3.0	2.2	2.2	2.7	3.6	4.0	4.0	4.0	4.0	3.2	3.6
CSD (layers)		8.5	9.0	9.0	9.5	9.5	10.0	9.0	9.4	9.0	7.7	7.9	9.8	13.5	14.0	15.0	15.0	12.0	14.0	13.0
Contribution #1	Ab (%) 3W	57	62	63	66	63	65	69	55	42	35	9	3	4						
	2W	66	98	98	98	97.5	97	96.5	97	96.5	93	93	93	70						
	1 4 4 7		c	c	c	L	c	L		L	1	ſ	ſ							
	M1	-	N	N	N	C.7	n	c.5	n	c.5	_	~	~	30						
Contribution #2	Ab (%)	з	2	2	2	c S			22	30	46	35	16	15	20	31	21	20	29	28
	3W	85	82	80	70	65														
	2W	15	18	20	30	35			65	70	52	52	47							
	1W								35	30	48	48	50	06	8 06	39	87	80	80	75
	0W												3	10	10	11	13	20	20	25
Contribution #3	Ab (%)	24	26	25	22	25	21	17	17	11			22	33	33	28	52	64	69	64
	3W	27	25	25	25	20	20	18	18	18										
	2W	70	70	70	70	75	75	75	75	75			25	25	23	20	10	5	5	3
	1W	3	ъ	ß	5	5	5	7	7	7			73	72	72	75	85	92	92	91
	0W												2	3	ъ 2,	10	5	3	3	9
Contribution #4	Ab (%)	15	6	6	10	8	13	13	7	17	19	58	58	48	47 4	42	27	16	2	8
	3W	2	ß	ß	5	c S	5	2												
	2W	60	57	57	57	55	50	53	35	30	10	8	2	5	5	2				
	1W	35	38	38	38	42	45	45	65	70	90	92	97	97	97 97	. 26	66	66	66	50
	0W												1	1	1	_	1	1	1	50

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Table 4 Structural parameters used to fit experime	ental XRD pa	tterns of	Hect-O	H-1.6 as	a functio	n of rela	ıtive hun	nidity.												
Relative humidity %		95	06	85	80	75	70	65	60	55	50	45 ,	40 3	35	30	25 2	0 1	15	0	5
Number of H <sub>2</sub> O molecules per [O <sub>20</sub> (OH) <sub>4</sub> ]	1W layers	6.0 10.0	6.0 0 0	6.0 0.7	6.0 0.6	6.0	6.0	6.0	6.0 0.6	5.5	5.3	4.9	1.6 4 7.6 7	1.5	4.3	4.2 3	6.	3.7 3	3.4	3.3
Debye–Waller factor of $H_2O$ molecules $({\rm \AA}^2)$	Ewat1W	50	50	50	50	50	50	50	50	50	50	6. 8	6.4	10 T	45	44 4	7 13	<sup>42</sup>	01	38
I arrow to lorrow dictomore (Å)	Bwat2W	21	20	19	20	19	19	20	20	16 0.70	12	12	1	1	11	0 02 0	02	02.02	02.0	02.0
Layer-to-layer distances (A)	1W	13.30	13.25	13.20	12.90	12.75	12.73	12.70	12.70	9.70 12.61	9.70 12.59	9./U 12.58	12.57	1./U 12.565	9.70 12.55	۶./۱ ۶ 12.53 1	./u 2.49	12.43	1./U 12.335	9./U 12.20
	2W	15.66	15.55	15.52	15.49	15.44	15.41	15.36	15.32	15.31	15.29	15.28	15.27	15.26	15.255					
Adow (Å)	3W	1 47	18.0 1 46	18.0 145	18.0 145	18.0 145	18.0 1 44	18.0 1 42	1 40	1 40	1 25	. 33		30	1 30					
$\sigma_{z}$ (Å)		0.20	0.21	0.22	0.24	0.24	0.24	0.25	0.21	0.21	0.24	0.21	0.22	0.22	0.26	0.24 0	.26 (	0.27 (	0.27	0.25
o* (°)		5.6	7.8	9.0	9.0	8.6	8.6	7.4	7.0	6.9	8.0	8.0	3.0 8	3.2	8.4	3.0 5	0.	3.4 8	3.6	9.0
CSD (layers)		16.5	17.0	16.4	17.0	16.1	16.0	16.2	16.0	16.0	17.0	17.5	17.8	19.5	20.5	22.0 2	1.0	20.5	20.0	21.0
Contribution #1	Ab (%)	77	89	96	97	95	89	78	51	60	7									
	3W																			
	2W	96.5	96	95.5	95.5	95.5	95.5	95.5	94	93	06									
	1W	3.5	4	4.5	4.5	4.5	4.5	4.5	9	5	8									
	0W									2	2									
Contribution #2	Ab (%)	16	9	4	3	5	5	12	27	21	43	9	~		2			.,		4
	3W	25	25	20	20	11	10	10	33											
	2W	75	75	80	80	89	89	88	96	63	58	20	44	25	25					
	1W						1	2	1	35	40	47	52	20	70				20	70
	0W									2	2	, m			5 2				00	30
Contribution #3	Ab (%)						5	10	2	7	27	39	13				-	[5	12	45
	3 W						0		Î				ļ							
	2W						60	60	50	34	18	18	[]							
	1W						40	40	50	65	79	78	78				w	30	22	85
	0W									1	33	4						00	5	15
Contribution #4	Ab (%)	7	4						20	13	23	55	33	93	98	100 1	3 00	35 8	00	52
	3W																			
	2W	75	75						68	76	65									
	1W	25	25						32	23	34	66	86	98	97.5	5 26	7	86	80	98
	0W									1	1		~1	01	2.5		.,	~	~1	5

