XRD profile modeling approach tools to investigate the effect of charge location on hydration behavior in the case of metal exchanged smectite

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Abstract:

This work aims to investigate the hydration behavior and structural properties of two dioctahedral smectites with contrasting location charge (beidellite SbId-1 and montmorillonite SWy-2) according to the nature of the bivalent compensator heavy metal cations (i.e. Hg (II), Ni (II), Ba (II) and Mg (II)). This study is achieved using XRD profile modeling approach based on the simulation of the *00l* reflection which allowed us to determine structural characteristics along the c* axis related to the nature, abundance, size, position and organization of exchangeable cation and water molecule in the interlamellar space along thec*axis. The obtained results show that a heterogeneous hydration behavior is systematically observed in all studied samples and the structural models, used to fit samples with tetrahedral charge, are more heterogeneous than smectite with an octahedral sheets substitution. In the case of exchanged beidellite specimen, the proposed models are described by a mixed layer structure with variable abundance containing respectively, dehydrated (0W), mono-hydrated (1W) and bihydrated (2W) layers. Whereas, in the case of the montmorillonite, the absence of 0W hydration state is noted.

Key words:
Charge location, heavy metal cation, quantitative XRD analysis, hydration heterogeneities

I. INTRODUCTION

Dioctahedral smectites are 2:1 phyllosilicates with a main structure constituted by two tetrahedral sheets sandwiched by an octahedral one, often occupied with a trivalent cation (Grim, 1962; Brindley and Brown, 1980). The isomorphic substitutions in either the tetrahedral or octahedral sheets creates a charge deficit which is compensated by exchangeable cations located in the interlayer spaces. Water, polar molecules and hydrated exchangeable cation can penetrate the interlamellar spaces which bring the swelling clay properties. (Sato *et al.*, 1992**).** This swelling ability is controlled by several factors mainly, the nature of compensator cation, the amount, the charge location and also the environmental condition as temperature and the relative humidity. Several works showed that the hydration behaviors is strongly influenced by the equilibrium between repulsive forces created between adjacent 2:1 layers and other attractive forces between the negatively charged surface of 2:1 layers and the compensator cations (Norrish, 1954; Van Olphen, 1965; Kittrick, 1969; Laird, 1996; Laird, 1999). Based on these properties, this material type constitutes a potential candidate to be used as a surface barrier to immobilize the metallic pollutants through both ion exchange and adsorption mechanisms. Indeed, several researches, using variable approaches have developed the outstanding capacity of this soft material to remove heavy metal ions, occurring principally from industrial and household trash, using different methods such as chemical precipitation, sorption, electrolysis froth flotation, membrane separation and solvent extraction (Brigatti *et al.*, 2005**;** Sen Gupta *et al.*, 2008**;** Chávez *et al.*, 2010). Moreover, several studies are interested to characterize the hydration behaviors and the organization of hydrated interlayer space in the presence of divalent metal cations at different conditions. Ferrage *et al.*, (2007) investigates the hydration properties of Sr- and/or Ca-saturated dioctahedral smectites with different layer charge and charge location by modeling of X-ray diffraction profiles and showed the hydration heterogeneity evolution versus the interlayer cation amount, and location of layer charge.

In the work of Oueslati *et al.*, (2011), the hydration behavior of montmorillonite (SWy-2) saturated with Cu^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+} and Ni^{2+} us function of the relative humidity (%RH) is focused. The obtained result showed the possibility to distinguish between sample saturated with Cu and Pb for high RH values (≈75%). Whereas in the case of Ni, Zn, Cd and Co a similar hydration behavior is shown in all explored RH's ranges except the Ni^{2+} cation which presents a homogeneous 3W hydration state for 75%RH.

This study aims to investigate the hydration behaviors and the structural properties evolution of two dioctahedral smectites, which differ by the charge location (the montmorillonite SWy-2 and the beidellite SbId-1) and an intrinsic CEC (i.e. Cation exchange capacity) saturated with bivalent heavy metal cations Hg^{2+}, Ni^{2+}, Mg^{2+} and Ba^{2+}.

To achieve this an XRD profile modeling approach is used, which is based on the comparison between calculated and experimental XRD patterns. This method allowed us to determine structural parameters related to the nature, abundance, size, position of water molecule and the exchangeable cation in the interlamellar space along the c* axis.

