



## Physico-chemical and mineralogical characterization of clays collected from Akrach region in Morocco

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### Abstract

This study reports the physicochemical analysis of two deposit clays from the Akrach area (north-west, Morocco), Miocene deposit clay (MC) and Pliocene deposit clay (PC) (whole rock). Experiments were carried out to evaluate their potential applications. The clay fraction (particles smaller than 2 microns) from these deposits underwent a series of mineralogical, chemical and physico-chemical analyses. The results of X-ray diffraction (XRD), infrared spectroscopy (IR), differential scanning calorimetry (DSC) and elemental analysis by atomic absorption spectroscopy (AAS) show that examined samples should be mixtures of kaolinite, smectite, chlorite and large amount of muscovite-illite. Swelling clay is mainly found in the fraction <2  $\mu\text{m}$  with a clear presence in the Miocene clay (DRX analysis)

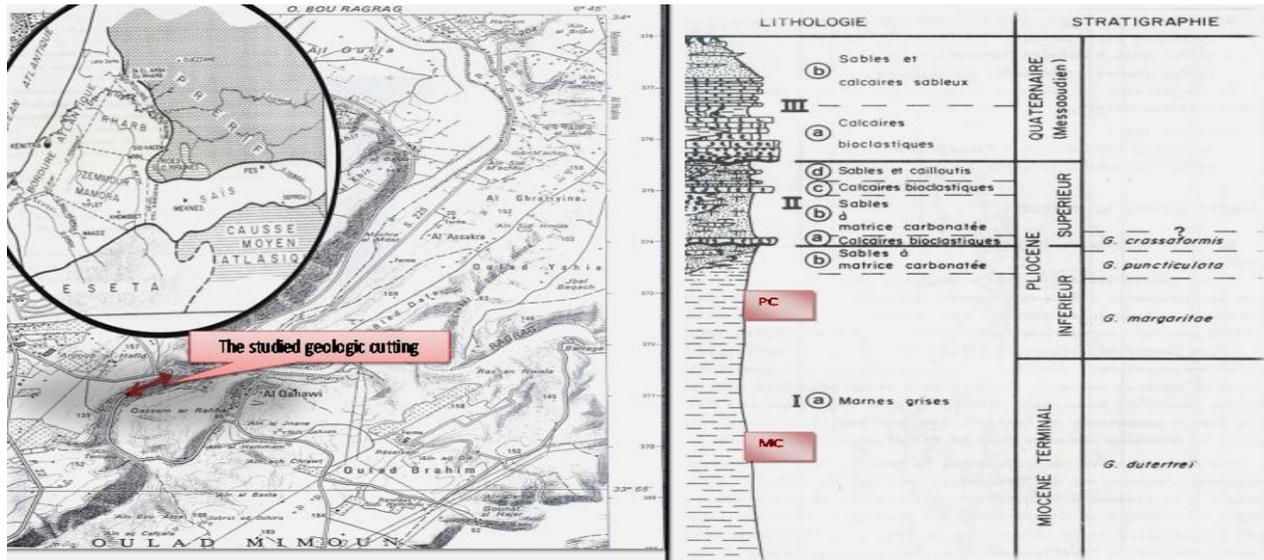
*Keywords:* Clays, Physico-chemical characterization, Akrach region.

