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Impact of Intrinsic Structural Properties on the Hydration of 2:1 Layer Silicates

Florian Schnetzer^{†,*}, Cliff T. Johnston[§], Gnanasiri S. Premachandra[§], Nicolas Giraudo[‡], Rainer Schuhmann[†], Peter Thissen[‡], and Katja Emmerich[†]

[†]Competence Center for Material Moisture, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[‡]Institute of Functional Interfaces, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[§]Department of Agronomy, Crop, Soil and Environmental Sciences, Purdue University, 915 West State Street, West Lafayette, Indiana 47907-2054, United States

Abstract

Several 2:1 layer silicates comprising di- and trioctahedral smectites of different layer charge between 0.2 and 0.4 per formula unit and a trioctahedral vermiculite were studied by an *in situ* method that allowed Fourier transform infrared spectroscopy (FTIR) spectra and water vapor sorption isotherms to be obtained simultaneously. The particle size and shape of the selected materials were determined using X-ray diffraction and gas adsorption analyses, which provided an estimate of the particle size with resulting edge site proportion. The aim of this study was to elucidate the hydration mechanism in 2:1 layer silicates during desorption and adsorption of water vapor. Domains in the desorption and adsorption of water vapor of the smectite samples with a slightly increasing slope were explained by a heterogeneous layer charge distribution, which enables the coexistence of different hydration states even under controlled conditions. Whereas hysteresis was observed over the entire isothermal range of the smectites, the isotherm of the vermiculite sample only showed hysteresis in the transition from the monohydrated state (1W) to the bihydrated state (2W). We also revealed that hysteresis is a function of the layer charge distribution, the achieved water content, and the particle size with resulting edge site contribution. Increasing the edge site proportions led to an increased hysteresis. The findings from the experimental FTIR/gravimetric analysis showed that the transition from 2W to 1W and backward is visible using infrared spectroscopy. The shifting of $\delta(\text{H}-\text{O}-\text{H})$ was influenced by the layer charge and octahedral substitutions. As a final point, we use water as a sensor molecule to describe

*Corresponding Author: florian.schnetzer@gmail.com.

ORCID

Florian Schnetzer: 0000-0002-9609-2928

Notes

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Supporting Information

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Material characterization including XRD patterns of the powdered samples stored at 53 and 86% rh, layer charge distribution, ESEM image of VT-2Na, and IR spectra of the selected 2:1 layer silicates as a function of humidity (from 85 to 2% rh) (PDF)

the OH groups of the octahedral sheet and show that the observed shifts result from a change in the tilting angle. Our experimental results were supported by *ab initio* thermodynamic simulations that revealed the different shifting behavior of $\delta(\text{H-O-H})$ and $\delta(\text{M}^{X+}\text{-OH-N}^{Y+})$ related to the differences in surface charge density and octahedral compositions.

Graphical Abstract

Keywords

clay; water; infrared spectroscopy; montmorillonite; smectite; hectorite; vermiculite

INTRODUCTION

Smectites and vermiculites are planar hydrous 2:1 layer silicates. They are among the most dominant minerals in many soils and clay deposits. These types of clay minerals impart unique properties as a result of their intrinsic shrink–swell characteristics.^{1–8} At low moisture content, crystalline swelling of 2:1 layer silicates proceeds in a stepwise expansion of the layer-to-layer distance.^{9–17} The swelling shows hysteresis and desorption, and adsorption of water proceeds differently.^{18–24} In this paper, we studied the hysteresis in clay swelling as a function of relative humidity (rh) using powder X-ray diffraction (XRD), gas adsorption analysis, and infrared (IR) spectroscopy and related these experimental results to the intrinsic properties (e.g., layer charge, charge location, octahedral composition, and particle size) of the clay minerals being studied. Besides their widespread importance in soils, clay minerals are also used in many different applications, such as construction materials or barrier materials in waste repositories.²⁵ For these applications, it is important to control and monitor their swelling behavior, and hence, understanding the molecular mechanism of hysteresis in clay swelling is a prerequisite.

Vermiculites are swellable 2:1 layer silicates with a net negative layer charge of 0.6–0.9 per formula unit (fu), which is higher compared to the layer charge of smectites.^{26,27} In addition to higher layer charge, the particle size of vermiculites is greater than that of smectites. Vermiculites are commonly coarse with a particle size of $>20\ \mu\text{m}$, and consequently,

vermiculite particles are often large enough for detailed structural studies.²⁸ Smectites can have a di- or trioctahedral character of the octahedral sheet. The montmorillonite–beidellite series are the most common dioctahedral smectites with a general structural formula of $M_{x+y/n}^{n+}(\text{Si}_4-x\text{Al}_x)-1, \text{Fe}_{2-y}^{3+}\text{Mg}, \text{Fe}_y^{2+})\text{O}_{10}(\text{OH})_2$.^{29,30} Hectorite is a trioctahedral smectite and has an ideal structural formula of $M_{z/n}^{n+}(\text{Si}_4)-g_3-z\text{Li}_z^{+})\text{O}_{10}(\text{OH})_2$. Here, $x+y$ and z represent the permanent layer charge resulting from substitutions within the tetrahedral and octahedral sheets ranging from 0.2 to 0.6 mol(+) per fu, respectively. M^{n+} represents the charge-compensating counterions in the interlayer of smectites, which is naturally Na^+ , K^+ , Ca^{2+} , or Mg^{2+} . In addition to the permanent layer charge, a variable charge is lying at the edge of the layers associated with amphoteric sites, such as Si-OH and Al-OH .³¹ These pH-dependent edge sites play a significant role in the stability of aqueous clay suspensions.³² On the basis of the theoretical studies on edge site properties of White and Zelazny, Tournassat et al. correlated edge site properties with the chemical character in few Na-saturated dioctahedral smectites.^{33,34} Delavernhe et al. used that approach and showed in a comprehensive characterization that edge site properties also differ within four representative dioctahedral smectites.³⁵ The reason for this was primarily the layer dimension, which determines edge site properties. With regard to the swelling hysteresis of 2:1 layer silicates, the edge site reactivity has thus far received little attention.

The crystalline swelling of 2:1 layer silicates is commonly described by XRD, where the main focus lies in the evolution of the basal-spacing (d_{001}) value under variable rh.^{16–18,36,37} The reversible swelling mechanism is induced by hydration of the exchangeable cations in the interlayer of swellable 2:1 layer silicates leading to discrete water layers, which increase in number from one to three.³⁸ These discrete hydration states are known as monohydrated (1W, layer thickness $\approx 11.6\text{--}12.9\text{ \AA}$), bihydrated (2W, layer thickness $\approx 14.9\text{--}15.7\text{ \AA}$), and trihydrated (3W, layer thickness $\approx 18\text{--}19\text{ \AA}$),^{36,39} with the latter being less common. Many studies have recognized that these hydration states usually coexist in smectites, even under controlled conditions.^{16,39,40} In such a coexistence, the stacking sequences are not periodic and induce aperiodic 001 reflections as well as a peak profile asymmetry at the transition between two hydration states.^{12,16,40} To quantify the amount of different layer types with different hydration states as a function of rh, XRD profile modeling procedures based on the algorithms developed by Drits and Sakharov were developed.⁴¹ The theoretical matrix formalism was extensively described by Drits and Tchoubar, and the fitting strategy was detailed by several authors, such as Ferrage.^{9,42} As a result of the higher layer charge of vermiculites, the interlayer expansion is limited to a 2W state with $d_{001} \approx 14.85\text{ \AA}$.²⁶

Beyond d_{001} spacings of $22\text{ \AA}$, osmotic swelling occurs, in which a competition of repulsive electrostatic forces and long-range attractive von der Waals (vdW) forces governs the interactions between adjacent layers.^{43,44} In this study, we focus on the influence of the particle size and layer charge and how vdW forces contribute to the crystalline swelling process.

