

Effect of interlayer cation and relative humidity on the hydration properties of a dioctahedral smectite

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Abstract. This paper aims at characterizing the structural evolution of a dioctahedral smectite (i.e. Wyoming montmorillonite) saturated by Na⁺, Cu²⁺ or Pb²⁺. Hydration properties of the <2µm size fraction of Wyoming montmorillonite smectite (SWy) source clay (low charge i.e. 0.35) were studied by modelling of X-ray diffraction (XRD) patterns recorded under controlled relative humidity (RH) conditions on Na, Cu or Pb saturated specimens. The Cation Exchange Capacity (CEC) of the starting sample was first Na⁺ saturated to guarantee better dispersion, followed by exchanges with the cations Cu²⁺ or Pb²⁺. The resulting complexes were respectively labelled Wy- Na, Wy-Cu and Wy-Pb. The qualitative analysis of XRD patterns obtained under room pressure and temperature conditions showed that all complexes have one water layer hydration state. In order to highlight the specific hydration properties of each complex, we studied the XRD patterns under controlled relative humidity (%RH). The quantitative analysis of XRD patterns is achieved using an indirect method based on the comparison of experimental XRD patterns with calculated ones. This quantitative study showed that for Wy- Na, Wy-Cu and Wy-Pb at low RH (≈15%) the d₀₀₁ spacing corresponds to a low hydration state characterized by one water layer, whereas for higher studied rates of relative humidity (75%), differences of hydration state can be distinguished for Wy-Na, Wy-Cu and Wy-Pb samples.

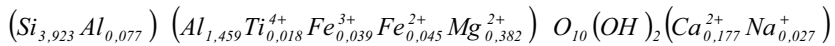
Introduction

Smectite is a 2:1 phyllosilicate with a layer structure consisting of an octahedral sheet sandwiched between two siliceous tetrahedral sheets. Isomorphic substitutions in either tetrahedral and/or octahedral sites induce a permanent negative layer charge which can be compensated by the presence of hydrated cations in the interlamellar space [1-2]. The observation of 00l basal reflections on XRD patterns has shown that with increasing relative humidity rates

smectite expands progressively due to the intercalation of 1,2 or 3 sheets of H₂O molecules in the interlamellar space[2-4]. In order to highlight the specific hydration properties of each sample, we studied the relative humidity (RH) effect on the hydration behaviour of Na⁺, Cu²⁺ or Pb²⁺ saturated specimens labelled respectively Wy_Na, Wy_Cu and Wy_Pb [3-5]. Several factors controlled the structural evolution such as the nature of interlayer cation, the layer charge and its location (octahedral or tetrahedral) [6]. The main objective of this study was to investigate the specific behaviour of the natural clay mineral characterized by an octahedral layer charge under controlled RH conditions. One of the most effective methods for identifying and determining these structural characteristics is X-ray diffraction. The XRD analysis is based on the comparison of the experimental *00l* reflections obtained from oriented films patterns with those calculated from structural models.

Materials and methods

The clay fractions were prepared according to the classic protocol of extraction [7]. The <2µm fraction of a crook montmorillonite (Wyoming, USA) were supplied by the Source Clay Minerals Repository Collection. Its half cell structural formula, as obtained by electron microprobe, is [8]:



It was dispersed in water and separated by sedimentation. The Na saturated clay minerals were prepared by washing suitable amounts of the clay suspension several times in 1N NaCl to disperse as well as possible the clay fraction. The Wy-Na samples were then washed several times with 1N lead chloride or cooper chloride respectively. This step aims to prepare reference samples named respectively Wy-Pb and Wy-Cu. The excess of chloride was eliminated by washing the clay in distilled water and by subsequent dialysis.

The XRD patterns of the oriented and air-dried specimens were obtained by reflection setting with a D5000 Bruker equipment using Cu-Kα radiation and a solid-state detector. Intensities were measured at 40-50s counting time per step of 0.04° (2-theta). Oriented preparations were prepared by depositing a clay suspension on a glass slide [9-10] as layered minerals crystallize usually as thin plates and tend to remain parallel to one another and to the plane of the sample holder. The diffracted intensity was calculated according to the matrix formalism [11] with expression

$$I_{00l}(2\theta) = Lp \cdot Spur \left(Re [\Phi] [W] \left\{ [I] + 2 \sum_n^{M-1} \left[(M-n)/M \right] [Q]^n \right\} \right)$$