contains 2W layers ('layer' is used hereafter to describe the 'unit structure', that is the assemblage of the layer plus the interlayer that defines the unit-cell motif) interstratified with minor 1W layers to fit the high-angle asymmetry of smectite 001 reflection. The other two contributions contain 2W interstratified with 3W layers to fit the lowangle asymmetry of this reflection. From 90 to 60% RH, XRD patterns are fitted with three contributions (Fig. S1), the main one including mostly ( $\geq$  97%) 2W layers interstratified with 1W layers, whereas the second contribution keeps a minor content of 3W layers down to  $\approx 70\%$ RH to account for the low-angle asymmetry of smectite 001 reflection. In the third minor contribution, 2W and 1W layers are interstratified in similar proportions. The overall proportion of 1W layers remains about stable (< 5%) over the 95–70% RH range and increases significantly ( $\approx$ 24%) at 55% RH as evidenced by the enhanced high-angle asymmetry of smectite 001 reflection, the low-angle asymmetry of 2W smectite 005 reflection, and the onset of 1W smectite 002 reflection at  $\approx$  14°2 $\theta$  (Fig. 2). At 55% RH, four contributions are thus necessary to fit XRD data (Fig. S1). The proportion of the main contribution, overwhelmingly dominated by 2W layers, strongly decreases from 67 to 41% (at 60 and 55% RH, respectively). The three additional contributions, containing 2W and 1W layers in contrasting proportions ( $\approx$  3:1, 1:1, and  $\approx$ 1:4 ratios), account for 10% or more of the scattered intensity. Dehydrated smectite layers are first detected at 55% RH, although in minimal proportion ( $\approx 1\%$  – Table 2). Down to 45% RH, the coexistence in the experimental patterns of reflections typical for both 2W and 1W smectite (e.g. peaks both at  $\approx 16$  and  $\approx 14^{\circ}2\theta$ ) requires four contributions to fit the data (Fig. S1). Over the 55-45% RH interval, the main contribution changes to an essentially periodic 1W smectite (contribution #4 in Table 2), whereas the proportion of the contribution dominated by 2W layers decreases (41 and 4% at 55 and 45% RH, respectively) together with its content of 2W layers (95 and 82% at 55 and 45% RH, respectively). The proportion of 1W layers consistently increases with decreasing RH in the other two contributions. From 40% RH, experimental XRD patterns are dominated by 1W smectite ( $d_{001} = 12.56$  Å), and the main contribution consistently is an essentially periodic 1W smectite (contribution #4 in Table 2). At 40% RH, the other two contributions to the diffracted intensity contain both 2W and 1W layers. With decreasing RH, the contribution dominated by 2W layers vanishes (contribution #1 is not detected at 35% RH), whereas the proportion of 2W layers steadily decreases to 0 at 25% RH. At 25 and 20% RH, the two contributions to the diffracted intensity contain only 1W and 0W layers (Fig. S1). The proportion of 0W layers exceeds 10% only at 5% RH, however ( $\approx 18\%$  – Table 2), the decreased proportion of the essentially periodic 1W smectite (49% at 5% RH) indicating the onset of smectite dehydration (Fig. S1).