The effect of layer charge on the interlayer water arrangement in natural dioctahedral smectites⁴⁵ and synthetic tetrahedral charged trioctahedral smectites (saponites)^{15,16} has been studied using XRD profile modeling. From the relative proportions of hydration states

upon dehydration, they demonstrated the influence of layer charge on smectite hydration. They showed that the smectite layer-to-layer distance decreases with an increasing layer charge because of the enhanced cation-layer electrostatic attraction. XRD studies of homoionic smectites also showed that the basal spacings are larger when the layer charge is located in the octahedral sheet than when it is in the tetrahedral sheet.¹² However, the limitation of XRD is that the proton has an exceptionally small X-ray cross section, and hence, questions regarding the orientation of interlayer water molecules cannot be answered by XRD studies.¹⁷ IR spectroscopy, on the other hand, allows us to probe the clay–water interface on the molecular scale and is the most sensitive tool to measure changes in hydrogen bonding.⁴⁶

The position and intensity of the vibrations of the structural OH groups, which means $\nu(\text{M}^{x+}\text{N}^{y+}\text{O}-\text{H})$ between ≈ 3700 and 3400 cm^{-1} and $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ between 950 and 550 cm^{-1} , are strongly influenced by their immediate chemical environment and allow for the determination of the chemical composition, isomorphous substitution, bonding, and structural changes upon chemical modification of clay minerals.^{46–52} The amount of the $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ vibration bands reflects partial substitutions of octahedral Al^{3+} by Mg^{2+} and Fe^{2+} in dioctahedral smectites. The position of $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ is strongly influenced by the occupancy of the octahedral sheet, and consequently, dioctahedral 2:1 layer silicates absorb in the $950\text{--}800\text{ cm}^{-1}$ region, while $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ of trioctahedral species is shifted to lower wavenumbers in the $700\text{--}600\text{ cm}^{-1}$ region. It was also confirmed that the structural OH groups of trioctahedral smectites are vibrating almost perpendicular to the basal surface and those of dioctahedral smectites are vibrating almost horizontally to the basal surface in the hydrated state.^{53–55}

The major vibrational bands of adsorbed H_2O occur in two regions of mid-infrared (MIR) corresponding to O–H stretching $\nu(\text{O}-\text{H})$ between ≈ 3700 and 2900 cm^{-1} and the H–O–H bending $\delta(\text{H}-\text{O}-\text{H})$ region.²² Analysis of the $\nu(\text{O}-\text{H})$ region is commonly impeded as a result of an overlap of bands produced by the structural OH groups and absorbed water.^{56,57} The $\delta(\text{H}-\text{O}-\text{H})$ region, however, is comparatively free from spectral interference. The $\delta(\text{H}-\text{O}-\text{H})$ band is sensitive to the extent of hydrogen bonding between H_2O molecules,⁵⁸ and hence, it can be used as a molecular probe for water–clay interactions.^{22,59–61} To relate the vibrational properties of clay–water interactions to water uptake, prior studies have coupled spectroscopic methods with quartz crystal or gravimetric microbalance measurements.^{22,61–63} These IR studies showed that the position of the $\delta(\text{H}-\text{O}-\text{H})$ band of adsorbed water changes as a function of the water content. At water contents of $>12\text{ H}_2\text{O}/\text{Na}^+$, $\delta(\text{H}-\text{O}-\text{H})$ was observed at 1635 cm^{-1} for Na^+ -exchanged SWy and SAz.⁶¹ At water contents lower than $6\text{ H}_2\text{O}/\text{Na}^+$, the $\delta(\text{H}-\text{O}-\text{H})$ band shifted to 1625 and 1629 cm^{-1} for Na^+ -saturated SWy and SAz, respectively.⁶¹ At such low water contents, the position of the $\delta(\text{H}-\text{O}-\text{H})$ band consistently shifted to lower wavenumbers, which was also observed using a thin clay film of montmorillonite on a silicon wafer.⁶⁴ Under these conditions, the water molecules are highly polarized by their proximity to the exchangeable cation. Inelastic neutron scattering data^{16,17,23} have also shown that the water molecules coordinated to the interlayer cation are in a constrained environment relative to those in bulk water.²² In addition, a correlation between $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ and the water content can also be found.⁶¹ Sposito et al. observed, at dehydration under vacuum, a change of the intensities of $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$,

which they interpreted as evidence that the OH groups contained within the clay structure itself are influenced by changes in the water content.⁶⁵ Xu et al. quantified the change in molar absorptivity upon lowering the water content and showed the influence of the water content on their band position.⁶¹ Interestingly, $\delta(\text{M}^{x+}\text{--OH--N}^{y+})$ corresponding to the isomorphous substitutions $\delta(\text{Al--OH--Fe})$ and $\delta(\text{Al--OH--Mg})$ were most perturbed by lowering the water content. In this study, we use water as a sensor molecule to describe the OH groups of the octahedral sheet and show that the observed shifts result from a change in the tilting angle.

Up to now, the occurrence of hysteresis is commonly associated with capillary condensation, depending upon the pore structure and adsorption mechanism.^{66,67} For swellable 2:1 layer silicates, the literature suggests different explanations for the origin of the hysteresis (e.g., structural rearrangements^{21,68,69} or phase transitions^{70,71}). Recent studies showed on a molecular scale that the swelling hysteresis has a kinetic origin in terms of a free energy barrier that separates the layered hydrates.^{24,72,73} This free energy barrier is dominated by breaking and formation of hydrogen bonds within water layers.⁷² To the best of our knowledge, no study has described the hysteresis in clay swelling as a function of the chemical and morphological parameters of di- and trioctahedral 2:1 layer silicates.

Here, we will first compare the particle size of the selected materials using the approach described by Delavernhe et al. Additionally, the shape of the micrometer-sized particles will be determined by environmental scanning electron microscopy (ESEM) and XRD. Subsequently, we will investigate the influence of the intrinsic structural heterogeneity of the 2:1 layers on hydration properties using Fourier transform infrared spectroscopy (FTIR), with emphasis on the sorbed water bands. We focus on the transition from 2W to 1W and the influence of layer charge and octahedral composition. The deformation mode of water $\delta(\text{H--O--H})$ reflects the change from a bi- to monohydrated state and can, therefore, be used as a molecular probe for water–smectite and –vermiculite interactions. Because these experiments allow for the collection of IR spectra and water vapor sorption isotherms simultaneously, a relationship between gravimetric sorption and IR data can be made. Additionally, we will employ state-of-the-art calculations using the density functional theory (DFT) to support our experimental findings from FTIR. With the help of first principles calculations, we will explain the different shifting behavior of $\delta(\text{H--O--H})$ related to the differences in surface charge density and octahedral compositions.