II. MATERIALS AND METHODS

A. Starting Samples

The beidellite SbId-1(extracted from Glen Silver Pit, DeLamare Mine, Idaho, USA) and the montmorillonite SWy-2 originated from bentonites of Wyoming (Wyoming, USA) are the dioctahedral smectites selected for this study. The starting samples are supplied by the Source Clay Minerals Repository Collection (Moll, 2001**)**. The SbId-1 sample is characterized by a most isomorphic substitution in tetrahedral sheets, whereas, SWy-2 exhibits a major octahedral charge and extremely limited tetrahedral substitutions. The half-cell structural formula respectively for SbId-1 and SWy-2 are as following:

$(Si^{4+}_{3.772},\ Al^{3+}_{0.228})\ (Al3^{+}_{1.786},\ Fe^{3+}_{0.104},\ Mg^{2+}_{0.046},\ Mn^{3+}_{0.001},\ Ti^{4+}_{0.048})\ (Na^{+}_{0.012},\ K^{+}_{0.159})\ (O_{10})\ (OH)_{2}$

(Post et al., 1997)

$(Si^{4+}_{3..392},\ Al^{3+}_{0.077})\ (Al^{3+}_{1.459},\ Ti^{4+}_{0.018},\ Fe^{3+}_{0.039},\ Fe^{2+}_{0.045},\ Mg^{2+}_{0.382})\ (O_{10})\ (OH)_{2}\ (Ca^{2+}_{0.177},\ Na^{+}_{0.027})$

(Oueslati et al., 2011**).**

B. Pre-treatment and Experimental procedure

According to the classical protocol (Tessier, 1984), a sodium exchange is conducted in order to saturate all exchangeable sites with homoionic cations and to guarantee better dispersion. After that, an exchange process with divalent metallic cations (i.e. Hg (II), Ni (II), Mg (II) and Ba (II)) is started .

The experimental exchange process protocol is reported in Fig. 1. All obtained samples are hereafter referred to as

- SbId-1-Hg, SbId-1-Ni, SbId-1-Mg, and SbId-1-Ba for specimen with tetrahedral charge location
- SWy-2-Hg, SWy-2-Ni, SWy-Mg, and SWy-2-Ba for specimens with octahedral charge location.

An oriented preparation, for XRD analysis, is prepared by depositing a clay suspension onto a glass slide and drying it at room temperature for a few hours (Srodon et al., 1986**).**