#### 3.2.2. Hect-1.3-OH

At 95% RH, four contributions are needed to fit XRD data (Fig. 3), the main contribution (contribution #1 in Table 3) being an essentially periodic 2W smectite. Two additional contributions account for the low- and high-angle asymmetry of smectite 001 reflection (contributions #3 and #4, respectively, in Table 3). These two contributions are also dominated by 2W layers but contain a significant (> 25%) proportion of 3W and 1W layers, respectively. A fourth minor contribution is dominated by 3W layers at these high RH conditions. Decreasing RH value to 65%, the overall contributions to the diffracted intensity remain stable. The most significant evolution is the decreasing proportion of 3W layers in contributions #2 and #3, and the increase of 1W layer proportion in contribution #4 (Table 3). Contribution #2, which is dominated by 3W layers, is not detected at RH values lower than 75% RH. At 60% RH, the onset of 2W-to-1W transition is characterized by the prevalence of 1W layers in contribution #4 as a result of the steady increase of their proportion in this contribution. At this RH value, the essentially periodic 2W smectite remains the main contribution, however, despite a significant decrease of its relative abundance (from 65-70% to 55% at > 60% RH and 60% RH, respectively - Table 3).

Two other contributions, both dominated by 2W layers, are necessary to fit the data. 3W layers persist in contribution #3, whereas only 2W and 1W layers are present in the fourth contribution (contribution #2 in Table 3). The XRD pattern collected at 55% RH was fitted with the same four contributions, although the relative abundance of contribution #4, which is dominated by 1W layers is increased from  $\approx 10$  to  $\approx 20\%$  (at 60 and 55% RH, respectively - Table 3). Reflections typical for 1W smectite are visible in the XRD pattern collected at 50% RH (Fig. 3) and are accounted for by a contribution overwhelmingly dominated by 1W layers (90% of 1W layers in contribution #4 - Table 3). On the other hand, contribution #1 remains dominated by 2W layers (93%), the main contribution to the diffracted intensity at this RH value containing 2W and 1W layers randomly interstratified in almost equal proportions. however. At 45% RH, the same three contributions are present. Their relative abundances are significantly modified, however with the prevalence of the essentially periodic 1W smectite (contribution #4 in Table 3), whereas the contribution of the essentially periodic 2W smectite becomes marginal (6% - Table 3). This contribution decreases further (3%) at 40% RH. At this RH value, 1W layers prevail in the other three contributions, the main one being an essentially periodic 1W smectite (contribution #4 in Table 3), whereas the other two account for hydration heterogeneity. Contribution #2 contains only dehydrated layers interstratified with 1W layers, whereas both 0W and 2W layers coexist with prevailing 1W layers in contribution #3 (Table 3). These three contributions allow fitting XRD data down to 5% RH. With decreasing RH, the proportion of 2W layers in contribution #3 decreases steadily to become marginal (< 10%) at 15%RH, whereas the proportion of dehydrated layers increases in contribution #2, whose relative abundance increases with decreasing RH (from  $\approx 15\%$  to  $\approx$  30% at 35% RH and 5–10% RH, respectively – Table 3).

# 3.2.3. Hect-1.6-OH

As for the other two hectorite samples, XRD patterns collected at high RH values (Fig. 4) are dominated by the contribution of an essentially periodic 2W smectite (> 90% of 2W layers - contribution #1 in Table 4). Additional contributions that contain either 3W and 2W (contributions #2 and #3) or 2W and 1W layers (contribution #4) account for the low- and high-angle tails, respectively, of smectite 001 reflection. With decreasing RH conditions, the relative abundance of the most hydrated contributions decreases together with their content of 3W layers. At 75% RH, the two contributions allowing fitting XRD data are a major contribution of essentially periodic 2W smectite and a minor contribution with  $\approx 10\%$  of 3W layers interstratified with 2W layers. Contributions having similar composition contribute also to XRD patterns collected at 70 and 65% RH. A third contribution in which 2W layers are randomly interstratified with 1W layers accounts for the high-angle asymmetry of smectite 001 reflection that starts developing at these RH values. This asymmetry increases further at 60% RH, and requires the addition of a fourth contribution incorporating a significant proportion (> 30%) of 1W layers (contribution #4 in Table 4). At the same time, the proportion of 3W layers in contribution #2 becomes minimal (3% - Table 4). At 55% RH, 1W layers become prevalent in contribution #3, although peaks typical for 1W smectite become visible only at 50% RH (Fig. 4). Consistently, the relative abundance of contribution #4, in which 1W layers prevail, increases from 12 to 23% (at 55 and 50% RH, respectively - Table 4) whereas that of contribution #1, which is still dominated by 2W layers (90%) becomes marginal (7% - Table 4), the main contribution including both 2W and 1W layers in similar proportions (58:40 ratio - contribution #2 in Table 4). At 45% RH, the XRD pattern is dominated by 1W smectite, the main contribution to the diffracted intensity being an essentially periodic 1W smectite (contribution #4 in Table 4), whereas the other important contribution is also dominated by 1W layers. A third contribution with equivalent proportions of 2W and 1W layers accounts for the limited low-angle asymmetry of smectite 001 reflection. Contributions with similar compositions allow reproducing XRD data collected