MATERIALS AND METHODS

Materials

The 2:1 layer silicates with an equivalent sphere diameter (esd) of either 0.2 or 2 μm were selected concerning their layer charge, charge location (octahedral versus tetrahedral charge), and octahedral composition. BV-M0.2Na was separated from the blended bentonite Volclay (supplied by former Süd-Chemie AG, Germany). SAz-M2Na and SHCa-0.2Na were separated from SAz-1 and SHCa-1,⁷⁴ respectively, of the Source Clays Repository of the Clay Mineral Society. The <2 μm size fraction (esd) of SAz-1 exhibited no impurities, and therefore, the materials were considered to be sufficient for the following experiments. VT-2Na was separated from an industrial vermiculite produced by Thermax, Austria. As a

result of the large grain size of selected vermiculite, it was not possible to separate the 0.2 μm esd fraction. Accordingly, VT-2Na has an esd of $<2 \mu\text{m}$. All samples were Na^+ -exchanged and pretreated according to Steudel and Emmerich.⁷⁵ A detailed description of the chemical pretreatment and separation of the $<2 \mu\text{m}$ fraction of ground vermiculite is given by Steudel et al.⁷⁶ The cation-exchange capacity (CEC) of the resulting materials was measured using the Cu–triethylenetetramine (Cu–trien) method.⁷⁷ The CEC measurements were performed at the resulting pH of ≈ 7 . The mean layer charge (ξ) was determined by the alkylammonium method.^{78–80} For vermiculite, the layer charge distribution was measured on the basis of the extended Olis et al. “shortcut” ($n_c = 12$, and $n_e = 18$).⁸¹ The chemical composition of the samples was determined by X-ray fluorescence (XRF) analysis. The structural formula of the 2:1 layer silicates was then calculated from chemical composition adjusted with respect to layer charge and impurities in the samples.⁸²

XRD Analysis

XRD patterns of the samples were recorded from random powder with a Bruker D8 Advance diffractometer (Bragg–Brentano geometry, $0.02^\circ 2\theta$ step size from 2 up to $80^\circ 2\theta$ with 3 s per step). Cu radiation (Cu $K\alpha$) was implemented. Before the XRD measurements, the powdered samples were stored above a saturated KCl solution ($\approx 86\%$ rh). Equilibration was obtained after 48 h. To compare the chosen starting conditions from IR spectroscopy, the rh of 86% was chosen. For all measurements, the same sample holder was used. The size of the coherent scattering domains (CSDs) was calculated by the Scherrer equation

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where L is the mean crystallite size (average of the CSD thickness in $\text{\AA}$) in the direction normal to the reflecting planes, K is the Scherrer constant (near unity), λ is the wavelength of Cu $K\alpha$ radiation in $\text{\AA}$ and β is the full width half maximum (fwhm) after subtracting the instrumental line broadening and expressed in radians of 2θ . To avoid peak broadening and peak shift effects as a result of low CSDs in the low-angle ($<10^\circ 2\theta$) range, the (003) reflection in the 2W state was used for calculation. Also, the effect of mixed layering on the peak width was eliminated using the (003) reflection in the 2W state.⁸³

Particle Size Characterization

The procedure of Delavernhe et al. was used to study the proportions of the edge sorption sites of the selected 2:1 layer silicates.³⁵ An argon adsorption isotherm at 87 K using a Quantachrome Autosorb-1-MP instrument was measured. The samples were outgassed at 95°C for 12 h under a residual pressure of 0.01 Pa. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) model ($a_{s,\text{BET}}$) in the adsorption range from 0.02 to 0.20 p/p_0 .⁸⁴ As a result of the turbostratic arrangement of the smectite particles, the adsorption of argon concurrently occurs on external and micropore surfaces in this low-pressure region.⁸⁵ As described by Delavernhe et al., we considered a layer stacking model [n layers per stack of diameter d (nm)] with the specific edge surface area [$a_{s,\text{edge}} = 4/(\rho_s d) \times 10^6 \text{ (m}^2/\text{g)}$] and the specific basal area [$a_{s,\text{basal}} = 4/(\rho_s h n) \times 10^6 \text{ (m}^2/\text{g)}$] with $h = 0.96 \text{ nm}$

and $\rho_s = 2700 \text{ kg/m}^3$. An overestimation of about 20% of the layer stacking was considered.³⁵ The determination of the mean weighted equivalent diameter (d) of the coarse VT-2Na was performed with ESEM XL 30 FEG (Philips, Germany). For a representative overview, the perimeter and basal area were measured from 50 single particles. The images were recorded in the gaseous secondary electron (GSE) detector mode at a chamber atmosphere of 0.9 Torr and an acceleration voltage of 20 kV. For BVM-0.2Na, SAz-M2Na, and SHCa-0.2Na, the values for their mean particle size were taken from the literature.^{86,87}

FTIR/Gravimetric Cell

The FTIR spectra were recorded on a Thermo Scientific Nicolet iS 10 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. FTIR spectra were obtained by co-adding 64 scans in the $4000\text{--}650 \text{ cm}^{-1}$ spectral range with a resolution of 4 cm^{-1} . The FTIR spectrometer was controlled using the OMNIC Series software. A 16 cm path length gas cell was placed in the sample compartment of the FTIR spectrometer. The cell was fitted with two $50 \times 3 \text{ mm}$ ZnSe windows and sealed with O-rings. The gas cell was connected to a Cahn microbalance. For all experiments, the flow rate was constant at 100 standard cubic centimeter per minute (sccm). To regulate the wet and dry N_2 flow and to adjust the rh, two MKS mass flow controllers were used. The rh was monitored online with a Vaisala model HMP35A humidity sensor (Figure 1).

The sample film was deposited at the ZnSe window from a sonicated dispersion (1 mg/1 mL H_2O) and dried at $60 \text{ }^\circ\text{C}$ ($\approx 12 \text{ h}$) in a vacuum oven. Additionally, a “second” powder sample ($\approx 10 \text{ mg}$) was placed in the weighing arm of the Cahn microbalance (Figure 1). Both the film and powder samples were subjected to the following treatments: Equilibration of the sample at $85 \pm 1\%$ rh for 12 h. The mass of the sample was recorded simultaneously from the microbalance, and the spectra were collected every 5 min. After equilibration at $85 \pm 1\%$ rh, the rh was decreased stepwise from 85 to 0% (nominal). The increments were set to 10% rh from 80 to 40% rh and then 5% rh between 40 and 0% rh by controlling the relative proportions of the dry N_2 and H_2O -saturated N_2 gas. To ensure equilibration of the sample, the rh was kept for 2 h at each step. For the adsorption and to examine hysteresis, the rh was again increased stepwise from 0 to $85 \pm 1\%$ following the same data collection as in the desorption branch. After the recording of the water vapor desorption and adsorption isotherm, the sample was dried under dry N_2 purging for 48 h. All spectra were recorded at $25 \text{ }^\circ\text{C}$.