where Re means the real part of the final matrix; Spur, the sum of the diagonal terms of the real matrix; Lp, the Lorentz-polarization factor; M, the number of layers per stack; n, an integer varying between 1 and M-1; [Φ], the structure factor matrix; [I], the unit matrix; [W], the diagonal matrix of the proportions of the different kinds of layers and [Q], the matrix representing the interference phenomena between adjacent layers. This method allows determining the abundance of the different types of layers (Wi), the mode of stacking of the different kinds of layers and the mean number of layers (\bar{M}) per coherent scattering domain (CSD). Within a CSD, the stacking of layers is described by the set of junction probabilities (P_{ij}). The relationships between the abundances Wi of the different types of layers are given by $\sum W_i = 1$. The XRD patterns were calculated using the z coordinates of [11]. The origin of

these coordinates was placed on the plane of surface oxygen atoms. The RH conditions used in this work extends from almost saturated (80%) to extremely dry (15%), the latter being obtained by connecting the Anton Paar chamber to a secondary vacuum ($\sim 10^{-4}$ Pa). For all samples, XRD patterns were recorded first under room conditions (297K, and $\sim 35\%$ RH). Then, XRD patterns were recorded for all samples following the same sequence of RH's (15, 35, 45, 55 and 75%). For each sample, all five experimental XRD patterns were recorded within a timeframe that did not exceed 48 hours after the drying of the oriented preparation. This procedure avoided any kinetically driven dehydration processes to occur [12-13].

Results and discussion

Qualitative XRD analysis

The experimental XRD patterns of the Wy-Na, Wy-Pb and Wy-Cu complexes are reproduced at figures 1a-c respectively for RH rates varying between 15% and 75%. The values of the corresponding observed d_{001} -spacings are reported in table 1. For RH $\leq 35\%$, the Wy-Cu, Wy-Na and Wy-Pb complexes show basal spacings between 12 Å and 13Å. This means that at these humidity rates, all samples are characterized by one water layer hydration state [14]. For RH = 45%, Wy-Pb keeps one water layer whereas for Wy-Na and Wy-Cu the 001 peak broadens and shifts towards lower angles with a weak peak at 14.91Å. This indicates that for these two compensating cations, a transition from 1W to 2W hydration state occurs. At RH=55%, complex Wy-Pb still exhibits little asymmetry of the 001 reflection while Wy-Na and Wy-Cu show a marked evolution from a 1W to a 2W state evidenced by the two peaks in the $5\text{-}10^\circ$ 2θ interval with d values equal to 12.59Å and 14.15Å. For 75%RH, Wy-Pb and Wy-Na, the respective basal distances d_{001} are 15.71Å and 15.31Å (i.e. 2W state). In the case of Wy-Cu, a weak reflection at $2\theta=4.76^\circ$ ($d_{001} = 18.54$ Å) appears indicating the starting of a 3W hydration state. A supplementary reflection appears in the diffraction pattern of Wy-Pb sample in the 2θ range (18-28°) due to the presence of Laurionite (PbOHCl: pattern reference 74-2022(C)) and Lead Chloride (PbCl₂: pattern reference 84-1177(C)) due to excess of salt in the solution.

Table1. Experimental basal spacings and 2θ values for complexes Wy-Pb, Wy-Cu and Wy-Na

sample	Wy-Pb		Wy-Cu				Wy-Na						
	%RH	d_{001} (Å)	2θ	d_{001} (Å)	2θ	d_{001} (Å)	2θ	d_{001} (Å)	2θ				
15		12.69	6.95	12.38	7.13			12.17	7.25				
35		12.92	6.83	12.64	6.98			12.68	6.96				
45		12.92	6.83	14.91	12.49	5.92	7.07	12.70	13.95	6.95	6.33		
55		13.01	14.13	6.78	6.25	14.93	12.69	5.91	6.96	14.15	12.59	6.23	7.01
75		15.71	5.62	18.54	15.88	4.76	5.56	15.31		5.76			

Quantitative XRD analysis

The comparison between experimental and calculated intensities I_{001} using the above expression allowed determining the structural parameters d_{001} , \overline{M} and W_i as a function of the RH for each complex i. The results are summarized in table 2. Examples of agreement between experimental and simulated patterns for 75% RH are reported in figure 2. Inspection of table 2 indicates that