**Fig. 5.** Evolution of the relative proportion of the different layer types (summing up all contributions to the diffracted intensity) along water vapor desorption isotherms for Hect-OH-0.8, Hect-OH-1.0, Hect-OH-1.3, and Hect-OH-1.6 (A). Color code as in Fig. 1. Squares, diamonds, triangles, and disks represent 0W, 1W, 2W, and 3W layers respectively. Evolution of the relative proportion of the different layer types for Hect-OH-0.8 and Sap-0.8-OH (B), and for Hect-OH-1.6 and Sap-1.4-OH (C). Patterns as for (A), red and black lines represent hectorite and saponite, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

at 40% RH, the relative contribution of the essentially periodic 1W smectite increasing significantly, however (from 55 to 83% at 45 and 40% RH, respectively). This contribution overwhelmingly dominates XRD patterns collected from 35 to 20% RH, coexisting only with a minor contribution in which 1W layers represent  $\approx$ 70% of the total layers at 35 and 30% RH (Table 4). When decreasing further the RH conditions, this essentially periodic 1W smectite remains the main contribution to the diffracted intensity, with additional contributions containing dehydrated smectite layers interstratified with prevailing 1W layers, accounting for the high-angle tails of smectite 001 reflection.

# 3.3. Evolution of synthetic hectorite hydration along the $H_2O$ vapor desorption isotherm

The XRD profile modeling approach used allows gaining quantitative insights into the overall hydration of investigated hectorites despite intrinsic heterogeneity. In particular, by plotting the relative proportions of the different layer types as a function of RH it is possible to evidence the transition between different hydration domains (Fig. 5). Plots obtained for all hectorites are similar (Fig. 5a), with two main plateaus corresponding to bi- and mono-hydrated domains extending from 90 to 60% RH and from 40 to 10% RH, respectively. Except for Hect-OH-1.3, the proportion of a given layer type exceeds 90% on these plateaus thus indicating a low hydration heterogeneity, consistent with previous reports on tetrahedrally substituted synthetic smectites (saponites - Ferrage et al., 2010) and in contrast with natural montmorillonites and beidellites (Ferrage et al., 2005b, 2007). In contrast to saponites, there is no significant influence of the amount of layer charge deficit on the 2W-to-1W dehydration behavior of hectorite which is similar to that of low-charge saponite  $[0.8 \text{ charge per } O_{20}(\text{OH})_4 -$ Fig. 5b]. When increasing layer charge, dehydration of saponite occurs at lower RH values, whereas hydration behavior of hectorite remains unchanged (Fig. 5a,c). The similarity of hectorite hydration behavior with that of low-charge saponite possibly indicates that the reduced charge undersaturation of surface O atoms in hectorite, compared to high-charge saponite, is responsible for the lack of influence of layer charge on hectorite hydration behavior. Relative proportion of OW layers decreases with increasing layer charge under low RH conditions (from 25.6% to 9.0% for Hect-0.8-OH and Hect-1.6-OH, respectively, at  $\approx$  5% RH), however, consistent with the increased stability of higher hydration states towards low RH conditions observed for saponites when increasing the layer charge. Finally, 3W layers are systematically reported in hectorites under high RH conditions, in contrast with saponites (Ferrage et al., 2010; Dazas et al., 2015). This difference most likely does not correspond to contrasting hydration behaviors related to charge location but is rather due to the lack of a structure model for 3W layers that prevented at the time an optimum fit of saponite XRD data recorded under these high RH conditions. In the present study, 3W layers were considered to fit the low-angle tails of the first smectite reflection despite the possible contribution of scattering effects over this angular range.



