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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 to 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 it mainly found in the fraction <2 µm 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 characteristic 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, $Si_4O_6(OH)_4$ [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

current research area in electroanalysis [7,8], photo-energy applications [9] , water purification [10], and ceramic applications [6,11].

Akrach region is made up of vast alluvial plains with abundant clay materials in their numerous valleys. Despite its high proportion, clay materials from Akrach region are only exploited for traditional pottery and local ceramic bricks. This is primarily because the potentialities of these clays are not evaluated. To date, no study that evaluates the potential applications of these materials is reported. It is then obvious that their mineralogical, chemical and physical properties need to be analyzed in order to ameliorate their use in ceramic products and to open ways for other potential industrial applications. Thus, this paper aims to contribute to the study of mineralogical and physicochemical properties of two clay samples from Akrach deposits (Miocene and Pliocene deposits clay) in morocco, to evaluate their potential as raw materials and to ascertain its suitability for industrial purposes.

2. Materials and methods

2.1. Samples and sampling techniques

Two clay samples were collected from two layers in a vertical section of the Akrach area terrace. The samples were designated as MC for the Miocene layer and PC for the Pliocene layer. The Akrach area is located in North West Morocco (Fig.1), specifically on the Atlantic coast in Rabat; it is traversed by Oued Akrach who notched his bed in the Miocene and Pliocene marl deposits (Fig.2). Special attention was devoted to this location due to the promising physicochemical characteristics of the deposits. Akrach region is very rich in clays.

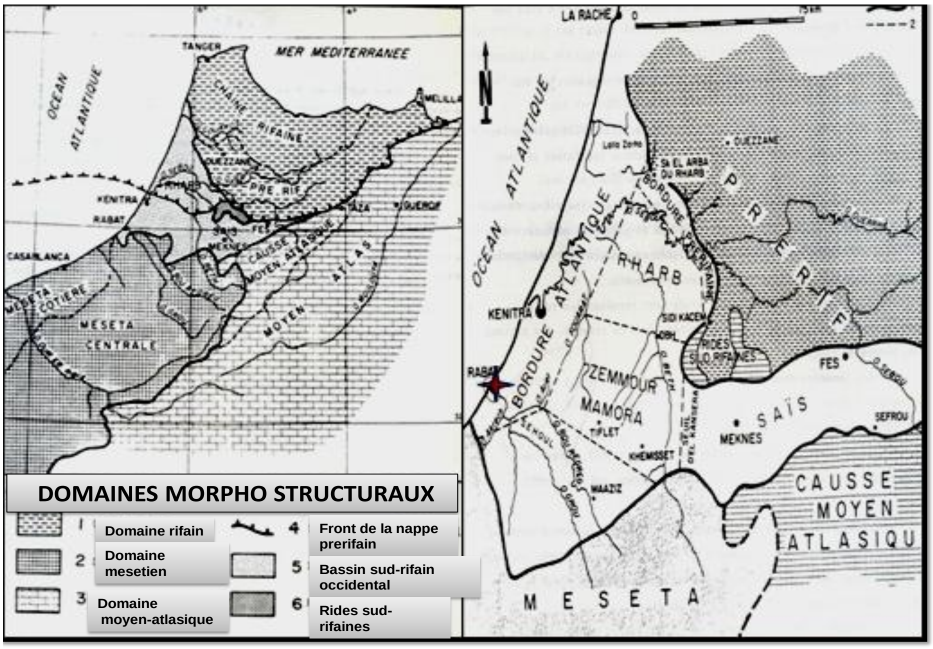

Figure 1: Localisation of Akrach Region [12]

2.2. Methods

2.2.1. Extraction method of fine fraction for XRD analysis

This technique consists essentially in a fine fraction (enriched in clays) from geological samples (figure 3). After the treatments of fine fraction the samples are presented to make the various analyses. The three X-ray patterns were recorded in sequence under air-dried or natural condition (N), after solvatation with ethylene-glycol for 24 h (EG), and heating to 500°C for 4 h (F)

2.2.2. Mineralization method for the AAS analysis

0.5 g of finely ground sample was weighed then we add 7.5 ml of hydrochloric acid and 2.5 ml of nitric acid for dissolution at warm for 2 hours, after the solution was filtered in a 100ml volumetric flask and completed to 100ml with distilled water. The assay was then performed.

