

# Structural formula determination of 2:1 Tunisian clay using XRD investigation

R. Chalghaf, S. Jebali, W. Oueslati, H. Ben Rhaiem,  
A. Ben Haj Amara\*

UR05/13-01- PMLNMH: Physique des Matériaux Lamellaires et Nano-Matériaux Hybrides  
Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia

\* Contact author; email: Abdesslem.bamara@fsb.rnu.tn

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**Abstract.** This work aims at determining the structural formula of a Tunisian 2:1 clay using PXRD analysis. To accomplish this goal, exchangeable site of the material was saturated respectively by  $\text{Li}^+$ ,  $\text{Cs}^+$  and  $\text{Ni}^{2+}$  cation. The octahedral charge rate and the structural iron amount were obtained using Li-saturated sample and based on the Hoffman Klemen method. The Cs exchange process was used to determine the total and the tetrahedral layer charge. The Si, Al, Fe and Mg rates were determined using XRD patterns. All these parameters allowed us to establish the structural formula. A Ni-saturated sample was studied to confirm the structural formula calculated above. All structural parameters were determined using an indirect method based on the comparison between experimental and simulated XRD patterns. Final results showed that the studied sample was characterized by an octahedral charge and the following structural formula:

$(\text{Si}_{4.00} (\text{Al}_{1.10} \text{Fe}_{0.50} \text{Mg}_{0.40}) \text{O}_{10} (\text{OH})_2 (\text{M}^+_{0.4}); \text{M}^+$  is a monovalent cation.

## 1. Introduction

The clay minerals are characterized by a wide variation in chemical structure defects and physical properties. The smectite group is characterized by a high structural charge (up to 1000 meq/kg) which involves important sorptive properties. Such a mineral is constituted by octahedral sheet sandwiched between two silica tetrahedral sheets. Isomorphous substitutions, either on tetrahedral or on octahedral sheets, for cations with lower charge species (such as  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , for  $\text{Al}^{3+}$ ;  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  for  $\text{Si}^{4+}$ ). The layer negative charge resulting from these isomorphous substitutions is balanced by exchangeable cations in interlamellar space. The Cation Exchange Capacity (CEC meq/100g) is an important characteristic of the mineral especially of bentonites. The determination of the structural formula is an important step for understanding the properties of the mineral in relation with CEC, charge and location charge (octahedral or tetrahedral) [1]. Generally such a determination is achieved using chemical analysis and requires large amounts of material. In order to determine the charge location, it is customary to use the Hofmann and Klemen effect [2]. The aim of this study is to determine accurately the clay elements such as Si, Al, Fe, Mg; the layer charge as well as its

location in order to establish the structural formula on the basis of quantitative XRD analysis. The method is based on the simulation of  $00l$  reflections patterns.

## 2. Materials and methods

### 2.1 Materials

The clay sample was collected from a marble quarry of BirElfei in Gafsa department (Southern Tunisia) in a geological fault (figure 1).



Figure 1. Clay in fault.

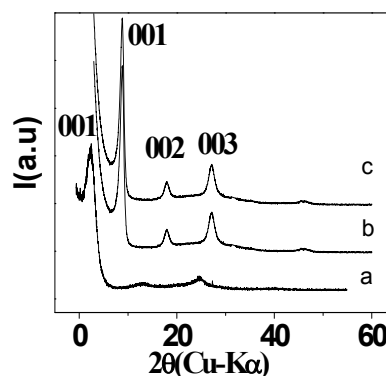


Figure 2. Experimental XRD patterns of ST-Li (a), ST-Li-H (b) and ST-Li-H-EG (c).

The crude starting sample (designed ST) was first Na exchanged according to the Tessier protocol [3] in order to obtain Na-rich specimen (ST-Na). ST-Na complex was prepared by dispersing suitable amounts (200g) of clay suspension several times (7 cycles) in 1N NaCl solution. The excess of salt was then removed by washing the material for several times with distilled water. Chemical analyses achieved on crude sample according to classical protocol are reported in table 1. The obtained results require large amounts of sample and show that results are qualitative.