### Introduction

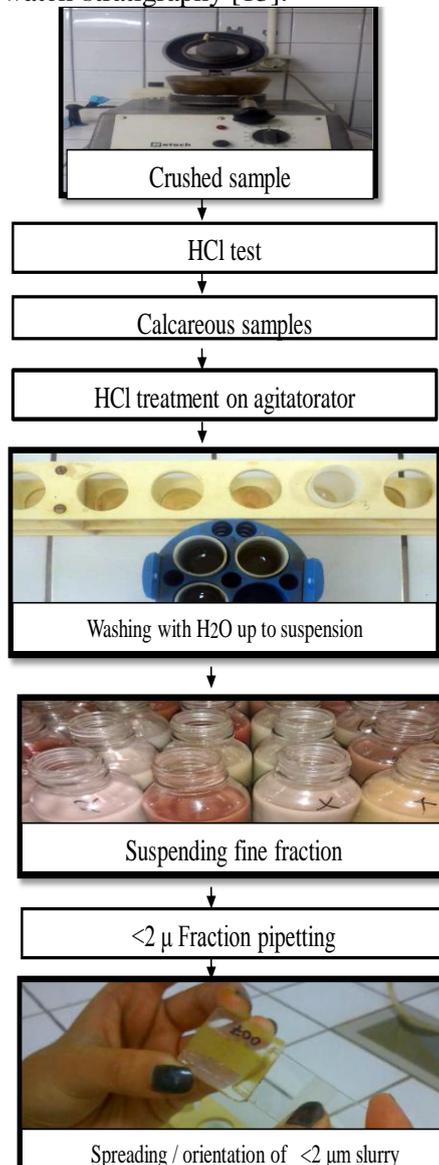
Clays are naturally occurring materials composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired [1]. They have varying chemical composition depending on both the physical and chemical changes in the environment where clay deposits are found [2]. Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption potential for ion exchange, clay materials are strong candidates as adsorbents [3]. Clay minerals share a basic set of structural and chemical characteristics and yet each clay mineral has its own unique set of properties that determine how it will interact with other chemical species. The variation in both chemistry and structure, among the clays leads to their applications in extremely diverse fields.

Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalies and alkali earths [4]. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygen or hydroxyls. The second unit is built of silica tetrahedrons. The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition,  $\text{Si}_4\text{O}_6(\text{OH})_4$  [4]. The specific clay minerals are identified by several techniques including thermal differential analysis, elemental analysis by atomic absorption analysis, infrared spectrometry and X-ray diffraction. Chemical analysis is an essential step to establish the nature of minerals [5]. In Morocco, the valorization of clay materials is a domain of growing interest [6]. The actual domains of interest are analytical applications the use of clay to modify carbon paste electrodes (CCPEs) is a





**Figure 2:** Synthetic cutting of the neogene series of the Margin upper Atlantic of the Westerner pond: Sequences, Lithology , Stopwatch-stratigraphy [13].



**Figure 3:** Extraction method of fine fraction

### 2.3. Apparatus

X-ray diffraction (XRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO operating with Cu K $\alpha$  radiation (K $\alpha$  0.15406 nm) generated at 40 kV and 20 mA. Scans were carried out at 0.02° min<sup>-1</sup> for 2 $\theta$  values between 3 and 40. The differential scanning calorimetric (DSC) measurements were realized by using a DSC-kind SETARAM 121 apparatus, operating under an argon flow and at a heating rate of 10 °C min<sup>-1</sup>. The infrared spectra (IR) of clay samples mixed with KBr were recorded with a vertex 70 spectrophotometer, operating in the range 4000–400 cm<sup>-1</sup>. A model GBC 906 AA flame atomic absorption spectrometer operating with an air-acetylene flame was used for metals determination.

## 3. Results and discussion

### 3.1. XRD analysis:

XRD patterns of samples (MC and PC) are shown in Figures 4 and 5. These patterns indicate the characteristic peak of illite, kaolinite and chlorite as the major phase for tow samples, with presence of smectite and interlayer Illite/smectite in Miocene clay sample (MC). The oriented samples were analyzed to confirm the nature of the clay phases. The examination using X-ray diffractions shows that the reflection at 10A° and its harmonics are not affected by the heat treatment. This compartment is characteristic of illite-muscovite. Indeed the later is a non-swelling mineral and thermally stable to temperatures higher than 500°C.