The dry mass of the sample was determined by plotting the intensity of $\delta(\text{H-O-H})$ against the mass of the sample and extrapolating the plot to zero band intensity.²² To avoid the presence of different types of interlayer H_2O , $\delta(\text{H-O-H})$ intensities were only used at low rh. Then, the water content of the samples was calculated from each FTIR spectrum in dependence of rh. The amount of H_2O per Na^+ was calculated using the measured CEC as a structural intrinsic property of the 2:1 layer silicates. The CEC measurement uncertainties were set to 2% of the measured values, and therefore, the error bars were calculated for $\text{H}_2\text{O}/\text{Na}^+$.

Computational Chemistry

The total energy and ground-state structure calculations in the present work were performed using DFT as implemented in the Vienna *ab initio* simulation program (VASP).⁹⁰ The electron–ion interaction was treated within the projector-augmented wave (PAW) method.⁹¹ The valence electron wave functions were expanded into plane waves up to a kinetic energy cutoff of 360 eV. The Brillouin zone sampling was performed with a $1 \times 1 \times 1$ mesh of Monkhorst–Pack k points.⁹² The electron–electron exchange and correlation (XC) energy was approximated within the generalized-gradient approximation (GGA), using the XC potential developed by Perdew et al.⁹³ The PW91 functional was found to describe the structure and energetics reliably, especially of hydrogen-bonded water molecules.^{94–96} The optimization of the atomic coordinates and unit cell size/shape for the bulk materials was performed via a conjugate gradient technique, which uses the total energy and the Hellmann–Feynman forces on the atoms and stresses on the unit cell. In addition to the k -point density, the convergence in calculations of clay minerals was also dependent upon the thickness of the mineral layer. For every atomic configuration, we checked convergence by running a series of calculations with different layer thicknesses. The thermodynamic minimum was then constructed by solving the Birch–Murnaghan equation of state.

The stoichiometric description of the supercells is given in Table 1. MMT0.25 and MMT0.5 are described by Emmerich et al.³⁸ The two dioctahedral models were chosen to cover the range of the layer charge per fu of the selected natural materials. The model system for hectorite is HCT0.25 as a trioctahedral structure.

RESULTS AND DISCUSSION

Mineralogical and Chemical Characterization

BV-M0.2Na and SAz-M2Na were identified as dioctahedral smectite by a d_{060} at 1.50 Å. SHCa-0.2Na is a trioctahedral smectite, which was confirmed by the observed d_{060} peak at 1.52 Å on the XRD pattern of the powdered sample (see Figure SII of the Supporting Information).⁹⁷ VT-2Na was classified as a trioctahedral 2:1 layer silicate and characterized by Steudel et al.⁷⁶ BV-M0.2Na has a lower mean layer charge [0.26 mol(+)/fu] with substitution in both the octahedral and tetrahedral sheets and exhibits a lower CEC [89 cmol(+)/kg] compared to SAz-M2Na [CEC = 130 cmol(+)/kg] with almost no tetrahedral charge and a mean layer charge of 0.37 mol(+)/fu. SHCa-0.2Na has a mean layer charge of 0.25 mol(+)/fu, a CEC of 76 cmol(+)/kg, and Li^+ substitutions in the octahedral sheet. The mean layer charge from both montmorillonites and hectorite was derived from a heterogeneous layer charge distribution of BV-M0.2Na, SAz-M2Na, and SHCa-0.2Na (see Figure SI2 of the Supporting Information). In contrast to smectite samples, VT-2Na required a longer reaction time for the complete exchange with alkylammonium (>1 month), and thus, the rapid mean layer charge estimation was applied.⁸¹ The d_{001} peak observed at 22.8 Å in the pattern of the alkylammonium-exchanged sample (chain length $n_c = 12$) showed a low-charged vermiculite with a layer charge of 0.70 mol(+)/fu, whereas the basal spacing $d_{001} = 32.8$ Å for $n_c = 18$ indicated the presence of high-charged domains.⁷⁶ A CEC of 159 cmol(+)/kg for VT-2Na was measured. The negative charge is mainly in the tetrahedral layer as a result of the exchange of Si^{4+} by Al^{3+} .

BV-M0.2Na contains 2% cristobalite,³⁵ and VT-2Na contains 14% phlogopite and 2% calcite.⁷⁶ In SAz-M2Na and SHCa- 0.2Na, no impurities were found. With 38% tetrahedral charge of total charge, BV-M0.2Na was classified as low-charged beidelitic montmorillonite, whereas SAz-M2Na was classified as medium-charged montmorillonite.⁹⁸

Structural formulas were $\text{Na}_{0.26}(\text{Si}_{3.90}\text{Al}_{0.10}) - (\text{Al}_{1.61}\text{Fe}_{0.19}\text{Mg}_{0.22})\text{O}_{10}(\text{OH})_2$ for BV-M0.2Na, $\text{Na}_{0.37}\text{Si}_4(\text{Al}_{1.41}\text{Fe}_{0.08}\text{Mg}_{0.58})\text{O}_{10}(\text{OH})_2$ for SAz-M2Na, $\text{Na}_{0.24}\text{Si}_4(\text{Mg}_{2.61}\text{Li}_{0.315}\text{Al}_{0.055}\text{Fe}_{0.02})\text{O}_{10}(\text{OH},\text{F})_2$ for SHCa- 0.2Na, and $\text{Na}_{0.70}(\text{Si}_{3.04}\text{Al}_{0.96})(\text{Mg}_{2.65}\text{Fe}_{0.31}\text{Al}_{0.01})\text{O}_{10}(\text{OH})_2$ for VT-2Na.

Particle Size Characterization—For VT-2Na, individual particles were easily identified by ESEM, and the perimeter and basal area could be measured directly. The particle size distribution of VT-2Na ranged from 0.934 to 2.588 μm equivalent diameter, with a mean weighted equivalent diameter of 1.73 μm (see Figure SI5 of the Supporting Information). For single particles, the mean weighted equivalent diameter for BVM0.2Na was measured to be 277 nm. For the two other smectite samples, the particle size ranged from 100 to 300 nm (Figure 2).^{86,87} Considering the layer stacking model from Delavernhe et al.,³⁵ between 30 and 50 layers per stack were estimated for BV-M0.2Na. For SAz-M2Na and SHCa-0.2Na, around 6–8 layers per stack were assessed. For VT-2Na, 20–30 layers per stack were estimated. The resulting $a_{\text{s,edge}}$ contribution ranged from 5 to 30% for the smectite samples. In contrast, VT-2Na has a noticeable lower edge site contribution of 2–4% (Table 2).

