Continuous water adsorption states promoted by Ni$^{2+}$ confined in a smectite

M. A. S. Altoé$^{1,2}$, L. Michels$^{2,*}$, E. C. dos Santos$^{2,3}$, R. Droppa Jr$^{4}$, G. Grassi$^{1}$, L. Ribeiro$^{5}$, K.D. Knudsen$^{6,2}$, H. N. Bordallo$^{3,7}$, J. O. Fossum$^{2,*}$, G. J. da Silva$^{1}$

$^1$Instituto de Física, Universidade de Brasília, 70.919-970, Brasília – DF, Brasil

$^2$Department of Physics, Norwegian University of Science and Technology – NO-7495, Trondheim, Norway

$^3$Niels Bohr Institute, University of Copenhagen, 2100, Copenhagen, Denmark

$^4$Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09.210-580, Santo André – SP, Brasil

$^5$Unidade Universitária de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, 75.132-903, Anápolis – GO, Brasil

$^6$Physics Department, Institute for Energy Technology, IFE, Kjeller, Norway

$^7$European Spallation Source, Tunavägen 24, 22100, Lund, Sweden

*Correspondences: leander.michels@ntnu.no

jon.fossum@ntnu.no

Abstract:

The water adsorption isotherms of the smectite Ni-fluorohectorite have been obtained from the relative humidity dependence of X-ray diffraction intensities, and it was observed that the transitions between the stable hydration states are continuous; a behavior which is markedly different from previous studies of Na-fluorohectorite and Li-fluorohectorite smectite. It was also observed that the environmental history of the clay samples is important for the detailed behavior displayed by these isotherms. In addition, based on thermogravimetric and differential scanning calorimetry measurements, a complete Ni-fluorohectorite dehydrated state only can be reached at long (several hours) isotherm times at 70 °C, or at shorter times (minutes) above 150 °C. Our observations are consistent with the existence of various forms of Ni$^{2+}$H$_2$O complexes in Ni-fluorohectorite, and we suggest that the present observations can be extended to other smectites with transition metals as interlayer charge compensating cations, and consequently have significant practical consequences in materials science and other areas where smectite clays are important.

Graphical Abstract:
Introduction

Smectites or clay minerals are among the most abundant minerals on Earth and are rarely found in nature without intercalated H\textsubscript{2}O. The large scientific and technological interest in smectites is connected to their ability to swell, most commonly caused by their interactions with H\textsubscript{2}O. Therefore whether smectites are used for CO\textsubscript{2}, nuclear waste storage, heavy metal removal, or drug delivery, understanding their interactions with H\textsubscript{2}O is of paramount importance.

Smectite contain charge-compensating cations in their nano-sized quasi 2-dimensional interlayers (pore width less than 2 nm). These cations balance the negative surface charge of the smectite sheets, and as a whole this system is responsible for the well-known swelling dynamics. Either crystalline (intercalation), or osmotic (exfoliation) swelling occurs when clay particles interact with foreign molecules, such as H\textsubscript{2}O or CO\textsubscript{2}. The variation of the basal spacing of hydrated smectites is connected primarily to the number of H\textsubscript{2}O molecules intercalated within the layers, and equilibration at different relative humidity and temperatures. The H\textsubscript{2}O molecules may be arranged within the smectite interlayer space in structures corresponding to integral number of water layers (WL) or more complex H\textsubscript{2}O structures. In order to study this crystalline swelling process many methods have been employed, such as quasi-elastic neutron scattering (QENS), Neutron Diffraction, X-ray diffraction (XRD), and Quasi-Elastic Neutron Scattering (QENS).
Synthetic clay minerals have the advantage that they possess a more homogeneous charge distribution, and also contain significantly fewer impurities (e.g. carbonates, (hydr)oxides, silica, and organic matter) than their natural counterparts (Bergaya and Lagaly, 2013). Fluorohectorites (Fh) have often been used as a representative and clean model system of natural smectite clays (Ayyappan et al., 1996; da Silva et al., 2003; Dazas et al., 2013; Hansen et al., 2012; Hemmen et al., 2010; Malikova et al., 2007; Tenorio et al., 2010). Hectorite is a 2:1 phyllosilicate, meaning that the layers are formed by two inverted silicate tetrahedral sheets, sharing their apical oxygen with one octahedral sheet sandwiched in between and it is classified as a trioctahedral smectite since Li$^+$ substitutes for Mg$^{2+}$ in the octahedral sheet sites, which are fully occupied. The proportion $x$ of the Li$^+$ ions in the clay sheet structure itself determines the surface charge of the layers, which are held together in the stacked structure by sharing the interlayer cation.