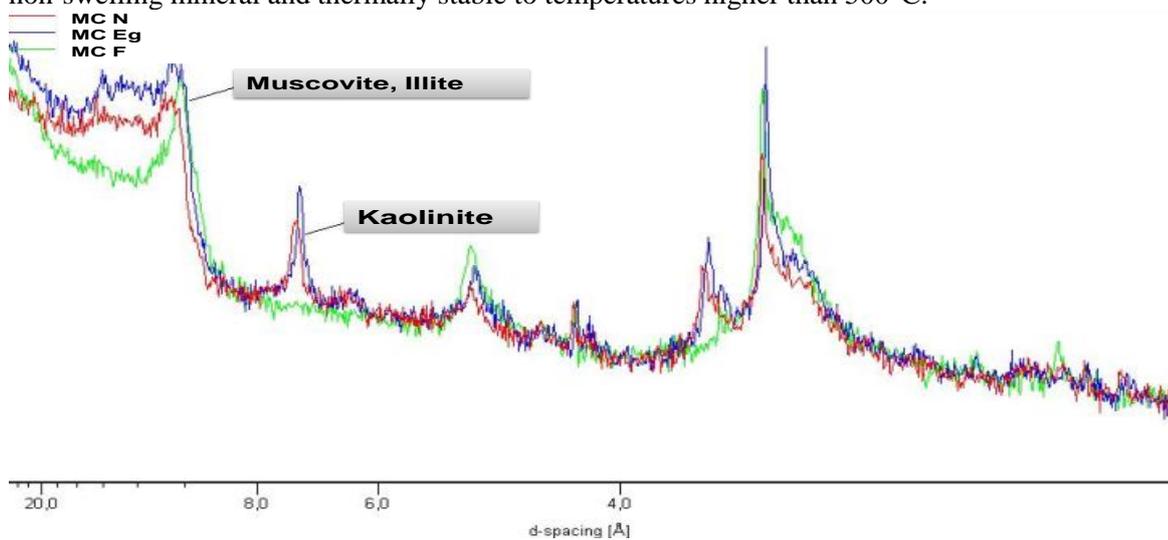


Figure 4: X-ray diffraction pattern of the Miocene clay material.