To support our results from gas adsorption analysis and to determine the shape of the selected powder particles after equilibration at 85% rh, peak shape analysis of the XRD patterns was performed. Differences in peak width resulted from a change of the size of the CSD. For smaller particles, the width of the XRD peaks became broader and was calculated by the Scherrer equation. As a result of the turbostratic arrangement of the smectite particles, the average CSD thickness of the smectite samples was clearly found below the measured particle size (Table 2). In contrast, the layers per stack estimated from the CSD of VT-2Na was above the values calculated from $a_{\text{s,BET}}$, which resulted from its ordered stacking sequences of layers.

Initial Hydration State and Dry Mass—For the samples equilibrated at $\approx 86\%$ rh, d_{001} spacings for BV-M0.2Na, SAz-M2Na, and VT-2Na were 15.3, 15.5, and 14.85 Å, respectively, corresponding to the 2W hydration state (see Figures SI3 and SI4 of the Supporting Information). d_{001} of SHCa-0.2Na was observed at 15.8 Å, indicating a beginning of the transition into the 3W state (see Figure SI3 of the Supporting Information). The lowest humidity achieved with the FTIR/gravimetric cell was 2% rh. Even at this low rh value, the FTIR spectra showed that some H₂O was retained by the sample (see Figure SI6 of the Supporting Information). The dry mass of the sample was obtained by plotting the intensity of the $\delta(\text{H}-\text{O}-\text{H})$ band against the gravimetric mass of the sample. On the basis of the measured CEC, the water content in H₂O per Na⁺ was calculated.

Water Vapor Sorption Isotherms—The calculated water content was correlated to each rh step (Figure 3). Continuous decreasing of the rh resulted in reducing the number of H₂O per Na⁺ (Figure 3). At 86% rh, a water content of 12.3 H₂O/Na⁺ was calculated for BV-

M0.2Na. First, a nearly linear decrease of the water content was observed from a rh of 85 to 50% with a water content ranging from 12.3 to 9.2 H₂O/Na⁺. At 43% rh, the water content decreased significantly to 7.5 H₂O/Na⁺. Subsequently, an almost linear decrease of the water content was observed again (from 35 to 8% with H₂O/Na⁺ ranging from ≈7 to 4), followed by a drop with a resulting water content of 3 H₂O/Na⁺ at 2% rh. The adsorption of water vapor proceeded differently. Three different slopes could be identified in water adsorption. At low rh (from 2 to 40%), a nearly linear increase could be observed. The correlated water content ranged from 3 to 4 H₂O/Na⁺. The first change of the slope in the adsorption branch was observed at 50% rh. Here, the water content changed from 4 to 7 H₂O/Na⁺. At 70% rh, the slope changed significantly and reached a water content of 10.5 H₂O/Na⁺ at 85% rh.

The desorption branch of the isotherm of SAz-M2Na exhibited a similar shape compared to the isotherm of BVM0.2Na. At 85% rh, a water content of 13 H₂O/Na⁺ was calculated for SAz-M2Na. First, the water content decreased nearly linear down to 9 H₂O/Na⁺ at 50% rh. A transition point at ≈40% rh was observed, followed by a linear decrease of the water content (from 33 to 11% rh with H₂O/Na⁺ ranging from ≈7 to 6). At < 10% rh, a drop in the water content was observed. The lowest water content was 2 H₂O/Na⁺ at 2% rh. The adsorption branch of the water vapor sorption isotherm of SAz-M2Na proceeded differently, and hence, hysteresis could be observed. A significantly larger hysteresis was observed for BV-M0.2Na compared to SAz-M2Na. Between 2 and 18% rh, a first nearly linear increase in the water content could be observed, followed by a change in slope at ≈20% rh and correlated water content of 4 H₂O/Na⁺. A second change of slope in the adsorption branch was observed at 35% rh. Here, the water content changed from 5 to 9 H₂O/Na⁺. At ≈60% rh, the gradient changed significantly. At 84% rh, the highest water content of 12.5 H₂O/Na⁺ was achieved.

The hysteresis observed on the water vapor sorption isotherm for SHCa-0.2Na was similar to those of the two dioctahedral samples. At 85% rh, a water content of 12.4 H₂O/Na⁺ was calculated for SHCa-0.2Na. Only small changes in the water content could be observed at high rh (between 85 and 70%). Then, a nearly linear decrease of the water content was observed from a rh of ≈60 to 40% with a water content ranging from ≈11 to 7 H₂O/Na⁺. Subsequently, an almost linear decrease of the water content with a changed gradient was observed from ≈6 to 3 H₂O/Na⁺ between ≈40 and 10% rh. Similar to the two dioctahedral smectites, on the desorption branch of SHCa-0.2Na, a drop in the water content was observed at <10% rh with a minimum water content of 1 H₂O/Na⁺ at 2% rh. In the case of water adsorption, a marked change in the gradient at ≈50% rh could be observed. In the beginning, the water content increased from ≈1 to 5 H₂O/Na⁺ (from 3 to 40% rh) and then from ≈6 to 11 H₂O/Na⁺.

In contrast, on the desorption branch of the isotherm of VT- 2Na, two ranges and a clear transition could be identified: from 8 to 6 H₂O/Na⁺ and second from 4 to 2 H₂O/Na⁺. The transition from these two nearly linear ranges was observed between ≈40 and 30% rh. Up to 25–30% rh, the adsorption of water vapor followed the same water content as in the desorption branch. From 30% rh, the adsorption of water vapor proceeded differently, and hence, hysteresis was observed. However, the extent of hysteresis is noticeably smaller compared to the smectite samples (Figure 3).

For theoretical models of dioctahedral smectites with only one layer charge, discrete hydration states were formed upon desorption and adsorption of water.³⁸ In contrast, the selected natural smectites exhibit a heterogeneous layer charge distribution (see Figure SI2 of the Supporting Information), and accordingly, different hydration states can coexist even under controlled conditions. As a result of this coexistence, we observed ranges in the desorption and adsorption of water vapor with a slightly increasing slope. In contrast, high-charged VT-2Na exhibits a nearly monodisperse layer charge, and accordingly, dehydration steps with a clear transition between 6 and 4 H₂O/Na⁺ could be assigned. These transitions could not be clearly identified in the smectite isotherms. However, our results indicated that, along these water vapor sorption isotherms from the montmorillonite and hectorite samples, at least two hydration states (2W and 1W) with different hydration dynamics could be observed. On the desorption branch, water contents ranging from 13 to 8 H₂O/Na⁺ and from 8 to 4 H₂O/Na⁺ correspond to domains dominated by 2W and 1W states (Figure 3C). Both adsorption branches of the low-charged samples (BV-M0.2Na and SHCa-0.2Na) showed a noticeable change in the gradient at 50% rh, indicating the transition from the 1W to 2W state. For higher charged SAz-M2Na, the transition from the 1W to 2W state shifted to a lower water content of 3 H₂O/Na⁺. On the desorption branch of all smectite isotherms, a marked change in the gradient was observed at <10% rh, indicating the transition from 1W to 0W. Reaching a water content below the 1W state also caused hysteresis at low rh, which was not observed for VT-2Na. Whereas hysteresis was observed over the entire isothermal range of the smectites, the isotherm of VT-2Na only showed hysteresis in the transition from 1W to 2W (Figure 3D). These findings indicated that hysteresis is a function of the layer charge distribution and the minimum achieved water content. In addition, the particle size of the selected materials revealed that the extent of hysteresis also depends upon the morphological character because a larger hysteresis was observed for coarser BV-M0.2Na compared to the other smectite samples. As a result, increasing the edge site proportion resulted in an increased hysteresis.