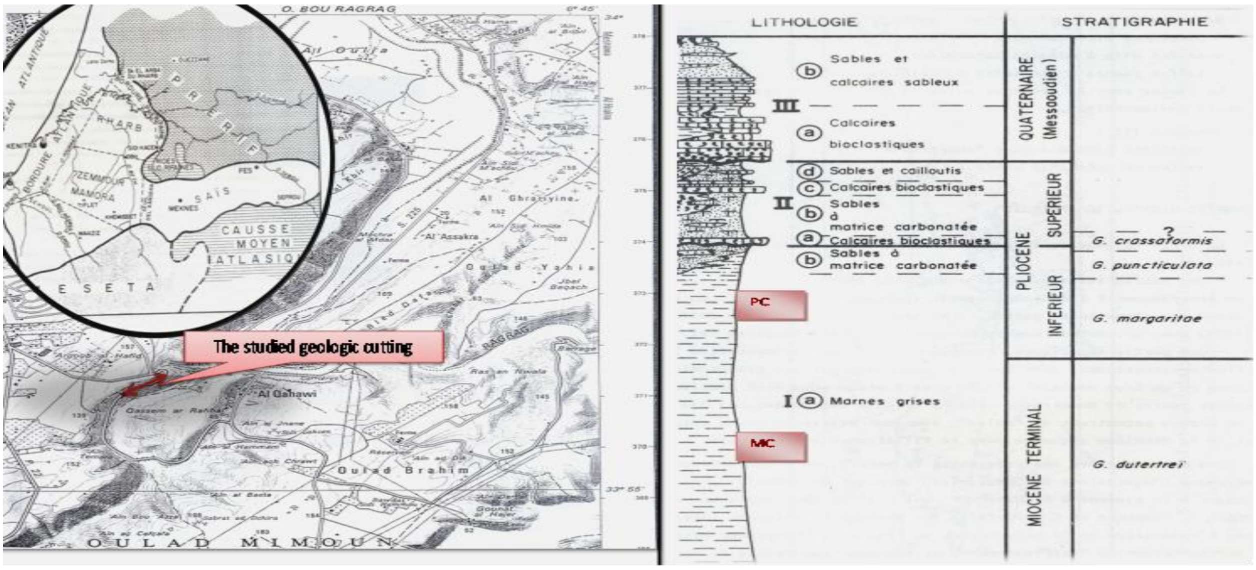

Figure 2: Synthetic cutting of the neogene series of the Margin upper Atlantic of the Westerner pond: Sequences, Lithology , Stopwatch-stratigraphy [13].

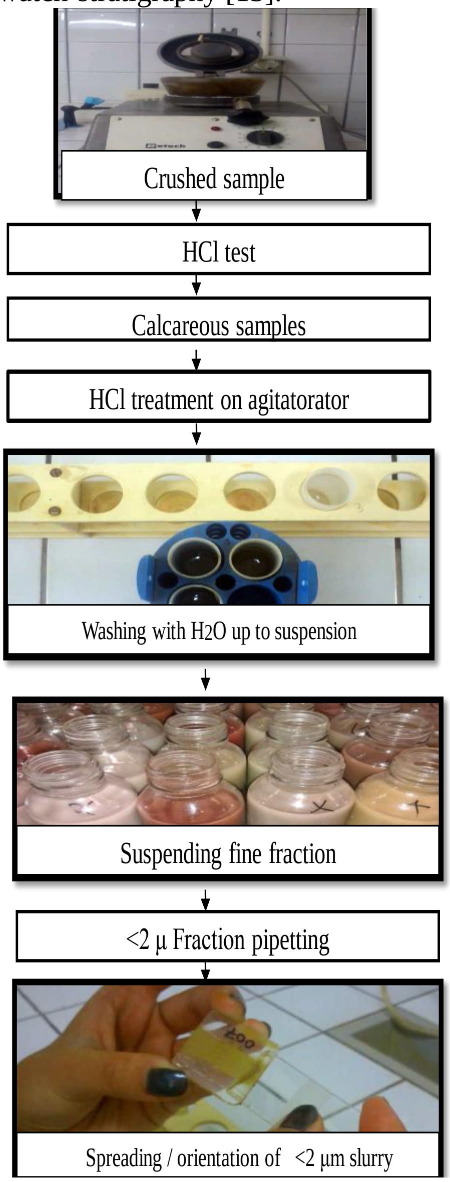

Figure 3: Extraction method of fine fraction

2.3. Apparatus

X-ray diffraction (XRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO operating with Cu Kα radiation (Kα 0.15406 nm) generated at 40 kV and 20 mA. Scans were carried out at 0.02° min^{-1} for 2θ 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^{-1}. The infrared spectra (IR) of clay samples mixed with KBr were recorded with a vertex 70 spectrophotometer, operating in the range 4000–400 cm^{-1}. 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 comportment is characteristic of illite-muscovite. Indeed the later is a non-swelling mineral and thermally stable to temperatures higher than 500°C.