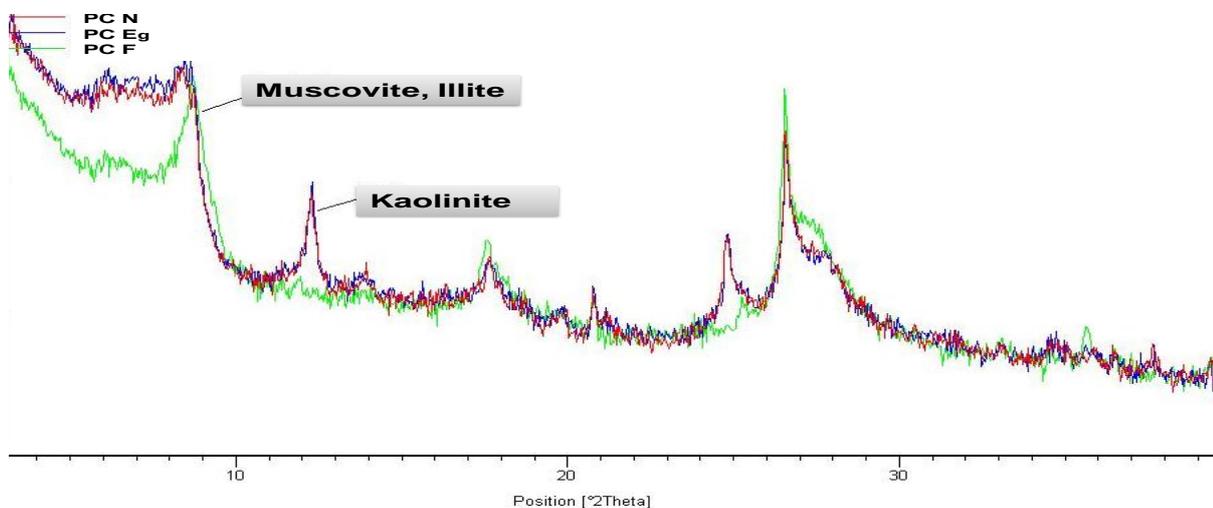
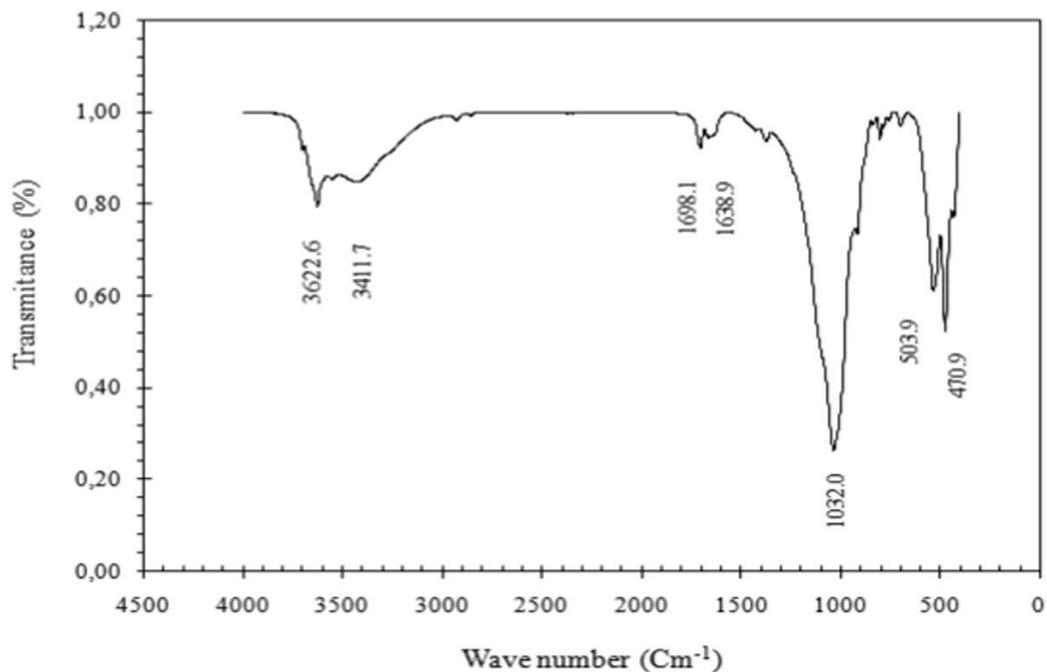


Figure 5: X-ray diffraction pattern of the Pliocene clay material.