Table 1. Chemical composition of the sample ST.

oxide	A1 : Wt%	A2 : Wt%	A3 : Wt%	A4 : Wt%
SiO <sub>2</sub>	52.98	59.7	50.73	52.33
Al <sub>2</sub> O <sub>3</sub>	16.32	23.75	14.74	15.3
Fe <sub>2</sub> O <sub>3</sub>	7.26	2.21	9.66	9.70
MgO	3.86	0.54	3.81	3.96
CaO	2.52	0.1	3.21	2.45
Na <sub>2</sub> O	0.5	0.17	-	-
K <sub>2</sub> O	0.5	1.05	0.05	0.03
Loss ignition	14.20	11.24	6.72	6.28

In order to establish more accurately the structural formula using quantitative PXRD analysis, the sample was submitted to several treatments to determine the charge location, dioctahedral character and chemical composition.

ST-Na sample was then exchanged with  $\text{Li}^+$ ,  $\text{Ni}^{2+}$  and  $\text{Cs}^+$  cations using respectively 1N Lithium chloride, Nickel chloride and caesium chloride solution. Obtained samples were labelled respectively ST-Li, ST-Ni and ST-Cs. ST-Li, ST-Ni complexes were heated at 300°C (ST-Li-H) and 400°C (ST-Ni-H) and exposed to the Ethylene Glycol vapour under 50°C (ST-Li-H-EG and ST-Ni-H-EG). These treatments permitted us to determine the amount and location of layer charge. In order to determine the structural characteristics along the normal to the layer using the  $00l$  reflexions, oriented films were prepared by depositing a clay suspension into a glass slide [3-4].

## 2.2 Methods

The XRD patterns of oriented and air-dried specimens were obtained by reflection setting with a D8 advanced Bruker installation using Cu-  $K\alpha$  radiation. Intensities were measured at  $2\theta$  intervals of  $0.02^\circ$  and 30 s counting time per step. The absolute precision of the Bragg angles was better than  $2\theta$  equal  $0.01^\circ$  over the whole angular range. The quantitative determination of structural parameters along the normal to the layer by comparing the experimental patterns to theoretical intensities calculated from the matrix expression [6].

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

Where: Re indicates the real part of the final matrix; Spur the sum of the diagonal terms of the real matrix;  $L_p$  the Lorentz-polarization factor;  $M$  the number of layers per stack;  $n$  an integer varying between 1 and  $M-1$ ;  $[\Phi]$  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 phenomenon between adjacent layers. All simulated XRD patterns were calculated using the  $z_n$  coordinates used by H. Ben Rhaïem and al. [4, 7] for the Wyoming montmorillonite.

The qualitative chemical composition was obtained using a transmission electron microscope (TEM) (FEI Tecnai G2) operating at 200 KV. Chemical analysis was performed using the energy dispersive X-ray spectroscopy (EDXS) system attached to the TEM

## 3. Results and discussion

### 3.1 Dioctahedral type

The dioctahedral character of the ST sample was highlighted using XRD patterns by examining the  $(06l, 33l)$  reflection situated at  $d=1.50\text{Å}$  [8].

### 3.2 Chemical analysis using EDX method

This step concerns the qualitative determination of the layer composition in order to facilitate the simulation of XRD patterns. Chemical analyses realized on different points of the same particle are reported on table 2. Examination of these analyses (table2) shows that the ST-Ni sample is formed by Si, Al, Mg, Fe and Ni and indicates that an heterogeneous charge distribution within the particle.

Table 2. chemical composition using the EDX method for ST-Ni sample.

Element	A1: weight %	A2: weight %	A3: weight %
MgK	3.5	4.1	2.6
AlK	14.8	14.8	12.8
SiK	53.4	59.5	59.8
FeK	11.1	9.3	9.6
NiK	17.2	12.2	15.3

### 3.3 Charge determination using the simulated PXRD patterns

In figure 2 we reported the experimental XRD patterns of ST-Li (fig. 2a), ST-LiH (fig. 2b) and ST-Li-H-EG (fig. 2c). The examination of figure 2 shows that  $d_{001}$  basal spacing value decreases from 14.62 Å (fig. 2a), (attributed to a two-water layer hydration state 2W), to 9.83 Å (fig. 2b) (corresponding to anhydrous state 0W). The XRD pattern of heated ST-Li at 300°C and ethylene glycol treated (fig. 2c) exhibits no change (basal spacing value  $d_{001}$  = 9.83 Å) indicating that the layer charge is located on octahedral sites [9]. A first structural formula can then be given as follow:  $(\text{Si}_4) [(\text{Al}, \text{Mg})_{2-x} \text{Fe}_x] \text{O}_{10} \text{OH}_2 \text{Li}_x$  (since Mg and Al have the same diffusion factor and cannot be distinguished by XRD in this step)