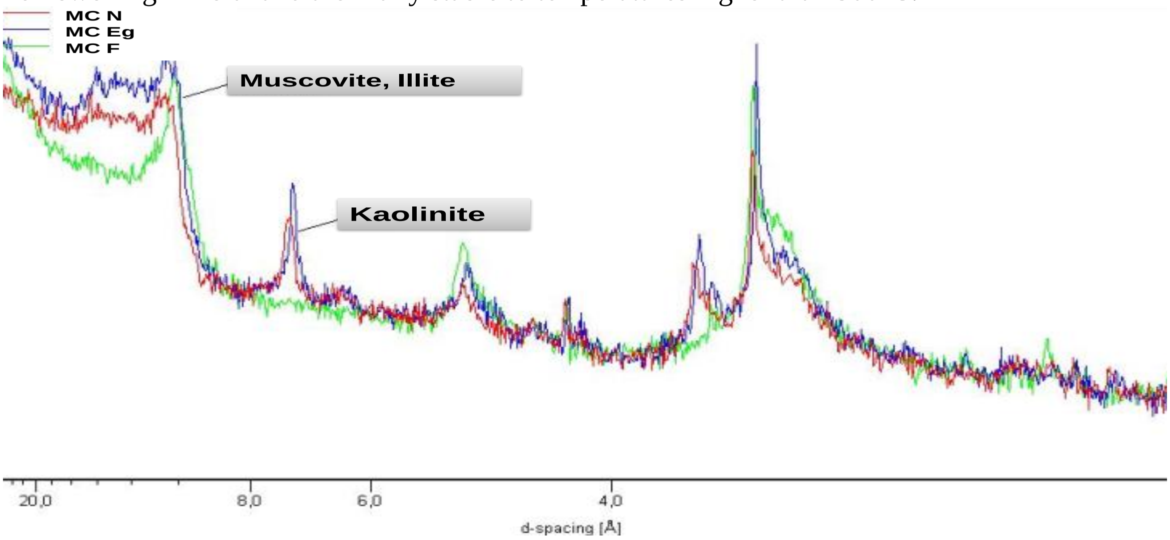

Figure 4: X-ray diffraction pattern of the Miocene clay material.

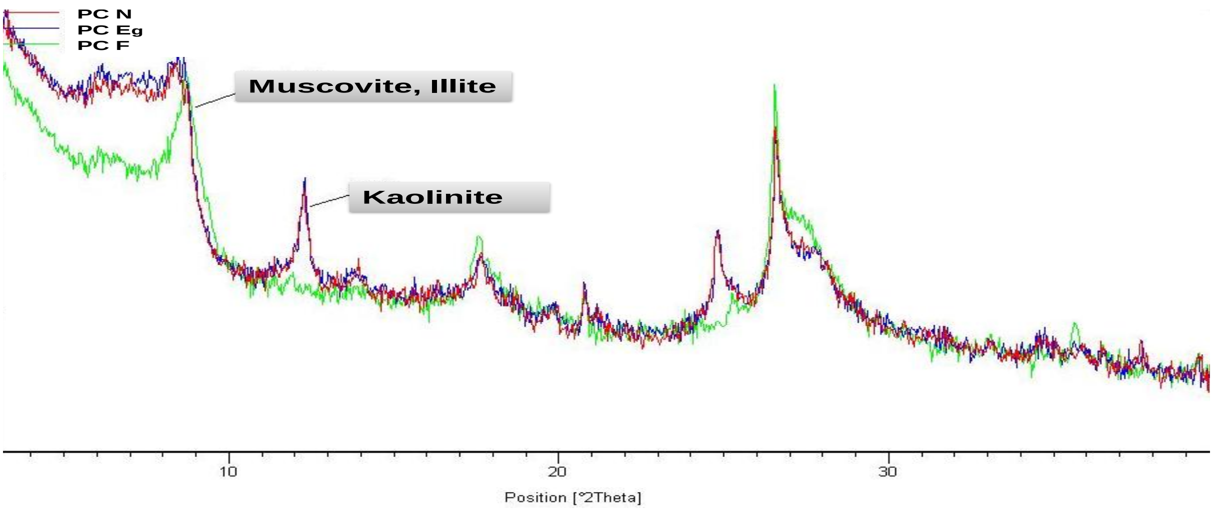

Figure 5: X-ray diffraction pattern of the Pliocene clay material.