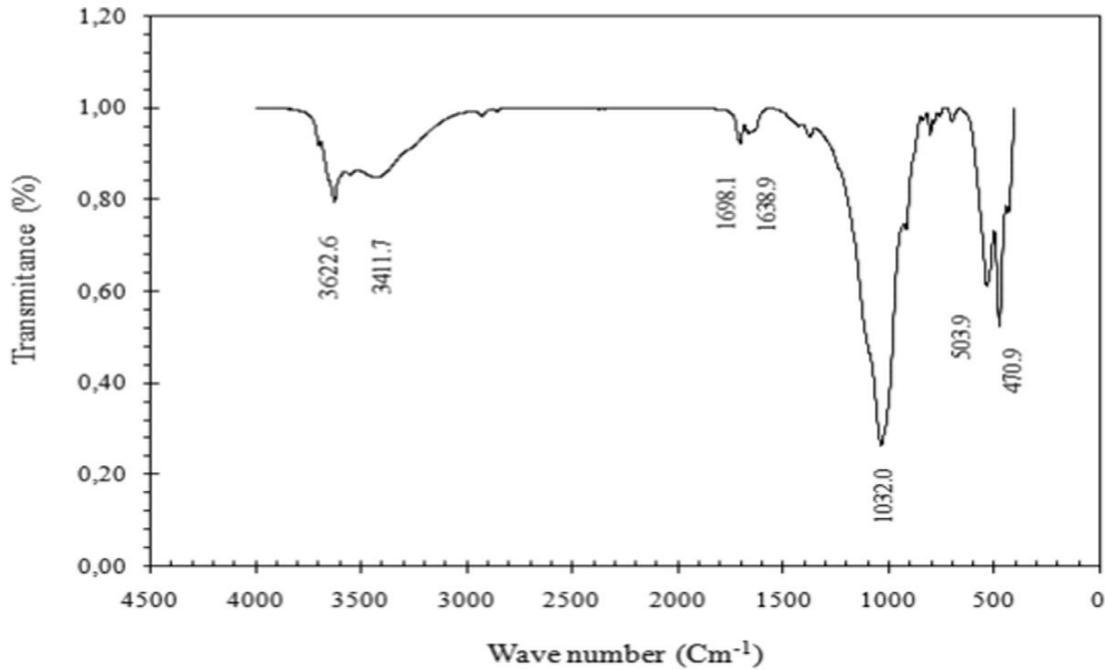
The heat treatment of the tow samples causes the disappearance of the reflection at  $13^\circ$  and its harmonics. This comportment is characteristic of kaolinite. The diffraction reflections at  $10^\circ$  and  $12.5^\circ$  are not displaced during glycolation and further confirm the presence of illite and kaolinite. The peak at  $14A^\circ$  following treatment with ethylene glycol and heating at  $500^\circ\text{C}$  confirmed the presence of clay mineral of the smectite group and chlorite. Through the 001 peak for to  $17A^\circ$  ( $2\theta = 5.2$ ) and break down to  $10A^\circ$  ( $2\theta = 8.8$ ). If the mineral is pure the peak  $14A^\circ$  passes in the peak  $17A^\circ$  and  $18A^\circ$  which explains the low intensity of the peak  $14A^\circ$ . The peak at  $4,26A^\circ$   $3,33A^\circ$  and  $3,25A^\circ$  suggest the presence of quartz and feldspath respectively in the raw material. The composition of this clay is comparable to that of African clays which is dominated by kaolinite, muscovite-illite and smectite [14].

### 3.2. IR analysis

The infrared spectra of the Akrach area clays was also investigated in Figures 6 and 7. The OH stretching vibration band that manifests at  $3698.1\text{ cm}^{-1}$ ,  $3622.6\text{ cm}^{-1}$ ,  $3411.7\text{ cm}^{-1}$ ,  $1638.9\text{ cm}^{-1}$ ,  $1032.2\text{ cm}^{-1}$ ,  $914.3\text{ cm}^{-1}$  and  $799.2\text{ cm}^{-1}$  indicate the presence of kaolinite [15, 16]. The characteristic band of illite at  $834\text{ cm}^{-1}$  was also observed [17]. The intense band occurring at  $3622.6\text{ cm}^{-1}$  and  $914.3\text{ cm}^{-1}$  is associated with the presence of a mineral 2/1 dioctahedral [18]. The Si-O stretching bands at  $1095\text{ cm}^{-1}$  and the Al-O bending at  $912\text{ cm}^{-1}$  are characteristic of alumino-silicate minerals. The stretching and bending of hydration water are observed at  $1630\text{ cm}^{-1}$ .