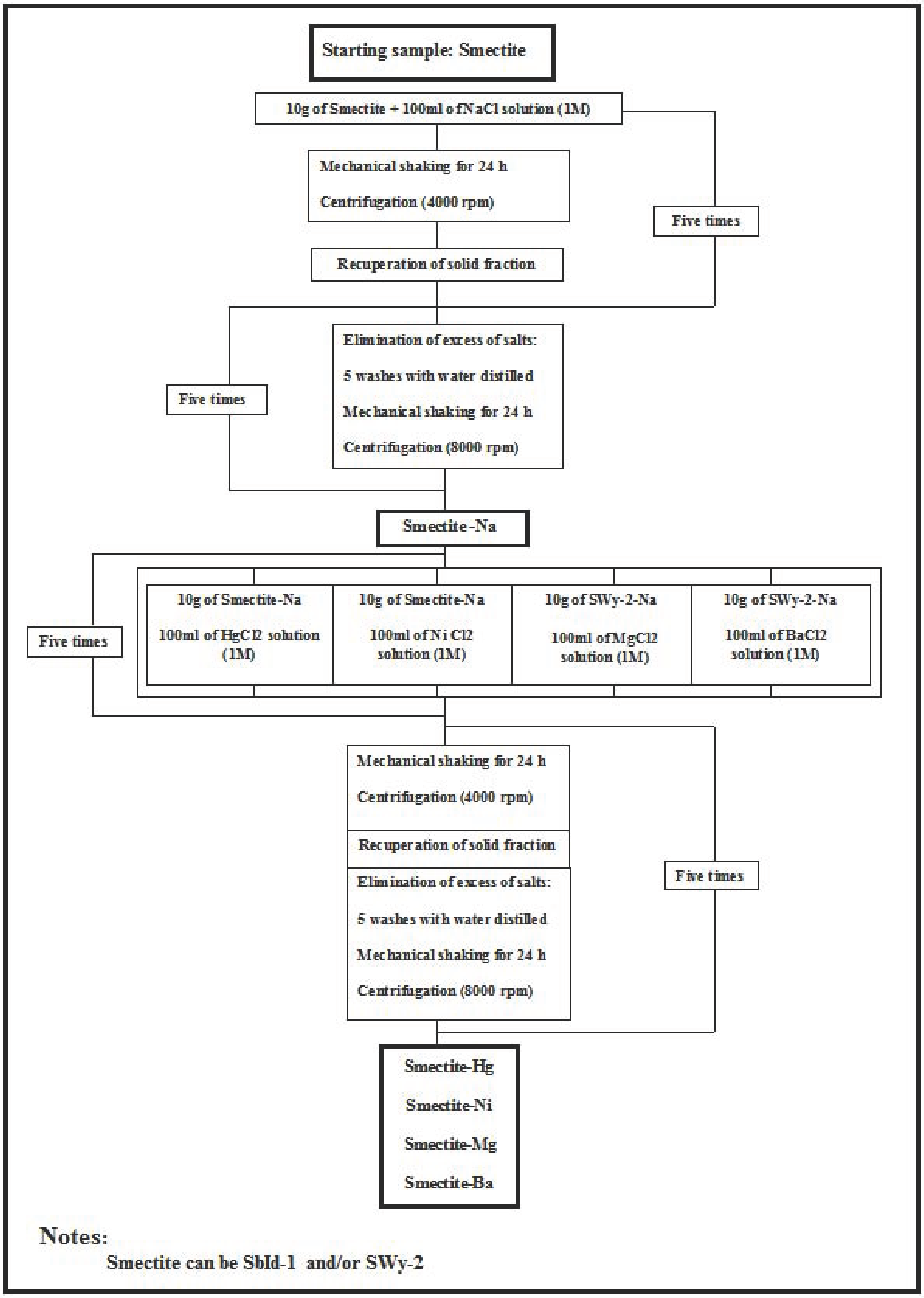


Figure 1. Experimental protocol for the ionic exchange process

C. Experimental.

XRD patterns of the oriented and air dried specimens are recorded under room condition (297 K, an ~40%RH), by reflection setting with a D8 Advance Brüker installation using Cu-Kα radiation equipped with a solid-state detector and operating at 40 KV and 30 mA.

The usual scanning parameters were 0.04 °2θ as step size and 6 s as counting time per step over the angular range 2–40 °2θ. The divergence slit, the two Soller slits, the antiscatter, and resolution slits were 0.5, 2.3, 2.3, 0.5, and 0.06°, respectively.

D. X-ray diffraction analysis

1. Qualitative XRD patterns investigation

A preliminary idea about the hydration state of the studied samples mainly based on the examination of the 00l basal reflections position and the global description of the profile geometry of the XRD pattern (picks symmetry and/or asymmetry). The measure of the Full Width at Half Maximum intensity (FWHM) value and the standard deviation of the departure from rationality (ξ) of the *00l* reflection **(**Bailey, 1982**)**, (calculated as the standard deviation of the $l \times d(00l)$ values calculated for all X*i* measurable reflections over the explored 2θ° angular range) can supply information about the hydration character (homogenous or interstratified) .

Nevertheless, the information related to the quantification of the relative layers proportions with different hydration states which can coexist in the same "particle", cannot be provided through the qualitative interpretation, thus it is necessary to perform the quantitative analysis in order to acquire details about different structure parameters, such as the position and organization of exchangeable cations with H_2O molecule in the interlamellar space along the c* axis.

2. Quantitative XRD analysis

The modeling of the X-ray patterns is performed using the algorithms developed by Sakharov and Drits, (1973); Drits and Sakharov, (1976). This method consists of adjusting the experimental patterns (00ℓ peak series) to a theoretical ones calculated using the Z atomic coordinates of the interlayer space corresponding to those proposed by Drits and Tchoubar (1990). The interlamellar water molecule distribution used in this work is in accordance with the latest literature description (Ferrage *et al*,. 2005, Oueslati *et al.*, 2012)**.** The theoretical intensities were calculated according to the matrix formalism detailed by Drits and Tchoubar (1990).

$$I_{00}(2\theta) = L_p Spur(\mathrm{Re}[\phi][W]\left\{[I] + 2\sum_{n}^{M-1}[(M-n)/M][Q]^n\right\})$$