Considering that the type of intercalated cation substantially influences the physicochemical behaviors of the system (Chatterjee et al., 2004), the present work investigates the effects of intercalating Fh with the divalent cation Ni$^{2+}$, hereafter termed NiFh clay. Ni-intercalated cations in smectites have been extensively studied by the scientific community (Grassi et al., 2014; Michels et al., 2014; Oueslati et al., 2011; Pascual et al., 2014; Pitteloud et al., 2001; Skipper et al., 1991b; Zheng and Zaoui, 2011; Zheng et al., 2010), partly motivated by substantial increase of the amounts of heavy metals in the environment. Our interest in NiFh is also partly based in the well-known fact that Ni$^{2+}$ and water in basic pH conditions form a Ni-hydroxide (Ni-brucite) structure, with chemical formula Ni(OH)$_2$, and that the Ni-brucite structure coexist with the NiFh particles (Michels et al., 2014). Therefore new features related to simultaneous NiFh-water and the Ni-brucite-water interactions could be expected, and our aim in the present work is to investigate and understand the origin of such features.

We here report on two different types of X-ray diffraction (XRD) experiments that were performed on NiFh powder. The first type consisted in mapping small interlayer displacements measured from the (001) Bragg peak positions as a function of relative humidity (RH) at two different fixed temperatures. In the second type of XRD experiment, the particle thickness and the lattice strain were calculated using the standard Williamson-Hall analysis method, based on the evolution of the (001) as well as higher order Bragg peaks measured at selected values of RH. In addition, thermal analysis was performed, demonstrating that NiFh clay shows a quite distinct behavior compared to that observed in other smectites upon water adsorption. We explore this in detail and suggest possible explanations for these behaviors.
1. Materials and Methods

1.1 Sample Preparation

The Ni-fluorohectorite (NiFh) samples were obtained by a cation exchange protocol starting from Li-Fluorohectorite (LiFh), described by our group previously (Grassi et al., 2014; Michels et al., 2014). This consists in mixing LiFh and NiCl\textsubscript{2}·6H\textsubscript{2}O in a water solution and collecting the powder after centrifuging. The NiFh powder is then washed in deionized water several times in order to remove residual salt. The nominal chemical formula of the product thus obtained is:

\[
\text{Ni}_{0.6} \left[\text{Mg}_{(4.8)} \text{Li}_{1.2}\right] \text{Si}_{8} \text{O}_{20} \text{F}_{4} \text{per unit cell. The pH was measured to be 9.5 during the cation exchange process, as adjusted by the clay dispersion itself. The samples are left to dry and after evaporation of the water, the sedimented film is collected and placed in the sample chamber described in Figure 1.}
\]

Previous to the XRD analyses, two kinds of samples were prepared from the pristine NiFh:

A. Non-preheated NiFh: Two samples of clay mineral with the same initial relative humidity (RH) were placed under N\textsubscript{2} atmosphere and their structural change was monitored in-situ using XRD, at two different temperatures: one at 70 °C and another at 20 °C, without prior preheating of the samples.

B. Pre-heated NiFh: Two samples of clay minerals were placed on a heater plate and pre-heated at 150 °C under N\textsubscript{2} atmosphere until their dehydrated structure was obtained, which was monitored in-situ using XRD. After dehydration, the temperature of one sample was lowered to 70 °C and a number of XRD patterns were collected for various values of RH, as detailed below. In addition, this same procedure was repeated with the other set of pre-heated NiFh at 20 °C.

After the sample preparation described above, the treated NiFh powder was placed inside a sample cell, in which RH and temperature could be accurately controlled. This custom made cell consists of a closed cylindrical chamber with a small kapton window for XRD transmission, a heater plate as sample holder in the center and a humidity/temperature sensor inside. The RH was controlled by regulating a pure nitrogen (N\textsubscript{2}) flux into the chamber. The N\textsubscript{2} gas was separated into two branches: one going into a water container, where N\textsubscript{2} was saturated with water vapor, and the other conducting the dry N\textsubscript{2} gas to the chamber. Both channels had flow meters installed in their respective flow paths for reproducibility control of the applied RH. This apparatus allows for mixing humid and dry gases in a controlled manner. A sketch of this experimental setup is shown in Figure 1.
Figure 1: a) Schematics of the sample cell which consists of a heater plate, kept inside a closed cylindrical sample chamber together with a humidity/temperature sensor. b) Aligned sedimented film of smectite clay mineral particles. c) The layer structure of the fluorohectorite with the charge compensating cation Ni\(^{2+}\) confined in the unit cell interlayer space (\(d_{001}\)).

1.2 XRD Experiments

XRD measurements on non-preheated samples were studied using an in-house (NTNU, Trondheim) Bruker NanoSTAR X-ray scattering instrument, attached to a Xenocs X-ray source with a copper anode. Preheated samples were measured at the Brazilian Synchrotron Light Source Laboratory (LNLS) at the XRD2 beam line, using a wavelength of \(\lambda = 0.154991 \text{ nm}\).