**Fig. 6.** Evolution of the layer-to-layer distance of smectite 1W layers as a function of relative humidity (A), and of the number of interlayer  $H_2O$  molecules per cation (B). Color codes as in Fig. 1. Triangles and disks represent hectorite and saponite, respectively. Data for Hect-OH-0.8 and saponites from the literature (Ferrage et al., 2010; Dazas et al., 2013, 2015). Only data points for which the overall content of 1W layers exceeds 10% were considered.

# 3.4. Layer-to-layer distance and content of interlayer water

#### 3.4.1. 1W hectorite layers

The overall range of layer-to-layer distances (12.0–12.6 Å) and of interlayer H<sub>2</sub>O contents [2.5–5.5 H<sub>2</sub>O molecules per O<sub>20</sub>(OH)<sub>4</sub>] is similar in both hectorite and saponite, independent of the layer charge location (Fig. 6, Tables 2–4, and published data for Hect-OH-0.8 and Sap – Ferrage et al., 2010; Dazas et al., 2013, 2015). This similarity of layer-to-layer distances and water contents evidences the limited influence of the distribution of H<sub>2</sub>O molecules, present either as part of



Fig. 7. Evolution of the layer-to-layer distance of smectite 2W layers as a function of relative humidity (A), and of the number of interlayer  $H_2O$  molecules per cation (B). Patterns as in Fig. 6. Only data points for which the overall content of 2W layers exceeds 15% were considered.

the cation hydration sphere or filling interlayer voids, on layer-to-layer distances (Tables 2–4) although the relative proportion of these different types of  $H_2O$  molecules impacts their dynamical behavior (Michot et al., 2012). In addition, the layer-to-layer distance of 1W layers varies in a similar way along the  $H_2O$  vapor desorption isotherm for all hectorite samples (Fig. 6a, Tables 2–4), consistent with the limited influence of hectorite layer charge on their hydration behavior. Similarly, for a given content of interlayer  $H_2O$ , the layer-to-layer distance of 1W hectorites is increased compared to that of saponite (Fig. 6b), most likely as a result of the reduced electrostatic attraction between interlayer cations and the 2:1 layer. Minimal cation-layer electrostatic interactions in hectorite may be responsible for the



<sup>(</sup>caption on next page)

**Fig. 8.** (A) Electronic density profiles within hectorite interlayers determined from XRD and GCMC modeling (dashed and solid lines, respectively) at  $\approx 20$  and  $\approx 80\%$  RH (1W and 2W interlayers, right and left respectively). Positions are given relative to the interlayer mid-plane. Blue, red, and grey lines indicate electron densities related oxygen, hydrogen, and cations, respectively. Black lines represent total electron density. (B) Electronic density profiles within saponite interlayers determined from XRD and GCMC modeling at  $\approx 20$  and  $\approx 80\%$  RH (1W and 2W interlayers, left and right, respectively). Positions are given relative to the interlayer mid-plane. Patterns as in panel A. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contrasting evolutions of 1W layer-to-layer distance as a function of interlayer H<sub>2</sub>O content, compared to saponite. Hectorite layer-to-layer distance remains unchanged over a wide RH range ( $\geq 20\%$  RH) before decreasing sharply for lower H<sub>2</sub>O contents, whereas saponite layer-to-layer distance decreases steadily with decreasing H<sub>2</sub>O content over the whole 1W stability domain (Fig. 6). Despite the limited influence of layer charge on hectorite hydration behavior, the evolution of 1W layer-to-layer distance as a function of interlayer H<sub>2</sub>O content is influenced by layer charge. Fig. 6b shows indeed that an increased number of interlayer cations induces a faster decrease of the layer-to-layer distance with decreasing H<sub>2</sub>O content (normalized to the number of interlayer cations). This rate is specifically increased for both saponite and hectorite when layer charge is equal or higher than 1.2 charge per O<sub>20</sub>(OH)<sub>4</sub>, and/or when the number of H<sub>2</sub>O molecules is lower than  $\approx 3.5$  per interlayer Na<sup>+</sup>.