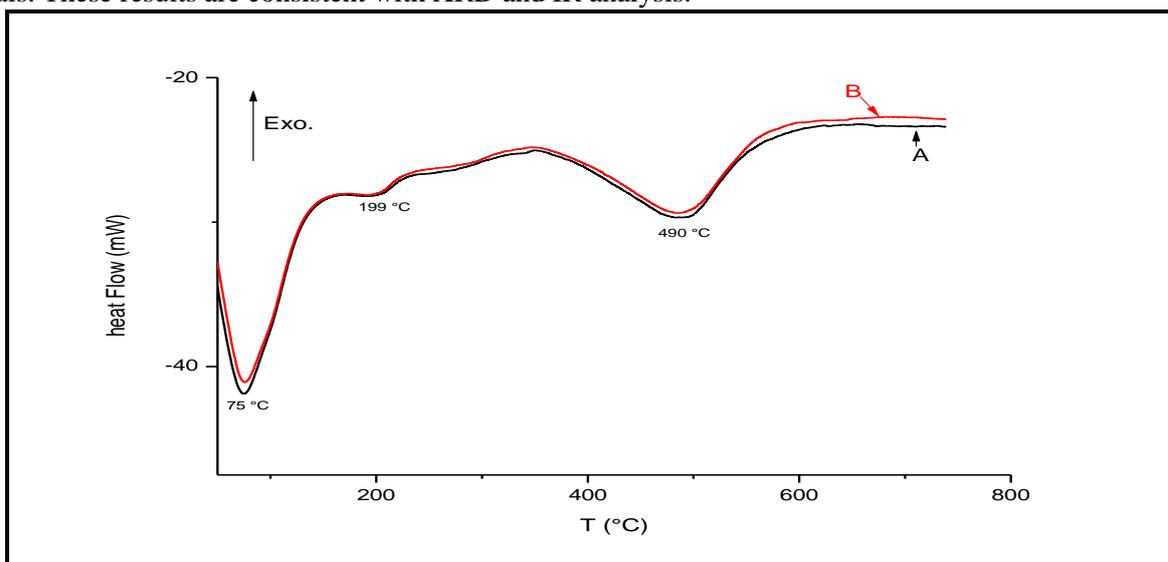
**Figure 6:** Infrared spectrum of the fraction  $<2\mu\text{m}$  of MC.



**Figure 7:** Infrared spectrum of the fraction <2μm of PC.

### 3.3. DSC analysis

Thermal curves, measured from ambient to 700 °C, are shown in Figure 8. The DSC curves of two samples show an intense endothermic peak at 75°C. These reactions were due to the removal of physically bound water. The peak observed at 199°C could be due to water molecules adsorbed in the interlayer or coordinated with exchangeable cations [19]. The form and position of this peak depend on the nature of the adsorbed cation and on the smectite clay mineral. In this case, these cations are probably Na<sup>+</sup> and K<sup>+</sup> [20]. Some thermal curves also showed an additional endothermic hump at 500°C, which was attributable to the dehydroxylation of clay minerals. These results are consistent with XRD and IR analysis.



**Figure 8:** Typical DSC thermogram of the fraction <2μm of Miocene sample (A) and Pliocene sample (B).

### 3.4. AAS analysis

Chemical composition of clays was obtained by atomic absorption spectroscopy, is shown in Table 8 . The clays contain CaO, K, Na and Mg oxides. Examination of the results of chemical analysis generally shows relatively

similar levels for most elements. This analysis revealed high levels of calcium (13.5%), a significant proportion of magnesium (1.29%) and sodium (1%). The presence of the potassium ion, which is a load balancer, indicates that it may be present in the leaf inter-layer of illite.

**Table 1:** Mineral composition of the MC and PC samples

		MC	PC
Concentrations ( IN 10 <sup>-3</sup> ppm)	Ca	9.7	12.7
	Mg	6.85	6.3
	K	4.25	1.6
	Na	4.75	4.65
Concentrations ( IN 10 <sup>-3</sup> ppm)	CaO	135.8	178.5
	MgO	10.96	10.08
	Na <sub>2</sub> O	12.92	12.65
	K <sub>2</sub> O	10.24	3.85
Weight percent (IN %)	CaO	13.58	17.85
	MgO	1.09	1.00
	Na <sub>2</sub> O	1.29	1.26
	K <sub>2</sub> O	1.02	0.38

The XRD and IR measurements were in accordance with the results of DSC and AAS. The purified material of the two samples consists of illite and kaolinite, with clear presence of smectite and chlorite in Miocene sample clay. These results are consistent with previous finding [21, 22]. In this work we have demonstrated that XRD and DSC combined with IR and AAS are a powerful method for the study of different fractions of clay minerals and were able to determine the distribution of the different minerals in each of the fractions.