The scattered X-ray intensities are plotted in terms of the scattering vector defined as \(q = \frac{4\pi\sin(\theta)}{\lambda}\), where \(\theta\) is the scattering angle. In order to obtain the peak positions and de-convolute the peak widths, which are intrinsic to the sample, a pseudo-Voigt peak shape function was used. For our purpose this function provides a good approximation to the convolution of Lorentzian and Gaussian functions (Wertheim et al., 1974):

\[
\Phi(q) = \mu \frac{2}{\pi} \frac{\Gamma}{4(q-q_{c})^2 + \Gamma^2} + (1-\mu) \frac{\sqrt{4\ln 2}}{\sqrt{\pi} \Gamma} \exp \left[ -4\ln 2 \frac{(q-q_{c})^2}{\Gamma} \right] 
\]

(1)

\(\mu\) is the proportional constant that ranges from zero to one and it is responsible for peak shape curve being more Lorentzian or Gaussian while \(\Gamma\) denotes the experimental peak width of curves.
\[ \mu = 1.36603 \left( \frac{\omega_L}{\Gamma} \right) - 0.47719 \left( \frac{\omega_L}{\Gamma} \right)^2 + 0.11116 \left( \frac{\omega_L}{\Gamma} \right)^3 \]

\[ \Gamma = \left( \omega_G^2 + 2.69269\omega_G^4\omega_L + 2.42843\omega_G^2\omega_L^2 + 4.47163\omega_G^2\omega_L^3 + 0.07842\omega_G^4\omega_L^4 + \omega_L^6 \right)^{\frac{1}{2}} \]

\[ \Phi(q) \] is the interference function related to the measured intensity by \( I(q) = C(q)\Phi(q) \). The \( C(q) \) parameter is related to the scattering structure factor and to the Lorentz-polarization factor, and in the region around each \((00\ell)\) peak, \( C(q) \) can be approximated by a constant since its value fall steeply at low \( q \) and varies slowly with \( q \) in the range of the peak widths. The \( \omega_L \) and \( \omega_G \) denotes the peak widths of the Lorentzian and Gaussian components that represent the sample and instrumental contribution to the line broadening respectively. At NTNU the FWHM Gaussian instrumental resolution width, obtained from the fittings, was \( \omega_G \approx 0.196 \pm 0.005 \text{ nm}^{-1} \) (Cases of Figures 2 (b) and (d) below), and at LNLS it was \( \omega_G \approx 0.043 \pm 0.009 \text{ nm}^{-1} \) (Cases of Figures 2 (a), (c) and Fig. 3 below).

Only for the Williamson-Hall procedure (Case of Figures 5 and 6 below) a Ge (111) single crystal analyzer was utilized at LNLS in front of the diffracted X-ray beam detector in order to sharpen the instrumental resolution, thus reducing the effects of instrumental broadening on the diffractograms but also reducing significantly the XRD intensity. This setup allows the data to be fitted with only a Lorentzian i.e. the instrumental width contribution can be neglected, and the pseudo-Voigt function is not needed.

1.3 Thermogravimetric Analysis

Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements were performed using respectively a TG 209 F1 LIBRA and a DSC 214 Polyma from NETZSCH. The experimental conditions were: N\(_2\) atmosphere \(\approx (40 \text{ ml/min})\), heating rate \(10 \text{ °C.min}^{-1}\), platinum top-opened crucible (TGA) and aluminum pierced crucible (DSC). The samples weights were approx. 20 mg. The results allowed quantifying the amount of initial H\(_2\)O in the clays layers as well as to describe the different phases as follows. Two types of measurements were performed using the TGA: one to measure the mass loss as a function of temperature carried out between 25 °C to 400 °C and the other to observe the evolution of the mass loss at constant temperature. The former can give the temperature where the H\(_2\)O populations de-adsorb from the sample, while in the latter (by fixing the temperature at 70 °C and 150 °C) one can determine the mass loss as a function of time. Consequently, the isotherm method allows us to directly compare the relation between the initial H\(_2\)O content and the XRD Bragg peak position. On the other hand, the differential scanning calorimetry (DSC) measurements, performed between room temperature and 400 °C, allows to quantify the H\(_2\)O transitions in the samples.
2. Results

A. XRD: It is well-known that smectite clays at finite values of RH expand (swell) in the z-direction (001). Therefore, the peak positions $q_{\alpha}$, obtained from Eq. (1), for a given RH are related to the hydration state, which depends on the type of interlayer cation. As reported in several previous publications (da Silva et al., 2002; Ferrage et al., 2010; Ferrage et al., 2005; Ferrage et al., 2011; Gates et al., 2012), for Na$^+$ the stable hydration states correspond to zero water layer (0WL) (dehydrated peak), one water layer (1WL) and two water layers (2WL). For the case of Li$^+$ as interlayer cation (Tenorio et al., 2010), the stable hydration states are 0WL, 1WL, one-and-a-half WL (1.5 WL) and 2WL.