Where Re is the real part of the final matrix; Spur, the sum of the diagonal terms of the real matrix; M, the number of layers per stack; n, an integer varying between 1 and M_1; [f], 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. The relationship between the different kinds of layer proportions and probabilities are given by Oueslati *et al.,* (2011). During the simulation of the XRD patterns, some experimental corrections must be taken into account, such as the Lorentz-polarization factor and the preferred orientation Reynolds (1986), Ben Haj Amara *et al.,* (1998). The XRD profile modeling approach is achieved following the fitting strategy detailed by Ferrage et al. (2005) , Oueslati *et al.,* (2011). Through this method several structural parameters such as the abundances of the different types of layers *(Wi),* the mode of stacking of the different kinds of layers and the mean number of layers per Coherent Scattering Domain (CSD) (Ben Rhaiem *et al.,* 2000) can be determined. Within a CSD, the stacking of layers is described by a set of junction probabilities (*Pij*). The relationships between these probabilities and the abundances *Wi* of the different types of layers was detailed by Drits and Tchoubar, (1990

In addition, the profile fitting approach is very useful for the characterisation of interstratified structures, containing essentially layers with the same hydration state, so additional contributions from (MLSs) structure of the mixed layer can be introduced to improve the agreement between theoretical and experimental XRD models. Therefore, layers with the same hydration state, present in the different MLSs contributing to the diffracted intensity, are assumed to have identical properties (chemical composition, Layer Thickness, Z-coordinates of atoms).

III. RESULTS

The best agreement between calculated and experimental XRD patterns, obtained under room condition (297 K, and ~40%RH), is illustrated in (Fig. 2). All structural parameters deduced from the qualitative XRD analysis including the d_{001} spacing values, the FWHM of the 001 reflection and the ξ parameter (i.e. Which are calculated for 3 or 4 measurable reflections over the 2–40°2θ angular range) are summarized in Table I.

TABLE I. Qualitative XRD investigations

Smectite with tetrahedral charge deficit

Sample	d_{001}(Å)	FWHM(°2θ)	ξ, Xi	Character
SbId-1-Ni	14.86	0.88	0.64 ,3	I
SbId-1-Hg	14.68	1.55	0.67 ,3	I
SbId-1-Mg	14.88	0.89	0.60 ,3	I
SbId-1-Ba	14.58	1.49	0.76 ,3	I

Smectite with octahedral charge deficit

Sample	d_{001}(Å)	FWHM(°2θ)	ξ, Xi	Character
SWy-2-Ni	15.47	1.20	0.15 ,3	I
SWy-2-Hg	15.20	0.77	0.05 ,3	H
SWy-2-Mg	15.52	1.03	0.77 ,3	I
SWy-2-Ba	14.94	1.55	0.97 ,3	I

A. Case of Idaho Beidellite specimen

1. Qualitative analysis

The qualitative XRD analysis, related to the sample saturated respectively with Ni Hg and Ba cation, shows that the *001* reflection is characterized by an asymmetric peak profile indicating the heterogeneous hydration character (Fig.2.a, Fig.2.b and Fig.2.d). The examination of the d_{001} values (i.e. 14.86 Å (Ni), 14.68 Å (Hg) and 14.58 Å (Ba)) shows an intermediate “1W-2W” hydration state with a major contribution of bihydrated layers. The irrationality for all measurable reflection positions is accompanied by a high ξ parameter value (i.e. 0.64 Å(Ni), 0.67 Å(Hg) and 0.76 Å(Ba)) which confirms the interstratified hydration character. On the other hand, the **SbId-1-Mg** is characterized by d_{001}=14.88 Å, which is recognized to a quasi-homogeneous 2W hydration state. The presence of a little "shoulder" near the elevated angle range, (Fig.2.c) is probably related to the presence of a few proportion of the dehydrated layer (i.e.0W) which confirm the supposed heterogeneous hydration behavior.

2. XRD profile modeling:

The hypothesis related to the heterogeneous hydration character for the homoionic exchanged **SbId-1** sample**,** determined through the qualitative XRD investigation, is confirmed by the quantitative study where, in the major case, the optimum structural models are determined assuming the presence of several MLSs within smectite crystallites. Indeed, in the case of **SbId-1-Ni**, the experimental XRD pattern is reproduced using three interstratified MLSs (i.e. 0W, 1W and 2W) with various contributions (Fig.2.a). The proposed theoretical model includes in total a major proportion of the bihydrated layers (52.90%) and mono hydrated ones (45.10%) mixed with a few contributions of dehydrated ones (2%) (Table II).