# 3.4.2. 2W hectorite layers

Layer-to-layer distances observed for 2W hectorite layers (15.10–15.65 Å) are larger compared to those reported for saponite (14.80–15.40 Å – Fig. 7) despite similar overall H<sub>2</sub>O contents [8.0–10.0 H<sub>2</sub>O molecules per  $O_{20}$ (OH)<sub>4</sub> – Tables 2–4]. In addition, layer-to-layer distances determined for hectorites are all akin and similar to those reported for low-charge saponite (Sap-OH-0.8 – Ferrage et al., 2010) indicative of a weak electrostatic attraction between the 2:1 layer and interlayer cations. On the contrary, 2W layer-to-layer distances steadily decrease for saponite with increasing layer charge (Fig. 7b). For all 2W hectorite and saponite samples, the 2W layer-to-layer distance decreases steadily with the decreasing number of H<sub>2</sub>O molecules hydrating interlayer cations, the range of distances for a given layer charge being more restricted for saponites compared to hectorite, however (Fig. 7b).

# 3.4.3. Comparison with volumetric $H_2O$ vapor isotherms and GCMC calculations

Consistent with the constraints imposed on the modeling, overall H<sub>2</sub>O contents determined from XRD modeling and from volumetric desorption isotherms are in general agreement, except under high RH conditions ( $\geq$ 70% RH) for which capillary condensation becomes significant (Fig. 1b). XRD modeling leads indeed to H<sub>2</sub>O contents ranging from 4.8 to 5.1 mmol per g of dry smectite and from 11.7 to 12.5 mmol per g of dry smectite in 1W and 2W hectorite layers, respectively. Similar H<sub>2</sub>O contents were determined from GCMC calculations for 2W layers (11.9-13.7 mmol H<sub>2</sub>O per g of dry smectite - Figs. 1b and 8). Both GCMC and XRD profile modeling suggest a slight increase of H<sub>2</sub>O content with increasing layer charge in these 2W layers, whereas an opposite trend is obtained from desorption isotherms, possibly as the result of sample texture (Cases et al., 1997). For 1W layers, H<sub>2</sub>O contents derived from GCMC calculations (5.5-6.4 mmol H<sub>2</sub>O per g of dry smectite) are systematically slightly higher than those determined experimentally (Figs. 1b and 8).

# 3.5. Organization of interlayer species

#### 3.5.1. 1W hectorite layers

Overestimation of  $H_2O$  contents derived from GCMC calculation compared to experimentally determined values (Figs. 1b, 8 and 9) possibly results from the use of the SPC/E model for water, this model leading to higher  $H_2O$  contents compared to the SPC model (Ferrage et al., 2011). Although leading to a slight overestimation of  $H_2O$  contents, the SPC/E water model allows a robust determination of  $H_2O$  organization in saponite over a range of layer charge similar to the one investigated in the present study (Ferrage et al., 2011). Alternatively, experimentally determined  $H_2O$  contents may be slightly underestimated by an incomplete release of  $H_2O$  molecules after sample degassing (Michot et al., 2005; Rinnert et al., 2005; Ferrage et al., 2010). Additional experimental measurements, from infrared spectroscopy and/or neutron diffraction on samples equilibrated with  $D_2O$ , would be needed to assess further the accuracy of present experimental constraints.

The overall agreement between interlayer electron density distributions derived from GCMC calculations and from modeling of XRD data (Figs. 8 and 9) is satisfactory however, especially for high layer charges. For low values of layer charge, the overestimation of  $H_2O$ contents from GCMC calculations leads to significantly higher electron density at the interlayer mid-plane (Fig. 8). In all cases, modeling of XRD profiles leads to a significant broadening of interlayer electron density distribution, consistent with the breadth of computed distributions. The latter distributions indicate however that the broadening is mainly due to the splitting of the interlayer cation position, this splitting increasing with increasing layer charge.