![Figure 2: The diffraction peaks corresponding to the stable hydration states (see Figure 3) in NiFh with the corresponding RH for a sample that is (a) pre-heated T = 20 °C, (b) non-pre-heated T = 20 °C, (c) pre-heated T = 70 °C and (d) non-pre-heated 70 °C. The thin continuous lines represent transition states in between the stable hydration states (i.e. peaks I, II, III and IV). The non-pre-heated samples measured at NTNU have broader peak widths due to the instrumental contribution as explained in the text.](image)

In this work, the expansion for NiFh was carefully followed by monitoring the position of the (001) Bragg peak for increasing values of RH. Figure 2 shows the Bragg peak position as a function of $q$ for different values of RH. The value of $d_{001}$, i.e., the distance between the basal planes, was then calculated using the relation:
The peak at $q_c \approx 5.5 \text{ nm}^{-1}$ (blue ○) found in all diagrams, represent the dehydrated condition corresponding to basal distance $d_{001} = 1.14 \text{ nm}$, implying that there is not enough space between the clay layers to accommodate $\text{H}_2\text{O}$ molecules. The other peaks, hereafter denoted as peak I to peak IV, correspond to the conditions where the $\text{H}_2\text{O}$ intercalates into the interlayer space.

For the pre-heated and non-pre-heated samples measured at $T = 20 \degree C$ (two upper panels), the peak positions in Figure 2 are: peak I with $q_c \approx 4.55 \text{ nm}^{-1}$ at RH = 4%, peak II with $q_c \approx 4.31 \text{ nm}^{-1}$ at RH = 53%, peak III with $q_c \approx 3.96 \text{ nm}^{-1}$ at RH 96% and finally peak IV with $q_c \approx 3.44 \text{ nm}^{-1}$ at RH = 100%. On the other hand, for samples pre-heated and non-pre-heated and measured at $T = 70 \degree C$ (two lower panels) the low q peaks (III and IV) are not observed. Moreover, although the peak positions related to stable peaks remain the same when compared with the samples at 20 °C they are shifted to different RH values. In addition, for the non-pre-heated sample measured at $T = 70 \degree C$ a transition from peak I to peak II is observed, while the range around peak II (green ◊) contains multiple peaks for various RH values. This can be considered as a continuum of transitions between peak I (orange □) and peak III (cyan ▽).

In order to check whether these peaks are stable hydration states or not, a pseudo-Voigt function, Eq. (1), was used to fit the diffractograms depicted in Figure 2. The resulting FWHM values, $\omega_L$, for the pre-heated sample measured at 20 °C are plotted as a function of $q_c$ in Figure 3.
Figure 3: FWHM ($\omega_{L}$) as a function of the position of the Bragg peak $q_c$ for pre-heated sample at $T = 20 ^\circ C$. The stable hydration states (large symbols) show narrower FWHM compared to that of the transient peaks.

It is known that the FWHM is related to the structural ordering of the crystalline material. More ordered and/or thicker structures will generally give smaller FWHM values. Therefore the peak positions, $q_c$, where the FWHM shows a minimum (large symbols in Figure 3) can be related to hydration states where the crystalline structure has a higher degree of ordering. This distinguishes them from the broader diffractograms of the mixed intercalated states, represented as transient states (yellow dots ◦) in Figure 3.

The average diameter of a freely rotating water molecule is approximately 0.29 nm (Israelachvili, 2011). When water is present in the interlayer space of clay minerals, the $d_{001}$ value is often related to the amount of H$_2$O “layers” present. For each hydration state there are intervals of corresponding $d_{001}$. If the $d_{001}$ value from the dehydrated state (1.146 nm) is subtracted from the average of the stable $d_{001}$ values, the resulting number is the effective interlayer space occupied by H$_2$O molecules. The results are shown in Table 1 for $T = 20 ^\circ C$.

Table 1: The average value of the $d_{001}$ corresponding to each peak type (defined as I to IV in Figure 2). The value of 1.146 nm, which is the $d_{001}$ of 0WL, is subtracted in order to calculate the amount of H$_2$O “layers” for stable hydration state.
<table>
<thead>
<tr>
<th>Peak</th>
<th>$d_{001}$ (nm)</th>
<th>$\sigma$ ($%$)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak I</td>
<td>1.3749 ± 0.0034</td>
<td>0.2289</td>
<td>0.80</td>
</tr>
<tr>
<td>Peak II</td>
<td>1.4439 ± 0.0040</td>
<td>0.2979</td>
<td>1</td>
</tr>
<tr>
<td>Peak III</td>
<td>1.5685 ± 0.0267</td>
<td>0.4225</td>
<td>1.5</td>
</tr>
<tr>
<td>Peak IV</td>
<td>1.8269</td>
<td>0.6809</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Now we turn to the analysis of peak positions of the diffractograms in Figure 2, which can be represented in terms of $d_{001}$ stacking distances using Eq. (2), as a function of RH. The results are shown in Figure 4.