The XRD pattern produced by **SbId-1-Hg sample** (Fig 2.b) was fitted using three MLSs with variable contributions detailed in Table II.

The best fit for **SbId-1-Mg sample** (Fig. 2.c) is obtained using three MLSs types with a variable layer abundance. Indeed, two layer type population related to 1W:2W ratio are mixed with a third one containing, in plus, a dehydrated (0W) layer type fraction. All structural parameters that made it possible to have this agreement are summarized in Table II.

For SbId-1-Ba sample, an arrangement of three MLSs, with variable abundance containing respectively 0W, 1W and 2W layers, were consistently used to fit XRD profiles (Fig 2.d). The proposed model is characterized by a main structure containing three layer types hydration states with a relatively significant proportion of 0W layers at 13.75%. The number of layers per stack is 8 and the optimum structural parameters used in the simulation are illustrated in Table II.

TABLE II. Optimum structural parameters used for modeling XRD profile in the case of homoionic exchanged beidellite.

Sample	L.T 0W 1W 2W	nH_2O 0W 1W 2W	Z H_2O 0W 1W 2W	Z n. 0W 1W 2W	%Abundance of layer type 0 W/ 1W /2W	M
SbId-1-Ni	10.30	-	-	8.90	2/45.10/52.90	8
	12.00	2.8	9.50	9.50		
	15.00	5.6	10.00/14.80	11.30		
SbId-1-Hg	10.20	-	-	9	7.50/50/42.50	6
	12.30	1.5	9.50	9.50		
	15.10	5	10.50-14.90	11.30		
SbId-1-Mg	10.20	-	-	8.90	3.50/44.50/52	10
	12.00	2.5	9.50	9.50		
	15.65	5.6	10.50/14.80	12.00		
SbId-1-Ba	10.20	-	-	9	13.75/29.75/56.50	8
	12.30	2.5	9.70	9.70		
	15.00	5	10.70/14.70	11.20		

Note: L.T: Layer thickness in Å. nH_2O: number of H_2O molecule per half unit cell. ZH_2O: position along c* axis of H_2O molecule. Zn: Position of exchangeable cations per half unit cell calculated along c* axis, 0W, 1W and 2W attributed to the layer hydration state M: average layer number per stacking

B. Case of Wyoming montmorillonite SWy-2

1. Qualitative analysis

The XRD pattern produced by **SWy-2-Ni** is characterized by an asymmetric peak profile (Fig. 2.e) and present a (*001*) basal reflection situated at 2θ=**5.70°** (d_{001}=15.47 Å). The examination of the ξ and FWHM values (i.e. 0.15 Å and 1.20) indicates the heterogeneous hydration state character (Ferrage *et al.*, 2005; Oueslati *et al.*, 2011). For **SWy-2-Hg** complex, the (001) reflection is characterized by a symmetric profiles (Fig. 2.f) and present a d_{001} basal spacing value (d_{001}=15.20Å) corresponding to a two water layer hydration state (Sato *et al.*, 1992).

The low ξ and FWHM values (i.e. 0.05 Å and 0.77) confirms the obtained rational reflections series, indicating the homogeneous hydration character. The qualitative examination of the experimental patterns related to **SWy-2-Mg,** shows a 001 basal reflection situated at 2θ=5.68° (d_{001}=15.52 Å). The ξ and FWHM value (i.e. 0.77 Å and 1.03) demonstrates an irrationality of the *00l* reflection positions attributed to the interstratified hydration character. In the case of **SWy-2-Ba** samples, the *(001)* reflection is characterized by an asymmetric profile (Fig. 2.h) with a d_{001} =14.94 Å corresponding to a quasi-homogeneous 2W hydration. This result is confirmed by ξ and FWHM investigation characterized by an eminent value (i.e. 0.97 Å and 1.55) indicating an irrationality of the *00l* reflection positions and the presence of more than one main hydrated phases.