### 3.4 Determination of the octahedral iron amount by XRD

The amount of iron (Fe III) in octahedral sites is obtained by modelling the XRD pattern of anhydrous ST-Li-H sample. We used the structural formula given below. Figure 3 represents XRD patterns of the 00l basal reflections calculated for different amounts of iron. Figure 3 shows an increase of the 002 and a decrease of the 003 reflection intensities when increasing the iron amount.

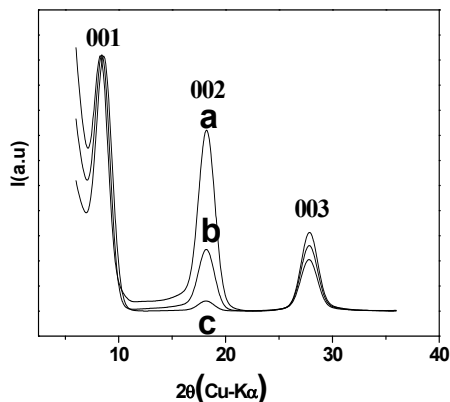


Figure 3. XRD patterns of various rate of iron placed at the octahedral sheet of the layer  
a : 0 Fe, b : 0.5Fe and c: 1.5 Fe.

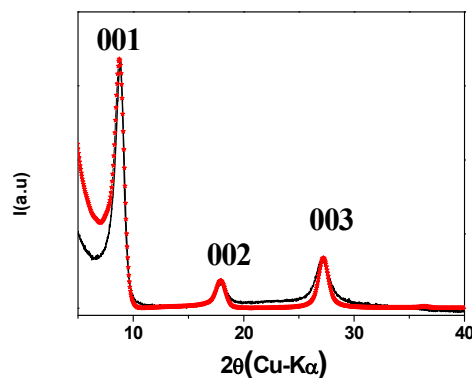
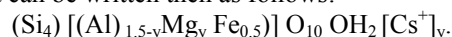


Figure 4. Best agreement between experimental (---) and theoretical (\*\*\*) XRD patterns of ST-Li-T.

The best agreement between the experimental and simulated XRD patterns (figure 4), using a single homogeneous phase characterised by  $d_{001}$  = 9.83 Å is obtained with: an average number of layers per stacking  $M = 15$  and 0.5 amount of iron.

### 3.5 Determination of magnesium amounts in the octahedral sheet and the mineral CEC

In order to determine accurately the magnesium amount and CEC, we studied the ST-Cs sample since the scattering factor of cesium is very high (about 54). Theoretical XRD patterns were calculated varying the cesium amount. To preserve the layer neutrality, we introduced the same amounts of magnesium and exchangeable  $\text{Cs}^+$  cations. The structural formula can be written then as follows:



In figure 5, we reported the simulated XRD using variable  $\text{Cs}^+$  amounts in the middle of the inter-lamellar space ( $z_n=9.44 \text{ \AA}$ ) and an hydration state of 2.5 molecules per  $\text{Cs}^+$ . We notice the increase of the 002 and decrease of 004 reflection intensities when increasing  $\text{Cs}^+$  amount.

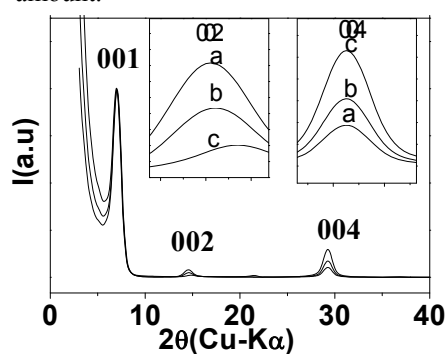


Figure 5. simulated XRD patterns of  $\text{Cs}^+$  rate: a : 0  $\text{Cs}^+$ , b : 0.1  $\text{Cs}^+$ , c : 0.3  $\text{Cs}^+$ .