**Figure 4**: Stacking distance $d_{001}$ as function of RH. The value of $d_{001}$ is related to the amount of H$_2$O within the interlayer space. The inset shows the continuous transition from peak I to peak II. The transition from peak II to peak III is not abrupt as is evident since $d_{001}$ grows continuously. The zoom window (right panel) shows the fit of an Avrami-like model (Eq. 4) to the data see description in the text. Pre-heated samples are exposed to pure dry N$_2$ and heated to 150 °C until the dehydrated Bragg peak position is reached and then the temperature is lowered to 20 °C or 70 °C. The non-pre-heated samples are dried at 20 °C or 70 °C in pure N$_2$ atmosphere until the dehydrated Bragg peak position is reached (see Methods).

As RH increases, $d_{001}$ increases as well. For low RH values, the transition from the dehydrated state to the state containing peak I is seen to be abrupt in all cases, whilst the transition from peak I to peak II displays an “S-shaped” change. The transition from peak II to peak III is not clearly visible, instead a continuous increment of $d_{001}$ is observed from 2% to 96% of RH until $d_{001}$ clearly changes to the peak IV position. The results indicate continuous peak shifts in the transition regions, which have not been observed in previous hydration studies of synthetic smectites (Hemmen et al., 2010; Tamura et al., 2000), and our results clearly differ from the abrupt stepwise expansion of the layer-to-layer distance with increasing water activity normally reported for smectites (Dazas et al., 2015). The change in temperature (20 or 70 °C) does not seem to affect either the continuous behavior or the presence of an abrupt transition for low RH values. However, the initial sample condition clearly influences the transition between peaks I and II. In the non-pre-heated case, this transition is observed...
to be shifted to higher RH values at T = 70 °C (yellow and green curves in the right panel of Fig. 4), whereas for the pre-heated sample at 70 °C the transition is not clearly observed.

For the sample pre-heated and measured at T = 20 °C (blue curve), the evolution of $d_{001}$, after the transition from peak I to II, could be fitted with a linear function, with slope $\eta$ as given by Eq. 3, up to approximately RH = 60%.

$$d_{001} = \eta \cdot RH$$  \hspace{1cm} (3)

In the case of the measurements performed at T = 70 °C, this linear behavior is also observed for the pre-heated sample (red curve), as well as for the non-pre-heated sample below the transition from peak I to peak II (green curve). In addition, the evolution of $d_{001}$, during the transition from peak I to peak II, was found to be well described by an exponential law:

$$d_{I\rightarrow II} = d_{II} - (d_{II} - d_{I}) \exp \left[-K(RH - RH_I)^\alpha\right]$$  \hspace{1cm} (4)

where, $d_{II}$ is the interlayer spacing of the hydration state corresponding to peak II, $d_{I}$ is the interlayer spacing of the hydration state corresponding to peak I, and $RH_I$ is the RH value at which the transition begins for the increasing RH. Thus the whole range shown in the right panel of Fig. 4 could be fitted with a combined equation, and the resulting parameters, represented by the continuous lines in the right panel of Figure 4, are shown in Table 2.

**Table 2: Fitting parameters obtained from Eq. (3) and (4).**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pre-heated T = 20 °C</th>
<th>Pre-heated T = 70 °C</th>
<th>Non-pre-heated T = 20 °C</th>
<th>Non-pre-heated T = 70 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$ (slope)</td>
<td>$(4.3 \pm 0.2) \cdot 10^{-4}$</td>
<td>$(4.8 \pm 0.6) \cdot 10^{-4}$</td>
<td>$(6.8 \pm 0.2) \cdot 10^{-4}$</td>
<td>$(6.4 \pm 0.6) \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$d_{II}$</td>
<td>$1.4410 \pm 0.0005$</td>
<td>$1.420 \pm 0.002$</td>
<td>$1.441 \pm 0.003$</td>
<td>$1.455 \pm 0.004$</td>
</tr>
<tr>
<td>$d_{I}$</td>
<td>$1.373 \pm 0.001$</td>
<td>$1.399 \pm 0.002$</td>
<td>$1.375 \pm 0.005$</td>
<td>$1.398 \pm 0.003$</td>
</tr>
<tr>
<td>$RH_I$</td>
<td>$3.5 \pm 0.6$</td>
<td>$38 \pm 1$</td>
<td>$0 \pm 1$</td>
<td>$36 \pm 1$</td>
</tr>
<tr>
<td>$K$</td>
<td>$(7 \pm 1) \cdot 10^{-3}$</td>
<td>$(2 \pm 1) \cdot 10^{-3}$</td>
<td>$(7 \pm 5) \cdot 10^{-3}$</td>
<td>$(2 \pm 1) \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