IR Spectroscopy—To examine the relationship between the desorption and adsorption isotherms and the spectroscopic data, all isotherms were compared to the corresponding IR data. For each data point shown in Figure 3, a corresponding FTIR spectrum was obtained using the FTIR/gravimetric cell described above (Figure 1). The position of the $\delta(\text{H-O-H})$ band was plotted in Figure 4 as a function of the water content. In accordance with earlier studies, our IR measurements showed that the position of the $\delta(\text{H-O-H})$ band of adsorbed water changes as a function of the water content.^{23,65} The wavenumber from $\delta(\text{H-O-H})$ provides information on the chemical structure of H₂O. The shifting of $\delta(\text{H-O-H})$ to a lower wavenumber indicated an ordered arrangement of the H₂O molecules at water contents of <4 H₂O/Na⁺. Our FTIR results also showed that the shift of the $\delta(\text{H-O-H})$ band was also influenced by the layer charge, charge location, and octahedral substitutions (Figure 4).

First, two montmorillonite samples with a different layer charge and approximately the same charge distribution will be compared. Second, with regard to its (de)hydration behavior, the exceptional position of vermiculite with a higher layer charge and specific charge distribution compared to the other studied samples will be discussed. Finally, di- and trioctahedral samples with about the same layer charge will be compared.

Influence of Layer Charge—SAz-M2Na and BV-M0.2Na are dioctahedral smectites with a different layer charge. In comparison to SAz-M2Na, $\delta(\text{H-O-H})$ of low-charged BVM0.2Na was observed at higher wavenumbers along the water vapor sorption isotherm. With the start of our experiment in the 2W state, $\delta(\text{H-O-H})$ was similar to liquid water for BVM0.2Na (Figure 4). For BV-M0.2Na, $\delta(\text{H-O-H})$ appeared at wavenumbers of $>1640 \text{ cm}^{-1}$ at water contents of $>6 \text{ H}_2\text{O/Na}^+$ and shifted to 1627 cm^{-1} by lowering the water content down to $2 \text{ H}_2\text{O/Na}^+$. By adsorption of water vapor, $\delta(\text{H-O-H})$ followed the same wavenumber steps with σ_x^2 of $\pm 2 \text{ cm}^{-1}$. A similar trend could be observed for SAz-M2Na; however, the wavenumber for $\delta(\text{H-O-H})$ was 6 cm^{-1} lower for water contents of $>6 \text{ H}_2\text{O/Na}^+$ compared to BV-M0.2Na. At water contents of $<6 \text{ H}_2\text{O/Na}^+$, $\delta(\text{H-O-H})$ shifted to 1618 cm^{-1} . σ_x^2 for SAz-M2Na was observed to be $\pm 3 \text{ cm}^{-1}$ (Figure 4).

These results indicated that increasing the layer charge from 0.26 to 0.37 per fu resulted in a highly ordered arrangement of H_2O molecules, which could be observed as a lower wavenumber position of $\delta(\text{H-O-H})$ (Figure 4). The effect of the wavenumber position of the $\delta(\text{H-O-H})$ band could also be derived from the two dioctahedral models in panels A and B of Figure 5.

Figure 5A shows a side view rotated 30° around $[001]$ of MMT0.25 and depicts a 1W state with $4 \text{ H}_2\text{O/Na}^+$. Three water molecules have a bond angle between 107.5° and 108.3° , showing the strongly polarized character in the 1W state. The fourth water molecule exhibits a lower bond angle of 105.5° , which indicates the start of reorientation. For MMT0.25, there are no water–water interactions at this stage of the hydration (Figure 5A), while at $4 \text{ H}_2\text{O/Na}^+$ for MMT0.5, water interacts with the basal surface as well with other adjacent water molecules by forming hydrogen bonds (Figure 5B). The picture clearly shows that, for the higher charged model MMT0.5 at $4 \text{ H}_2\text{O/Na}^+$, the interlayer cation–cation distances are reduced to $6.26 \text{ \AA}$ compared to the MMT0.25 model with $8.98 \text{ \AA}$ (panels A and B of Figure 5).

As a consequence, the interlayer cations are forced to move out of the midplane (Figure 5B) because the hydration of Na^+ with its high hydration enthalpy is, for water molecules, the most attractive interaction. As a result, the water molecules are in a constrained environment relative to those of MMT0.25 at $4 \text{ H}_2\text{O/Na}^+$, and hence, a lower wavenumber position of $\delta(\text{H-O-H})$ was observed for the higher layer charge.

Na^+ -Saturated Vermiculite—The shifting of $\delta(\text{H-O-H})$ from VT-2Na followed the same form as its water vapor sorption isotherm (Figures 3 and 4). At a water content between 8 and $6 \text{ H}_2\text{O/Na}^+$, a gradual shift from 1646 to 1638 cm^{-1} was observed for $\delta(\text{H-O-H})$, followed by a sharp drop in the water content from 6 to $4 \text{ H}_2\text{O/Na}^+$. Between 3 and $4 \text{ H}_2\text{O/Na}^+$, $\delta(\text{H-O-H})$ shifted from 1637 to 1631 cm^{-1} . σ_x^2 for VT-2Na was observed to be $\pm 1 \text{ cm}^{-1}$. The transition of these two stages was found on the intersection point of SAz-M2Na and SHCa-0.2Na.

The comparison of BV-M0.2Na and SAz-M2Na clearly showed that increasing the layer charge from 0.25 to 0.37 per fu resulted in an ordered arrangement of water molecules. VT-

2Na exhibits an even larger layer charge as SAz-M2Na, but a higher wavenumber of $\delta(\text{H}-\text{O}-\text{H})$ was observed. These results indicated that increasing the layer charge first resulted in an ordered arrangement of H_2O molecules. However, further increasing of layer charge turned into seemingly disordering.

We explain this by an additional disorder, in which the increased amount of Na^+ is brought into the water layer, resulting from the formation of the hydration shells. As a result of the increased layer charge, the interlayer cations with their hydration shell move out of the midplane (compare Figure 5B). Considering the interlayer cations as small point defects in the water layers, the interaction of water molecules behaves differently compared to the formation in an electric double layer model. The electronic structure calculations of MMT0.25 (Figure 5A) and MMT0.5 (Figure 5B) showed that the water layers are corresponding to a high chemical potential of Na^+ approaching the value of bulk water, which is in accordance with our experimental findings.