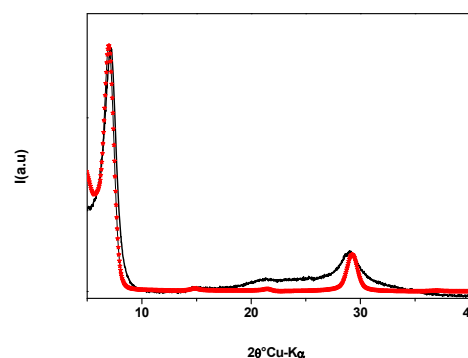


Figure 6. Best agreement between experimental (---) and theoretical (\*\*\*\*) XRD patterns of ST-Cs.

The best agreement between experimental and simulated XRD patterns is reported in figure 6. The obtained structural parameters are summarized in table 3. The final structural formula is then:  $(\text{Si}_4) (\text{Al}_{1.1} \text{Fe}_{0.5} \text{Mg}_{0.4}) \text{O}_{10} (\text{OH})_2 (\text{Cs}^+)_{0.4}$

To confirm this result, we studied the XRD pattern produced by heated ST-Ni sample at  $400^\circ\text{C}$  (STNi-H). A single homogeneous phase with  $d_{001} = 9.60 \text{ \AA}$  basal spacing related to an anhydrous homogenous state was used to calculate XRD intensities. The best agreement between theoretical and experimental XRD patterns is reported in figure 7. Structural parameters reported in table 3 indicate that the totality of nickel cations migrated into the vacant octahedral sites ( $z_n = 3.4 \text{ \AA}$ ). These results are in agreement with the structural formula given below and indicate that the layer charge is entirely octahedral.

Table 3. Structural parameters for ST-Li-T, ST-Cs, ST-Ni-T:  $n$ ,  $z_n$  ( $\text{\AA}$ ) number and position of exchangeable cations per half unit cell and  $M$ : layer number per stacking.

Sample	$d_{001}(\text{\AA})$	$n_{\text{CS}}$	$n_{\text{Mg}}$	$n_{\text{Fe}}$	$n_{\text{Ni}}$	$z_{\text{nFe}}$	$z_{\text{nNi}}$	$z_{\text{nCs}}$	$M$
ST-Li-H	9.83			0.5		3.31			15
ST-Cs	11.82	0.4	0.4	0.5		3.31		9.44	8
ST-Ni-H	9.6		0.4	0.5	0.2	3.31	3.40		11

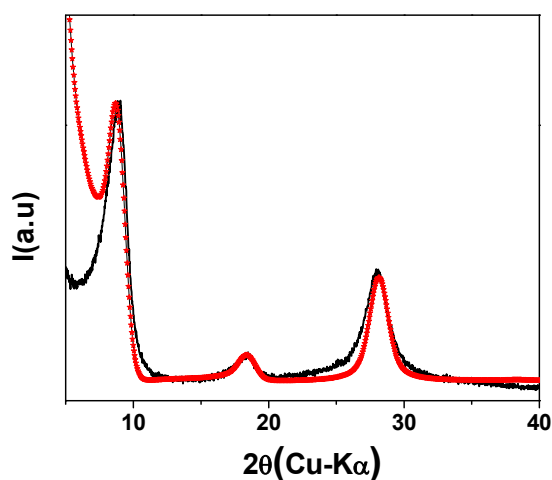


Figure 7. Best agreement between experimental (---) and theoretical (\*\*\*) XRD patterns of ST-Ni-T.

#### 4. Conclusion

In this paper, the structural formula of a dioctahedral sample was accurately determined using quantitative XRD analysis. This study was carried out through several steps by determining: The type of charge and location, the amount of iron in the octahedral sheet and the CEC. The structural formula per half unit cell thus determined is:

$(\text{Si}_{4.00}) (\text{Al}_{1.10} \text{Fe}_{0.50} \text{Mg}_{0.40}) \text{O}_{10} (\text{OH})_2 (\text{M}^+_{0.4})$  with  $\text{M}^+$  is a monovalent cation.

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