The slope, $\eta$, obtained by fitting in the linear regime, represents how H$_2$O intercalates into the interlayer space of NiFh in the continuous regime. Previous work performed at T = 15 °C on NaFh (Hemmen et al., 2010) gave an estimated slope in the same range as those obtained here. Furthermore, based on Table 2, the $\eta$ values are related to the initial condition of the clays. The pre-heated samples have approximately the same values of $\eta$, which are smaller than those observed for
the non-pre-heated samples. Thus our results indicate that the intercalation process in this region is temperature independent (at least in the temperature range probed in this study), i.e. the rate of H₂O intercalation (η) in the non-transition region seems to depend only on the environmental history of the clays. It is clear however that the temperature (20 or 70 °C) shifts the RH value for which the transition peak I → peak II occurs. This is reflected by the fitting parameter RH_i that shows that it is more difficult to intercalate H₂O at higher temperatures. Similar observations were reported by da Silva et al. in Na-fluorohectorite (da Silva et al., 2003).

The parameters α and K, defined in Eq. (3) may be discussed in terms of the Avrami equation (Gasparini et al., 2013), where K represents the transition rate constant, while α is an integer between 1 and 4, where α = 3 is normally interpreted as the case of 3-dimensional nucleation growth. However, while the standard Avrami model describes time dependent processes, the present case is an equilibrium process. The equation can however be adapted to the present case where the cation is already solvated and the water only fills the interlayer space. The fitting shows that K is independent of the initial condition of the sample (pre-heated or non-pre-heated) and is higher for T = 20 °C than at T = 70 °C.

Together, these considerations, taken with appropriate care, show that smectite clay hydration can be very sensitive to initial sample preparation and environmental history. Similar conclusions regarding preparation and environmental history were reported in a work on the synthetic smectite laponite by Cummins et al. (Cummins, 2007). We suggest that such behaviors also may apply to other of the transition metals intercalated smectites.

**B. Layer Thickness and Lattice Strain:** The obtained XRD peak intensities are shown in Figure 5 for the pre-heated sample at T = 20 °C.

![Figure 5: XRD (00l) intensities of the NiFh samples at different RH.](image-url)

Considering that the contributions to the FWHM of the peaks are average thickness of the clay particle stacks, plus the strain or disorder in the lattice spacing, we make use of a Williamson-Hall (W-H) (da Silva et al., 2002) plot to analyze these data as follows:
where \( \omega_L \) is the FWHM obtained from the Lorentzian fitting of the XRD curves shown in Figure 5, \( Nd \) is the average particle stack thickness, obtained from the extrapolation of the straight line to \( q = 0 \), and \( \xi \) is the average lattice strain, defined as \( \frac{\Delta q_L}{q_c} \), or disorder, obtained from the slope of the straight line. The results of this analysis, performed for four different values of RH, are presented in Figure 6.

\[
\omega_L = \frac{2\pi}{Nd} + \xi q
\]  

(5)

Figure 6: a) Williamson-Hall (W-H) plot, for RH values at 0%, 2.5%, 85% and 95%, with the slope and intercept giving the average strain and the average particle thickness respectively. b) The estimated particle thickness and lattice strain (inset).

Figure 6 (a) shows the W-H plots for 0%, 2.5%, 85% and 95% of RH for pre-heated samples studied at \( T = 20 \, ^{\circ}C \), from which both the average particle thickness and lattice strain were extracted and presented in Figure 6 (b). The particle thickness, \( Nd = 146 \pm 11 \), shown Figure 6 (b), remains approximately constant for 0%, 2.5%, 95% of RH. The exception is the case of RH = 85 %, where low particle thickness value may be attributed to the fact that at this condition the sample is in a transition between the regions of the peak II to peak III (as shown in Figure 4). In this case, the intercalated H\(_2\)O might not occupy the clay interlayers homogeneously, resulting in an increase of the lattice strain (see inset) and thus affecting the stability. The minimum strain, at low RH values, can be interpreted as a condition where the clay NiFh has its basal planes more ordered in the stacking layers, i.e. closer to each other due to the lack of intercalated H\(_2\)O. On the other hand, an increase of H\(_2\)O (higher humidity) disassociates the basal planes from each other allowing for more freedom and thus possibly a more disordered (higher lattice strain) layered orientation.
C. TGA and DSC: The H₂O adsorbed differentially in the sample can be identified by measuring the mass loss as function of temperature. Figure 7 (a) shows the mass loss of both NiFh and Ni-brucite as function of temperature and Figure 7(b) the quantifications of the H₂O transitions within the clay particles.