Influence of Octahedral Substitutions—The shift of $\delta(\text{H}-\text{O}-\text{H})$ of low-charged trioctahedral SHCa-0.2Na followed the same shape as the two dioctahedral smectite samples and intersected at $\approx 5 \text{ H}_2\text{O}/\text{Na}^+$ with the line of SAz-M2Na (Figure 4). Higher wavenumbers were observed above the point of intersection, and lower wavenumbers were observed below a water content of $5 \text{ H}_2\text{O}/\text{Na}^+$. $\delta(\text{H}-\text{O}-\text{H})$ shifted from 1632 cm^{-1} ($12 \text{ H}_2\text{O}/\text{Na}^+$) to 1619 cm^{-1} , which was comparable to the shift of $\delta(\text{H}-\text{O}-\text{H})$ from higher charged SAz-M2Na (from 1636 to 1618 cm^{-1}). In a previous study,⁶⁴ we showed that, at low water contents ($<3 \text{ H}_2\text{O}/\text{Na}^+$), the hydration shell around each Na^+ coincides with the surface/water interaction via hydrogen bonds and no water–water interactions exist for a low charged dioctahedral montmorillonite. The same can be observed for a trioctahedral hectorite. At a water content of $4 \text{ H}_2\text{O}/\text{Na}^+$, $\delta(\text{H}-\text{O}-\text{H})$ from SHCa-0.2Na was observed at 1625 cm^{-1} , while $\delta(\text{H}-\text{O}-\text{H})$ from BV-M0.2Na was observed at 1630 cm^{-1} (Figure 4). These findings implied that a trioctahedral structure leads to stronger interactions between interlayer water and the tetrahedral sheet compared to a dioctahedral composition. The calculation of HCT0.25 confirmed this result. Figure 5C shows an energetically favorable model of HCT0.25 and represents a 1W state with $4 \text{ H}_2\text{O}/\text{Na}^+$. The water molecules have an average bond angle of 107.5° and, accordingly, even larger compared to those of MMT0.25. As a result, a lower wavenumber position of $\delta(\text{H}-\text{O}-\text{H})$ was observed for SHCa-0.2Na. Finally, the calculation of the model HCT0.25 confirmed that the structural O–H groups of trioctahedral hectorite are vibrating almost perpendicular to the planar surface (Figure 5).

As a final point, we use water as a sensor molecule to describe the OH groups of the octahedral sheet and show that the observed shifts result from a change in the tilting angle (Figure 6).

For BV-M0.2Na, $\delta(\text{Al}-\text{OH}-\text{Al})$ and $\delta(\text{Al}-\text{OH}-\text{Mg})$ appeared at 920.6 and 846.4 cm^{-1} at water contents of $>6 \text{ H}_2\text{O}/\text{Na}^+$ and shifted to 921.3 and 848.6 cm^{-1} , respectively, by lowering the water content down to $2 \text{ H}_2\text{O}/\text{Na}^+$. By adsorption of water vapor, $\delta(\text{Al}-\text{OH}-\text{Al})$ and $\delta(\text{Al}-\text{OH}-\text{Mg})$ followed the same wavenumber steps with σ_y^2 of ± 0.28 and 0.74 cm^{-1} (Figure 6A). A similar trend could be observed for SAz-M2Na; however, the wavenumber

for $\delta(\text{Al-OH-Al})$ and $\delta(\text{Al-OH-Mg})$ was observed at 915.3 and 840.2 cm^{-1} , respectively, for water contents of $>6 \text{ H}_2\text{O/Na}^+$. At water contents of $<6 \text{ H}_2\text{O/Na}^+$, $\delta(\text{Al-OH-Al})$ and $\delta(\text{Al-OH-Mg})$ shifted to 916.0 and 842.1 cm^{-1} . σ_y^2 for SAz-M2Na was observed to be ± 0.1 and 0.58 cm^{-1} (Figure 6B). For the trioctahedral hectorite SHCa-0.2Na, $\delta(\text{Mg-OH-Mg})$ was observed at 652 cm^{-1} for water contents of $>6 \text{ H}_2\text{O/Na}^+$. At water contents of $<6 \text{ H}_2\text{O/Na}^+$, $\delta(\text{Mg-OH-Mg})$ shifted to 659 cm^{-1} (Figure 6C).

Both observed shifts of the dioctahedral smectites are in good correlation with the experimental findings of Xu et al.⁶¹ Small shifts of $<2 \text{ cm}^{-1}$ wavenumbers were observed for the structural OH groups upon changes in the H_2O content. Least affected was the $\delta(\text{Al-OH-Al})$ band corresponding to OH groups with no isomorphous substitution within the 2:1 layer. The band position of $\delta(\text{Al-OH-Mg})$ was more perturbed by changing the water content. In comparison to the small shifts of the dioctahedral smectites, a shift of 7 cm^{-1} wavenumbers was observed for $\delta(\text{Mg-OH-Mg})$.

The difference of the shift can be correlated to the tilt of the hydroxyl group incorporated in the octahedral sheet. In panels A and B of Figure 5, one can easily see that hydroxyl groups connected to aluminum are tilted very strongly in comparison to the [001] surface direction. This results in a low dipole moment upon this direction and is the reason for a small interaction with any water molecule. In other words, $\delta(\text{Al-OH-Al})$ does not shift a lot as a function of the water content. In contrast, $\delta(\text{Mg-OH-Mg})$ shifts a lot as a function of the water content. The reason is a strong interaction with the interlayer water, resulting from a very strong dipole moment of these hydroxyl groups in the [001] direction (this can be seen in Figure 5C).

The layer dimension determines the edge site properties. Di- and trioctahedral smectites display structural heterogeneities and variation in size. The particle size of VT-2Na is much larger, which was confirmed by the average CSD thickness, and accordingly, the coarser material had a noticeable lower edge site contribution. As proposed in earlier studies on osmotic hydrates,⁴⁴ the smaller basal spacings in 2W and 1W states for VT-2Na result from a larger number of layers per stack and, hence, a higher contribution of long-range vdW forces. Domains in the desorption and adsorption of water vapor of the smectite samples with a slightly increasing slope were explained by a heterogeneous layer charge distribution, which enables the coexistence of different hydration states even under controlled conditions. We also showed that hysteresis is a function of the layer charge distribution, the achieved water content, and the particle size with resulting edge site contribution. Increasing the edge site proportions resulted in an increased hysteresis. The findings from the experimental FTIR/gravimetric analysis showed that the transition from 2W to 1W and backward is visible using IR spectroscopy. The transition (forward and backward) from the bi- to monohydrated state is dominated by breaking and formation of hydrogen bonds within water layers. The shift of $\delta(\text{H-O-H})$ to lower wavenumbers was correlated to an increase of water-surface attraction. This shifting of $\delta(\text{H-O-H})$ was also influenced by the layer charge and octahedral substitutions. As the layer charge increases from 0.26 to 0.37 per fu, the wavenumber of $\delta(\text{H-O-H})$ decreases, corresponding to increased interactions from interlayer water and the surface of the tetrahedral sheet. The same increased water-surface

attractions were observed for Li^+ for Mg^{2+} substitutions in the octahedral sheet compared to Mg^{2+} for Al^{3+} substitutions. Increasing the layer charge above 0.5 per fu resulted in a disordered interlayer water arrangement similar to those of bulk water, and accordingly, a higher wavenumber of $\delta(\text{H}-\text{O}-\text{H})$ for VT-2Na was observed. This effect was explained by considering Na^+ as small point defects in the water layers. The hydration of Na^+ with its high hydration enthalpy is, for water molecules, the most attractive interaction.