2. XRD profile modeling

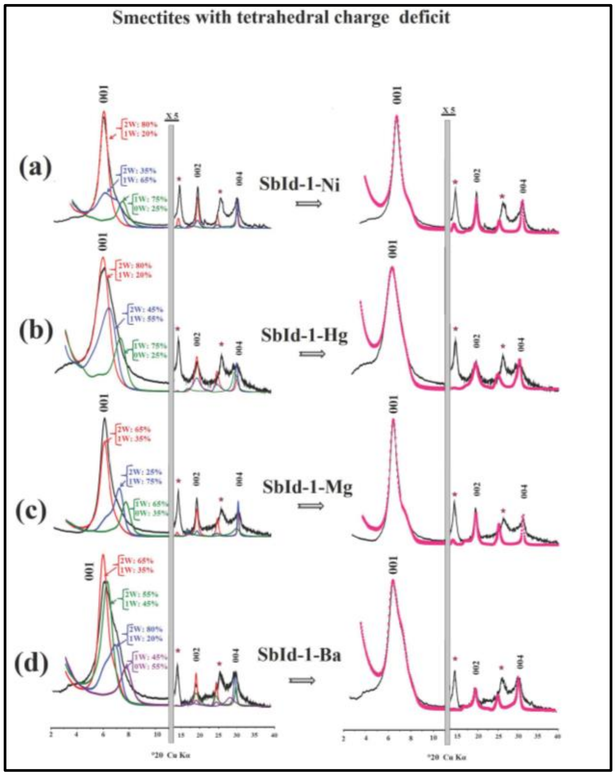
The qualitative XRD analysis supposes the presence of hydration heterogeneities in the case of sample exchanged with Ni^{2+}, Mg^{2+} and Ba^{2+} cation and predict a homogeneous hydration behavior in the case of SWy-2-Hg. To resolve problems related to structural heterogeneities the quantitative XRD analysis was imposed. Indeed, for **SWy-2-Ni**, the best agreement between theoretical and experimental profiles (Figs. 2.e) is achieved using two MLSs with different proportion of 1W and 2W layers. Indeed, the first MLS, characterized by **35%(1W) : 65%(2W)** ratio, is shared with a second MLS, containing **65%(1W) : 35%(2W)** ratio.

The theoretical XRD patterns (Fig 2.f) produced by **the SWy-2-Hg** sample is obtained assuming the presence of two MLSs including different contribution of 1W and 2W layer types randomly distributed within smectite crystallites. The first MLS is characterized by a major contribution of 2W hydration state (95%), whereas the second ones is described by the following ratio 55%(1W):45%(2W). This result is in discordance with the qualitative XRD analysis which suggests a main homogenous hydration character. The average number of layers per stack is 9. The structure of **the SWy-2-Mg** complex is reproduced using two distinct theoretical models with variable 1W and 2W proportion randomly distributed. In whole, the main structure is composed by 69% of bihydrated layers and 31% of monohydrated ones.

Two distinct MLSs with variable abundance containing respectively 1W and 2W layer hydration state are used to fit XRD patterns of **the SWy-2-Ba sample.** The first "particle" collection presents a major proportion of the bihydrated layers 85% (Figs. 2.g,) while the second one is relatively dominated by 1W at 65%. The structure is described in total by 47% of 1W mixed with 53% of 2W phases. All structural parameters that made it possible to have these agreements are summarized in Table III.

TABLE III. Optimum structural parameters used to fit XRD profile of homoionic exchanged montmorillonite.

Sample	L.T 0W 1W 2W	n_{H2O} 0W 1W 2W	Z $_{H2O}$ 0W 1W 2W	Z n. 0W 1W 2W	%Abundance of layer type 0 W/ 1W /2W	M
	-	-	-	-		
SWy-2-Ni	12.00	1.5	10.80	10.80	0/44/56	7
	15.45	3.6	11.30/14.50	12.80		
	-	-	-	-		
SWy-2-Hg	12.20	1	10.00	10.00	0/27.50/72.50	9
	15.20	4	11.00-14.60	12.70		
	-	-	-	-		
SWy-2-Mg	12.10	2	10.60	10.60	0/31/69	8
	15.65	3	10.00/14.50	12.40		
	-	-	-	-		
SWy-2-Ba	12.70	1	10.30	10.30	0/47/53	8
	15.50	4	11.40/14.60	12.20		