## Conclusion

Processed samples of used clay, located at the Akrach (Morocco), were qualitatively and quantitatively investigated by means of X-ray diffraction, differential scanning calorimetry, infrared spectroscopy and atomic absorption spectroscopy. The clay fraction of Akrach area samples is dominated by illite and kaolinite with variable contribution of chlorite, smectite. The results of the two samples Miocene clay and Pliocene clay showed that the purified material consists essentially of illite, kaolinite as minerals clay, with clear presence of smectite and chlorite in Miocene clay.

-The kaolinite which was the major mineral content makes it suitable in the paper production, pharmaceutical, in ceramics production and bricks production

-It can be good in making of animal dung due to the presence of smectite and illite minerals present in the clay.

-Chlorite and smectite found in the clay makes it suitable to be used in analytical applications.

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## References

1. Stephen.G., Martin R.T.; *Clays Clay Miner.* 43 (1995) 255.
2. Salawudeen T., Olalekan Isam Y., Qudsieh Nassereldeen A., Kabbashi, Maan Alkhatib, Suleyman A Muyibi, Faridah Yusof, Qusim H. Shah., *IJET – IJENS* .10 (2010) 23.
3. Elmoubarki R., Mahjoubi F.Z., Tounsadi H., Moustadraf J., Abdennouri M., Zouhri A., El Albani A., Barka N., *Water Resour. Ind.* 9 (2015) 16.
4. Ralph E Grim.; *Clay mineralogy.* (1968).
5. Newman A. C., *Mineralogical Society Monograph.* (1987) 480 .
6. Azzeddine Er-ramly and Abdelali Ider., *Int. J. Mater. Sci. Appl.* 3 (2014) 42.
7. Maghear A, Tertis M, FriteaL, Marian IO, Indrea E, Walcarius A, Șandulescu R., *Talanta* 125 (2014)36.
8. El Mhammedi MA, Achak M, Bakasse M, Bachirat R, Chtaini A.; *Mater Sci Eng.*, 30 (2010)833.
9. Lahcen Bouna, Benaissa Rhouta, and Francis Maury., *Int. J. Photoenergy.* Article ID 815473 (2013) 6 .
10. Ainane T., Abourriche A., Kabbaj M., Elkouali M., Bennamara A., Charrouf M., Talbi M., *J. Chem. Pharm. Res.* 6 (2014) 599.
11. El Ouahabi M., Daoudi L., Fagel N., *Clay Miner.* 49 (2014) 35.
12. Pierre C., *Mémoire de l'institut de géologie* (1987).
13. Wernli R. Editions du Service géologique du Maroc. (1988).
14. Fadil-Djenabou S., Paul Désiré N., Mbey JA., *J. Asian Ceram. Soc.* 3 (2015) 50.
15. Tuddenham W M, Lyon R J P. *Anal Chem.* 32 (1960)1630.
16. Frost R.L., Makó E., Kristóf J., Horváth E., Klopogge J.T., *J. Colloid Interface Sci.* 239 (2001) 458.
17. Wolf R G., *Am.Mineral.* 48 (1963)390.
18. Farmer V.C, Palmieri F. *Soils components.* NewYork: Springer-Verlag. (1975)107.
- 19 Odoma A.N., Obaje N.G., Omada J.I., Idakwo S.O., Erbacher. J., *J Afr Earth Sci.* 10 (2014) 013.
20. Alcides Wagner Serpa Guarino, Rosane A. S. San Gil, Helena Polivanov, Sonia M.C. Menezes., *J. Braz. Chem. Soc.* 8 (1997) 581.
21. Nwosu D.C., Ejikeme P.C.N., Ejikeme Ebere M., *Int. J. Multidiscip. Sci. Eng.*4 (2013) 11.
22. ElKasmi S., Lahrich S., Farahi A., Zriouil M., Ahmamou M., Bakasse M., ElMhammedi M.A., *J. Taiwan Inst. Chem. Eng.* 58 (2015) 165.

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