CONCLUSION

The purpose of this study was to investigate the influence of the structural heterogeneity of the silicate layers on hydration properties using FTIR, with emphasis on the sorbed H_2O bands. In the first part of this paper, the layer dimension and stacking were determined, which clarified the differences in edge site proportions of the selected 2:1 layer silicates. Whereas hysteresis was observed over the entire isothermal range of the smectites, the isotherm of VT-2Na only showed hysteresis in the transition from the 1W to 2W state. Hysteresis is a function of the layer charge distribution and the achieved water content. The particle size of the selected materials revealed that the extent of hysteresis also depends upon the morphological character. Increasing the edge site contribution resulted in an increased hysteresis.

The position of the $\delta(\text{H}-\text{O}-\text{H})$ band reflected the change from the 1W to 2W state and can, therefore, be used as a molecular probe for water–smectite and water–vermiculite interactions. With the help of first principle calculations, we could explain the different shifting behavior of $\delta(\text{H}-\text{O}-\text{H})$ related to the differences in surface charge density and octahedral compositions. At low water contents ($<4 \text{ H}_2\text{O}/\text{Na}^+$), interlayer water and the tetrahedral sheet form strong bindings via hydrogen bonds, which was observed as a shifting of $\delta(\text{H}-\text{O}-\text{H})$ to lower wavenumbers. At a layer charge of 0.37 per fu, strong interactions were clearly more distinct because we observed a larger shift for $\delta(\text{H}-\text{O}-\text{H})$ from SAz-M2Na compared to BV-M0.2Na. Low-charged trioctahedral SHCa-0.2Na had an equivalent shift as SAz-M2Na, which indicates that Li^+ for Mg^{2+} substitutions in the octahedral sheet compared to Mg^{2+} for Al^{3+} substitutions lead to strong interactions from interlayer water and the tetrahedral sheet. An interlayer water arrangement similar to those of bulk water was found for VT-2Na because the increased layer charge is followed by an additional disorder considering Na^+ as small point defects in the water layers. In addition, a correlation between $\delta(\text{M}^{x+}-\text{OH}-\text{N}^{y+})$ and the water content can also be found. Least affected was the $\delta(\text{Al}-\text{OH}-\text{Al})$ band corresponding to OH groups with no isomorphous substitution within the 2:1 layer. The band position of $\delta(\text{Mg}-\text{OH}-\text{Mg})$ was most perturbed by changing the water content. The reason is a strong interaction with the interlayer water, resulting from a very strong dipole moment of these hydroxyl groups in the [001] direction. As a result, the water arrangement in 2:1 layer silicates depends upon many factors, such as the structural intrinsic properties (e.g., layer charge and octahedral composition) and the layer dimension with resulting edge site proportions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic drawing of the FTIR/gravimetric cell, according to Johnston et al.^{88,89}

Figure 2.

Specific surface area of quasi-crystalline layer stacks as a function of the diameter, stack of layers, and $a_{s,edge}$ (dashed line), according to Delavernhe et al. Gray boxes are the selected 2:1 layer silicates with a representative area for the particle size diameter.

Figure 3.

Water vapor sorption isotherm from (A) BV-M0.2Na, (B) SAz-M2Na, (C) SHCa-0.2Na, and (D) VT-2Na at 25 °C. The precision of the humidity sensor was determined to be $\pm 1\%$ rh and, therefore, to be neglected. Arrows indicate the direction of the experiment.

Figure 4.

Evolution of $\delta(\text{H-O-H})$ as a function of the water content. An error bar (σ_x^2) for the band position of $\delta(\text{H-O-H})$ was observed for each sample. σ_x^2 was based on the highest possible variation upon desorption and adsorption of water vapor during the experiment.

Figure 5.

Side view rotated 30° around [001] on energetically favorable (A) $[\text{Na}_1(\text{Si}_{16})(\text{Al}_7\text{Mg}_1)\text{O}_{40}(\text{OH})_8] \times 4 \text{H}_2\text{O}$, (B) $[\text{Na}_2(\text{Si}_{16})(\text{Al}_6\text{Mg}_2)\text{O}_{40}(\text{OH})_8] \times 8 \text{H}_2\text{O}$, and (C) $[\text{Na}_1(\text{Si}_{16})(\text{Mg}_{11}\text{Li}_1)\text{O}_{40}(\text{OH})_8] \times 4 \text{H}_2\text{O}$ interfaces. Blue spheres represent Si; red spheres represent O of MMT0.25, MMT0.5, and HCT0.25; and white spheres represent H. (A and B) Mg defect is represented by a cyan sphere inside the dioctahedral sheet, and pink spheres represent Al. (C) Li defect is represented by a white sphere inside the trioctahedral sheet, and Na is represented as a yellow sphere.

Figure 6.

Evolution of $\delta(\text{M}^{\text{x}+}-\text{OH}-\text{N}^{\text{y}+})$ as a function of the water content of (A) BV-M0.2Na, (B) SAz-M2Na, and (C) SHCa-0.2Na. An error bar (σ_y^2) for the band position of $\delta(\text{M}^{\text{x}+}-\text{OH}-\text{N}^{\text{y}+})$ was observed for each sample. σ_y^2 was based on the highest possible variation upon desorption and adsorption of water vapor during the experiment.

Table 1

Stoichiometric Description of the Modeled Supercells with Solely Octahedral Charges

stoichiometric description	layer charge per fu	abbreviation
$[\text{Na}_1(\text{Si}_{16})(\text{Al}_7\text{Mg}_1)\text{O}_{40}(\text{OH})_8]$	0.25	MMT0.25
$[\text{Na}_2(\text{Si}_{16})(\text{Al}_6\text{Mg}_2)\text{O}_{40}(\text{OH})_8]$	0.5	MMT0.5
$[\text{Na}_1(\text{Si}_{16})(\text{Mg}_{11}\text{Li}_1)\text{O}_{40}(\text{OH})_8]$	0.25	HCT0.25

Table 2

Ar Gas Sorption Parameters, Diameter of Single Particles, Layers per Stack Estimated by a_{sBET} , Edge Surface Area Estimation, Mean CSD Thickness, the Basal Spacing d_{003} at 2W State, and Resulting Layers per Stack of the Selected 2:1 Layer Silicates

sample	a_{sBET} (m ² /g)	range of particle diameter (nm)	layers per stack, n estimated by a_{sBET}	$a_{\text{s,edge}}$ (%)	L (Å)	$3d_{003}$ at 85% rh (Å)	layers per stack, n
BV-M0.2Na	31	150–400	30–50	20–30	80 ± 10	15.35	5–6
SAz-M2Na	112	100–300	6–8	5–15	70 ± 10	15.40	4–5
SHCa-0.2Na	130	100–300	6–8	5–15	50 ± 10	15.48	3–4
VT-2Na	35	1000–2500	20–30	2–4	500 ± 30	14.85	32–36