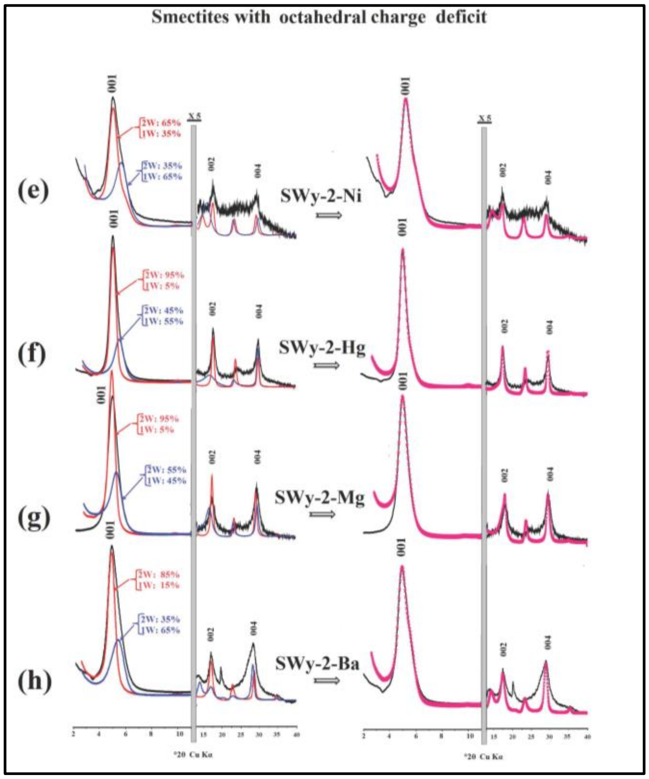


Figure 2. Qualitative and quantitative XRD investigations

IV. DISCUSSION

A. Hydration heterogeneity degree:

The quantitative investigation demonstrates the coexistence of varied MLSs types exhibiting different proportions of layers with contrasting hydration states, hence the hydration heterogeneity is the main deduced character for all studied specimens. The theoretical structural models related to the beidellite sample contain more complex structure than for montmorillonite in the presence of the same exchangeable heavy metal cation in interlayer spaces. In fact, for the exchanged **SbId-1 sample,** the best fit is obtained using the contribution of three dissimilar populations with a main interstratified structure including three hydration states (i.e. 0W, 1W and 2W). While, in the case of **SWy- sample,** all theoritecal models present two interstratified contributions involving the 1W and 2W layers types. This result is in agreement with the study of Ferrage *et al.,* (2007) where authors showed an increase of the hydration heterogeneity degree in the case of the beidellite structure (SbId-1) compared to the montmorillonite (SAz-1) saturated by Sr and/or Ca cations. This result is observed at different relative humidity (RH) conditions and the authors suggest that theses heterogeneities are due to the presence of the dehydrated and the monohydrated layer types.

B. Effect of the location charge

The impact of charge location (tetrahedral vs. octahedral) on the crystalline swelling of the studied dioctahedral smectites is clearly detected through both qualitative and quantitative investigations. Indeed , the montmorillonite and beidellite display a difference in the hydration behavior obviously observed from the qualitative examination of the d_{001} values where the SbId-1 present always the low basal spacing values comparing to SWy-2 when they are saturated with the same bivalent cation (Table1).

Furthermore, the comparison between the relative contribution of the different layer types (summing up all mixed-layer structures) derived throughout the quantitative analysis, shows the presence of the dehydrated layers (i.e.0W) in the case of the smectites with tetrahedral deficit charge (**SbId-1 specimen**). Whereas in the case of montmorillonite sample(i.e. octahedral deficit) all structures are modeled using only an arrangement between 1W and 2W layer type. The presence of dehydrated layer type in the case of beidellite sample can be explained by the significant attractive forces between hydrated exchangeable cations and the negatively charged surface which limits the hydration ability of the interlayer spaces and restrict the penetration of the H_2O molecule in interlamellar spaces. In fact the strong attractive interaction is assumed to decrease layer hydration (Laird 1996; Laird, 1999).