![Figure 7: Mass (a) and DSC (b) of NiFh and Ni-hydroxide (Brucite) as a function of temperature. The drops in the TGA correlates with the peaks observed in the DSC. The peak at 82 °C can be related to the H₂O present in the intraparticle meso-space, while the peaks at 150 °C and 270 °C to interlayer H₂O. The Ni-brucite has a peak at 100 °C and another at 310 °C that are related to H₂O desorption and Brucite degradation, respectively.](image)

It has been argued that Ni-brucite coexists with the clay mineral particles and that this is pH dependent (Michels et al., 2014). Although the TGA curves of NiFh and Ni-brucite are different, their DSC diagrams show some similarity. For NiFh the endothermic peaks at 82 °C and 150 °C are associated to different H₂O population that desorbs from the clay mineral, related to intraparticle and interlayer H₂O losses, respectively. The peak at 100 °C for Ni-brucite may be related to H₂O desorbing from the particle surface. These types of H₂O adsorbed in the clay minerals can be linked to previous interpretations in the literature (Bordallo et al., 2008; Gates et al., 2012). The NiFh sample and the Ni-brucite sample show peaks at around 260 °C and 320 °C respectively that can be attributed to the degradation of Ni-brucite, since the Ni-brucite particles are either at the surface or confined.
within the clay mineral pores, thus likely reducing the temperature threshold for this decomposition. It is well known that when smectites submitted to high temperatures, can have their structure modified in at least two ways: reduction of the layer charge or dehydroxylation. Layer charge reduction can be due to the migration of the interlayer cation into the octahedral sites, which has been observed in smectites saturated with small cations at temperatures as low as 125 °C (Skoubris et al., 2013), and it is known as Hofmann-Klemen effect (Komadel et al., 2005). Another type of known possible structure modification is the release at temperatures above 400 °C of the structural hydroxyl groups (OH) present in smectite layers (Green et al., 1970). However, it is important to notice that for the smectite clays studied in the present work the OH groups have been replaced by fluorine. This would imply that the DSC peak at 260 °C could also mean that the fluorine groups of the layer structure are being released.

In order to compare the dehydration of different NiFh samples, two isotherms with temperatures fixed at 70 °C and 150 °C (temperature of dehydration of the pre-heated samples) were measured in N₂ atmosphere. Both samples were prepared at room temperature at RH= 27 %, which are the same conditions used in the XRD experiments on non-preheated samples. The results are presented in Figure 8. In the asymptotic limit (125 min), for the sample heated at 70 °C the amount of mass lost is 8.7% while for the one heated at 150 °C the amount is 10.1%.

![Figure 8: The amount of mass loss based on the isotherm at 70 °C and 150 °C.](image)

### 3. Discussion

As described above, continuous peak shifts were found in the transition regions upon water uptake for this system. This can be related, to the existence of a Hendricks-Teller (HT) (da Silva et al.,
2002; Ferrage et al., 2007; Hendricks and Teller, 1942) type peak between two stable XRD peaks. In such a case, the positions of the HT peaks can be directly related to the amount of different states in the system. Simultaneously or alternatively, this continuous shift can be explained by different geometrical arrangements of Ni\(^{2+}\)-H\(_2\)O complexes in the interlayers, such as the presence of Ni-brucite (Ni(OH))\(_2\). Indeed Michels et al (Michels et al., 2014) reported that Ni-brucite was formed during the cation exchange process from LiFh to NiFh due to the natural high pH of clay minerals in solution, and it was shown that such structures may remain stable, which could possibly explain the differences between dehydrated NiFh and LiFh or NaFh. Similar possibilities were also discussed by Pitteloud et al. (Pitteloud et al., 2001), who found that Ni-montmorillonite at high hydration conditions forms a complex structure of Ni\(^{2+}\)hexaaqua, which is very close to what is found for Ni\(^{2+}\) in aqueous solution. Based on the results in Table 1, peak II can be label as 1WL. This is a stable hydration state which is in agreement with Figure 3. Peak I, like the transitions peaks, may be related to one type of confined Ni\(^{2+}\)-H\(_2\)O complex in which the free rotation of the H\(_2\)O molecule is limited. Furthermore, peak III has an interlayer space corresponding to approximately 1.5 WL, which was also reported by Tenorio et al. for LiFh (Tenorio et al., 2010). In sum all peaks I-IV may possibly be related to different stable situations (coordination numbers and orientations of H\(_2\)O molecules) of Ni\(^{2+}\)-H\(_2\)O complexes in the interlayers.

The dependence of the XRD isotherms on the sample history is not clear (i.e. why there are different XRD isotherm behaviors for the non-preheated and preheated samples). One explanation might be a partial, but nevertheless minor, change in the layer structure initiated while heating the samples at 150 °C. This has indeed been previously observed in smectites saturated with small-cations at temperatures above 125 °C (Komadel et al., 2005; Skoubris et al., 2013).