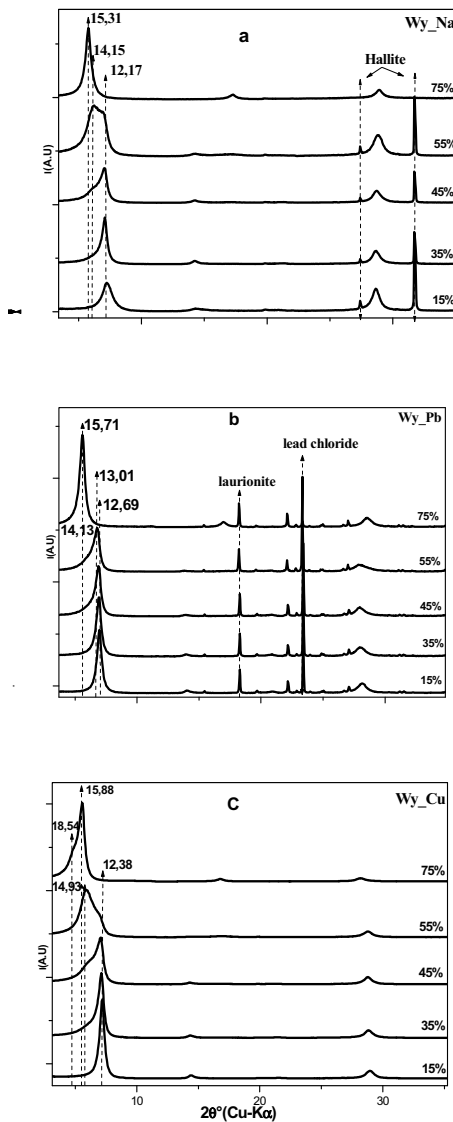


Figure 1. Experimental XRD patterns produced respectively by Wy-Na(a), Wy-Pb(b) and Wy-Cu (c) under controlled relative humidity. Basal spacing values are given in \AA .

(i) At low RH rates (15%), the Wy-Cu complex is characterized by a 1W homogeneous hydration state (12.3Å), although the Na or Pb saturated samples contain small amounts of 0W layers (10.0Å and 10.1Å dehydrated layers [13-14]). (ii.) For $35 \leq \text{RH} \leq 45\%$, the Wy-Na and Wy-Cu are characterised by a 1W state with a small amount of layers with 2W hydration state; the Wy-Pb complex keeps an homogenous hydration state (i.e. 1W). (iii.) When increasing RH to 55% and an evolution from 1W to 2W hydration occurs progressively for all complexes. (iv.) At 75% RH, the Wy-Na and Wy-Pb complexes reach an homogenous 2W state, whereas the Wy-Cu sample evolves towards a 3W hydration state.

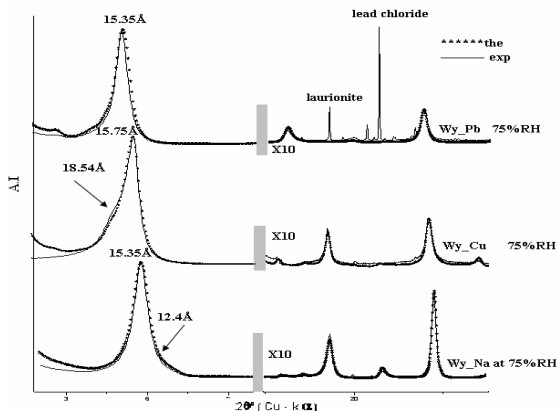


Figure 2. The best agreement between experimental (—) and calculated (***) XRD pattern: (a) Wy-Na 75%RH, (b) Wy-Cu 75%RH (c) Wy-Pb 75%RH

Table 2. Structural parameters obtained from XRD quantitative analysis.

Sample	Wy-Na			Wy-Pb			Wy-Cu		
	%RH	d_{001} (Å) (W_i)	\bar{M}	d_{001} (Å) (W_i)	\bar{M}	d_{001} (Å) (W_i)	\bar{M}		
15		10.0 (0.1) 12.4 (0.9)	9	10.1 (0.1) 12.95 (0.9)	8	12.3 (1)	8		
35		12.4 (0.9) 15.2 (0.1)	9	12.95 (1)	8	12.30 (0.9) 15.35 (0.1)	8		
45		12.4 (0.87) 15.2 (0.13)	8	12.95 (1)	6	12.30 (0.87) 15.35 (0.13)	6		
55		12.4 (0.1) 15.2 (0.9)	6	12.95 (0.95) 15.8 (0.05)	5	12.30 (0.12) 15.35 (0.88)	5		
75		12.4 (0.03) 15.4 (0.97)	9	12.95 (0.02) 15.8 (0.98)	7	15.35 (0.85) 18.3 (0.15)	6		

Conclusion

The objective of this work is to study the hydration properties of a montmorillonite saturated with Na^+ , Cu^{2+} or Pb^{2+} . For low RH rates (15%), Wy-Cu is characterised by a 1W hydration state, whereas Wy-Na and Wy-Pb have small amounts of 0W layers. For 45% RH, Wy-Pb exhibits a homogenous 2W state, while Wy-Cu and Wy-Na contain two types of layers (1W and 2W). Increase of the RH rates until 75% leads to homogenous 2W complexes for Wy-Na Wy-Pb; the Wy-Cu complex display a higher hydration state characterised by a three water sheets within the interlamellar space ($d_{001}=18.3\text{\AA}$). The present study allows concluding that at high RH conditions Na saturated and Cu saturated montmorillonites behave differently.

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