C. Effect of exchangeable cation nature

The effect of the exchangeable cation nature on the smectite hydration properties was treated by several previous work (Berend *et al.*, 1995; Case *et al.*, 1997; Ferrage *et al.*, 2005; Oueslati *et al.*, 2007) where the authors have shown the link between the Ionic potential of the exchanged cations and the associated interlamellar space swelling properties. The qualitative and quantitative XRD investigations show that the montmorillonite and the beidellite specimen display a special hydration behavior versus the exchangeable cation nature. Indeed, when the **SbId-1 sample,** is saturated by the alkaline earth metal ions (**Mg (II) and /or Ba (II)),** the structure presents an interstratified hydration character involving the 0W, 1W and 2W states, with a major contribution of bihydrated layer types, which confirm the qualitative analysis suggesting the elevated hydration degree. The presence of the dehydrated layers (i.e. 0W) indicates a restricted ion exchange process. This result is confirmed in the case of Ba cation, characterized by a high ionic radius value (Shanon, 1976), where an important relative contribution of the 0W phases (13.75 %) is used. In return, an absence of the dehydrated layer types is noted for SWy-2-**Mg and SWy-2-Ba** sample where a logical dominance of the bihydrated layers (i.e. 2W) is shown ,in particular, in the case of Mg cation which is characterized by an important ionic potential compared to Ba^{2+} cation. This result justifies the important interlayer water molecule content in the case of **SbId-1-Mg** (Fig. 3). In the others hands , the presence of the Ba cation in the **SWy-2** specimen is characterized by the dominance of the 1W layer type. For the transition metals (Hg and Ni), a specific hydration behavior is noted, in fact the cation with the elevated ionic radius (i.e. Hg) present an important 2W phase comparing to Ni^{2+} cation despite the important potential for this later. That can be explained by the Hg^{2+} cation properties which have a strong impact on the hydrogen-bond network of water that extends beyond the first coordination shell. (Valentina Miglioratiet *et al.*, 2011).

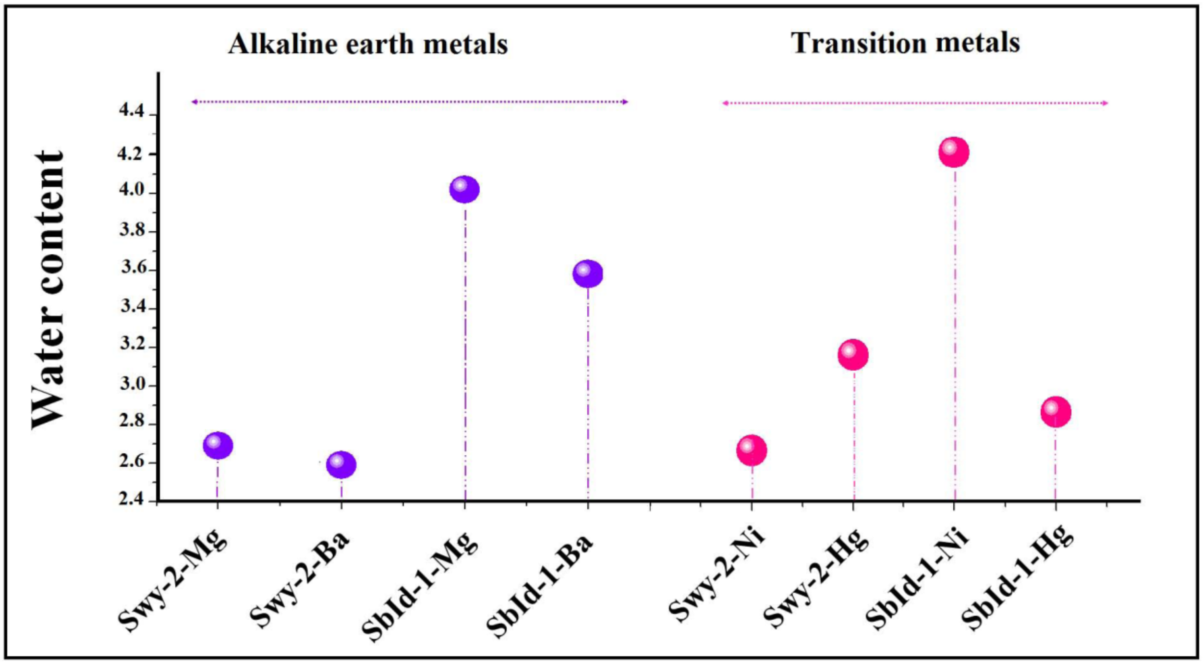


Figure 3. Water content versus exchangeable cations nature and the charge location.

V. CONCLUSION

The quantitative XRD analysis is used to characterize the effect of the charge location and the exchangeable cation nature on the hydration properties of montmorillonite and beidellite specimen. The modeling approach allows quantifying the different layers types (2W, 1W, and 0W) which present in the studied smectites structures. The obtained results show that the entire studied complex, are characterized by an interstratified hydration character. All exchanged beidellite specimen, presents the dehydrated, mono and bihydrated layers in their structure whereas, the montmorillonite contain an interstratified 1W-2W hydration states. This specific hydration behavior was explained by the effect charge location which limit the hydration ability in the case of tetrahedral deficit charge (i.e. SbId sample) particularly in the presence of the cation with high ionic radius [i.e. Hg (II) and Ba (II)].

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