From the TGA isotherm data at 150 °C the total mass loss is about 10.1%, and assuming that this is only due to H\(_2\)O loss, this corresponds to approximately 33.7·10\(^{20}\) H\(_2\)O molecules lost per gram of NiFh. Considering that there are approximately 0.6 Ni\(^{2+}\) cations per unit cell of Fh (Kaviratna et al., 1996) and that the number of unit cells per gram is the Avogadro’s number divided by the molar mass of the NiFh unit cell, one gets 7.71·10\(^{20}\) unit cells per gram. Thus one gets approximately 4.6·10\(^{20}\) Ni\(^{2+}\) cations per gram of NiFh, and if one considers that all the lost H\(_2\)O is associated with Ni\(^{2+}\) cations, the coordination number would be approximately 7.3 H\(_2\)O molecules per Ni\(^{2+}\) (corresponding to 4.4 H\(_2\)O molecules per unit cell). Interestingly, this value is only slightly above the Brucite structure coordination number, which is Ni\(^{2+}\) coordinated by 6 Oxygen atoms (Michels et al., 2014). On the other hand, for the isotherm measured at 70 °C, 8.7% of the mass is lost during the experiment, which corresponds to approximately 6.3 H\(_2\)O molecules per Ni\(^{2+}\), using the same calculation as above. This difference therefore amounts to about 1.0 H\(_2\)O molecules per Ni\(^{2+}\) cation left in the sample, which is less than 1.4% of the total mass, assuming that all and only H\(_2\)O is lost at 150 °C. Consequently, the TGA measurements show that diffraction data were not collected in fully dehydrated powders, indicating that the d\(_{001}\) value obtained using XRD does not directly represent the
amount of H$_2$O in the interlayer. Here it is important to point out that the detection limit of our XRD measurements is about 1.5% (signal to noise ratio) which can be estimated from the ratio of the dehydrated 0WL Bragg peak to the noise level in the 1WL peak position. Accordingly, if 1.5% of the crystallites are in the monohydrated state they are “invisible” in the XRD experiments.

4. Conclusion:

We have used XRD and TGA/DSC to study the intercalation of H$_2$O in the synthetic smectite clay fluorohectorite with Ni$^{2+}$ as interlayer cation using different sample preparation approaches, i.e. pre-heated and non-pre-heated clays. XRD results show that the transition upon water adsorption from the dehydrated state does not occur as an abrupt step, as commonly observed in other studies of hydration in smectites, but shows a relatively continuous change. The latter might be linked to the presence of various types of Ni$^{2+}$-H$_2$O complexes in the interlayers, such as Ni-brucite complexes or Ni$^{2+}$ hexaaqua and/or also to the coexistence with different hydration states within the scattering volume. As reported in our recent work (Michels et al., 2014), Ni-brucite complexes can be present in NiFh. If this behavior is common to smectite clays with transition metal cations, it will have significant practical consequences in materials science and other areas where smectite clays are used.

The TGA/DSC results highlights further the effect of the initial conditions of the NiFh in hydration experiments, suggesting that the sample pre-heated at 150 °C might have a reduced layer charge due to the migration of Ni$^{2+}$ to the layers (Hofmann-Klemen effect). This may explain the slightly different H$_2$O adsorption isotherms obtained using XRD for the samples pre-heated at 150 °C and the non-preheated samples.

Finally, via the Williamson-Hall analysis for four selected values of RH, the average particle stack thickness and the average lattice strain were obtained. The former was found to be $Nd = 146 \pm 11$ nm for all studied samples in their stable hydration states, and to decrease when the system is in transition between two hydration states. This observation may be attributed to an inhomogeneous distribution of the intercalated H$_2$O within the clay interlayers. The lattice strain was found to be proportional to the RH. This result indicates that the intercalation of H$_2$O in the basal planes cause disorder in the stacking layers.

Future work would be to perform QENS experiments in order to fully quantify the H$_2$O mobility (rotation and translation) within the interlayer space of the clay mineral and its relation to the number of H$_2$O layers obtained in the present work. Through the analysis of the elastic incoherent structure factor (Jacobsen et al., 2013), this technique might shed light on the identification of the different Ni$^{2+}$-H$_2$O complexes, like Ni$^{2+}$ hexaaqua and Ni-brucite, and their relation with the hydration stability.

Acknowledgements
The authors acknowledge the Brazilian Synchrotron Light Laboratory (LNLS) technical staff at the XRD2 beam line. We also wish to thank Antônio Gasperini, Fabio Zambello and Vinícius Fonseca for their helpful assistance at LNLS, also José Pereira for assistance in the TGA measurements. Mario Altoé acknowledges CAPES for PDSE Scholarship, process number BEX 4792/14-9. L. Michels, E. C. dos Santos, K. D. Knudsen, and J. O. Fossum appreciate support from the Research Council of Norway. H. N. Bordallo acknowledges support from the Carlsbergfondets (grant number Ref: 2013_01_0589).

References:


Oueslati, W., Ben Rhaiem, H., Amara, A.B., 2011. XRD investigations of hydrated homoionic montmorillonite saturated by several heavy metal cations. Desalination 271, 139-149.