# 3.5.2. 2W hectorite layers

The interlayer cation site is split also for 2W hectorite layers, although the highest cation density occurs at the interlayer mid-plane (Fig. 8). Despite their overall consistency, interlayer distributions of H<sub>2</sub>O molecules derived from GCMC calculations and from XRD profile fitting exhibit significant differences. A first difference arises from the sharpening of H<sub>2</sub>O molecule distributions determined from XRD profile modeling with increasing layer charge, whereas the breadth of O atomic distributions is essentially the same whatever the layer charge (Fig. 8). A second difference comes from the position of these distributions with respect to the interlayer mid-plane. H<sub>2</sub>O molecule distributions deduced from XRD profile modeling are systematically located at  $\approx 1.40-1.45$  Å ( $\Delta d2W$  in Tables 2-4) from the interlayer midplane. The same position was obtained from GCMC calculations performed for Hect-OH-0.8. For higher values of the layer charge, centers of O atomic distribution derived from GCMC calculations are shifted however towards the 2:1 layer by 0.15-0.20 Å. In all cases, planes of H<sub>2</sub>O molecules are located at a realistic distance of 2.8–3.0 Å from the 2:1 layer.

# 3.6. Comparison of synthetic hectorite and saponite hydration

No significant influence of the amount of layer charge on hectorite hydration behavior was evidenced in the present study, the dehydration from 2W to 1W layers occurring systematically over the same RH range (60–40% RH – Fig. 5). A slight shift of the 1W-to-0W transition towards lower RH values was observed however with increasing layer charge (Figs. 1 and 5). This latter shift is consistent with the increased stability of the most hydrated layers towards lower RH conditions observed for saponites (Ferrage et al., 2005b, 2007, 2010, 2011; Dazas et al., 2015). A similar shift was observed however for the 2W-to-1W transition (Figs. 5b, c), in contrast to hectorites. Despite their contrasting stability, the H<sub>2</sub>O content is systematically the same for a given hydration state and all smectites investigated, whatever the location and the amount of layer charge deficit (Fig. 1) with  $\approx$  4–6.5 and  $\approx$  10–13 mmol H<sub>2</sub>O per gram of dry smectite in 1W and 2W layers, respectively. These H<sub>2</sub>O contents are reduced by  $\approx$  30% by F-for-OH substitution in the anionic





**Fig. 9.** (A) Atomic density profiles within hectorite interlayers determined from GCMC modeling at  $\approx 20$  and  $\approx 80\%$  RH (1W and 2W interlayers, right and left respectively). Positions are given relative to the interlayer mid-plane. Patterns as in Fig. 8A. (B). Atomic density profiles within saponite interlayers determined from GCMC modeling at  $\approx 20$  and  $\approx 80\%$  RH (1W and 2W interlayers, left and right, respectively). Positions are given relative to the interlayer mid-plane. Patterns as in Fig. 8A.



framework of the 2:1 layer, however (Dazas et al., 2013).

Steric constraints imposed on these similar amounts of H<sub>2</sub>O molecules vary significantly as a function of the location and the amount of layer charge deficit. For hectorites, layer-to-layer distances are similar indeed for a given hydration state (H<sub>2</sub>O content) whatever the layer charge (Figs. 6 and 7). For a given H<sub>2</sub>O content, these distances are equal or slightly higher than those reported for Sap-OH-0.8 (Ferrage et al., 2010). On the other hand, layer-to-layer distances decrease significantly with increasing layer charge for saponites (Dazas et al., 2015). This contrasting evolution of layer-to-layer distances is most likely due to the lower electrostatic attraction between the 2:1 layer and interlayer cations in hectorite compared to saponite owing to the weaker local charge undersaturation of O atoms at the surface of hectorite layers. This lower local undersaturation, and the associated reduced need for local charge compensation, leads to interlayer species being located further away from the 2:1 layer surface (Figs. 8A, B) although the same LJ parameters were used for O atoms at the surface of the 2:1 layer for GCMC simulations of both saponites and hectorites. For hectorites, interlayer cations closest to the 2:1 layer are located indeed at  $\approx 2.5$  Å from this layer, compared to  $\approx 2.2-2.3$  Å for saponites, whereas H<sub>2</sub>O molecules are located at  $\approx 2.8-3.0$  Å, compared to  $\approx$  2.6–2.8 Å for saponites.

Both the lack of layer charge influence on the layer-to-layer distance observed for hectorites and the more diffuse charge undersaturation of O atoms at the surface of hectorite 2:1 layer, compared to saponite, result in similar distributions of interlayer species whatever the amount of hectorite layer charge. As a consequence, H<sub>2</sub>O contents, position of interlayer cations and H<sub>2</sub>O molecules with respect to O atoms at the 2:1 layer surface, and breadth of the distributions are indeed essentially similar for all hectorites whatever the layer charge (Fig. 8A and Fig. S2). By contrast, the decrease of the layer-to-layer distance observed for saponite with increasing layer charge induces steric constraints on the distribution of interlayer species. Constraints are enhanced by the stronger local charge undersaturation of O atoms at the surface of the 2:1 layer and the induced increased hydrophobicity of the layer surface (Ferrage et al., 2010, 2011; Dazas et al., 2015). Increased steric constraints in saponite compared to hectorite lead in turn to a stronger organization and to an increased polarization of H<sub>2</sub>O molecules (Fig. 9).

# 4. Conclusion

The overall range of interlayer H<sub>2</sub>O contents [2.5-5.5 and 8.0-10.0 H<sub>2</sub>O molecules per O<sub>20</sub>(OH)<sub>4</sub> for 1W and 2W hydrates, respectively] is similar in both synthetic Na-saturated hectorite and saponite, independent of their layer charge. The hydration behavior of both Nasaturated smectite varieties differs however as the transition from 2W to 1W layers systematically occurs over the same RH range for synthetic Na-saturated hectorite whereas the stability of 2W layers is increased towards lower RH conditions for high-charge synthetic Na-saturated saponites compared to low-charge ones. Consistent with this increased stability of most hydrated layers with increasing layer charge, a slight increase of 1W layer stability towards lower RH conditions is observed for high-charge Na-saturated hectorite compared to low-charge ones. 1W hydrates of synthetic Na-saturated hectorite and saponite also display similar layer-to-layer distances (12.0-12.6 Å), whatever their layer charge. Contrastingly, layer-to-layer distances of 2W Na-saturated saponite layers (14.80-15.40 Å) are shorter than those of Na-saturated hectorite 2W layers (15.10-15.65 Å). In addition, the amount of layer charge has essentially no effect on the layer-to-layer distance of Nasaturated hectorite 2W layers whereas a significant decrease of the layer-to-layer distance is observed with increasing charge for Na-saturated saponite 2W layers. The contrasting hydration behavior of Nasaturated saponite and hectorite is likely due to different electrostatic

attraction between the 2:1 layer and interlayer cations. The charge undersaturation of O atoms at the surface of hectorite 2:1 layer is indeed more diffuse compared to saponite, owing to the location of the charge deficit in the octahedral sheet. As a result, Na<sup>+</sup> cations are located further away from the surface of the 2:1 layer in hectorite compared to saponite. In addition, contrasting layer-to-layer distances of synthetic Na-saturated saponite and hectorite 2W layers lead to distances between interlayer H<sub>2</sub>O molecules and the surface of 2:1 layers shorter in the former compared to the latter despite unfavorable undersaturation of O atoms. Finally, the present article complements the dataset available for tetrahedrally charged synthetic Na-saturated smectites (saponites) to build comprehensive sets of data and samples with contrasting locations and amounts of layer charge deficits that provide key constraints to assess the validity of force fields simulating clay-water interactions. The present work being limited to Na-saturated hydroxylated smectites, its extension and applicability to other interlayer cations should be assessed to decipher the specific influence of the charge-compensating cation. Previous combined experimental and computational studies investigated the influence of interlayer cation nature on the structure and dynamics of interlayer species for alkali and alkaline earth cations (Michot et al., 2012; Bowers et al., 2014; Reddy et al., 2016). Michot et al. (2012) also demonstrated the validity for molecular dynamic studies of atomic potentials derived from the collation of experimental XRD profile modeling and of GCMC calculations for Na-saturated samples. Specific attention should be paid however to large alkali cation having low hydration energy (e.g., K<sup>+</sup>, Cs<sup>+</sup> -Bowers et al., 2011; Loganathan et al., 2016), owing to their specific properties.

# Declaration of competing interest

The authors declare no competing financial interest.

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# Authors contribution

BL, BD, and EF conceived the study, ML and DV performed the syntheses, VM and NF collected the sorption and diffraction data, respectively, DV, EF, BD, and BL contributed to XRD data modeling, BD and EF performed the molecular modeling, BL, DV, BD, and EF contributed to the writing of the article.

# Appendix A. Supporting information

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.clay.2019.105404. Comparison between experimental and calculated XRD patterns for a selection of Hect-1.0-OH Xray diffraction patterns with the respective contributions of the various interstratified structures to the calculated profiles. Comparison of the H<sub>2</sub>O contents determined from vapor sorption isotherms and from GCMC simulations. Specific surface area determined with the BET methods for all synthetic Na-saturated saponites and hectorites described.

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