The heat treatment of the tow samples causes the disappearance of the reflection at 13° and its harmonics. This comportment is characteristic of kaolinite. The diffraction reflections at 10° and 12.5° are not displaced during glycolation and further confirm the presence of illite and kaolinite. The peak at 14A° following treatment with ethylene glycol and heating at 500°C confirmed the presence of clay mineral of the smectite group and chlorite. Through the 001 peak for to 17A° (2θ =5.2) and break down to 10A° (2θ =8.8). If the mineral is pure the peak 14A° passes in the peak 17A° and 18A° which explains the low intensity of the peak 14A°. The peak at 4,26A° 3.33A° and 3, 25A° 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 cm^{-1}, 3622.6 cm^{-1}, 3411.7 cm^{-1}, 1638.9 cm^{-1}, 1032.2 cm^{-1}, 914.3 cm^{-1} and 799.2 cm^{-1} indicate the presence of kaolinite [15, 16]. The characteristic band of illite at 834cm^{-1} was also observed [17]. The intense band occurring at 3622.6 cm^{-1} and 914.3 cm^{-1} is associated with the presence of a mineral 2/1dioctahedral [18]. The Si–O stretching bands at 1095 cm^{-1} and the Al–O bending at 912 cm–^{1} are characteristic of alumino-silicate minerals. The stretching and bending of hydration water are observed at 1630 cm^{-1}.

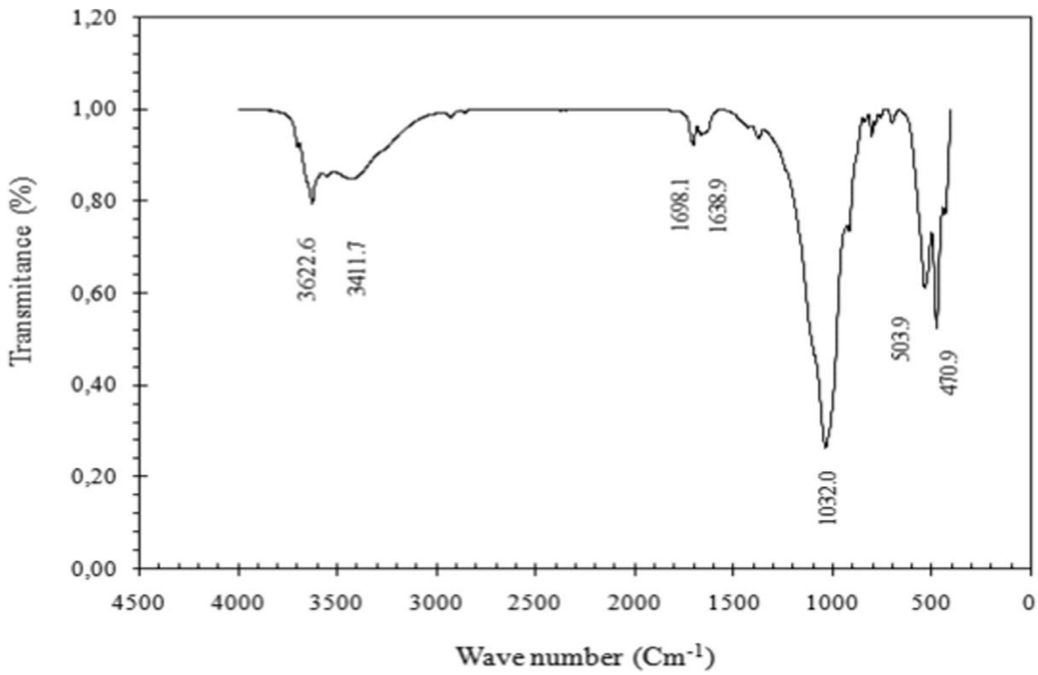

Figure 6: Infrared spectrum of the fraction <2μm of MC.

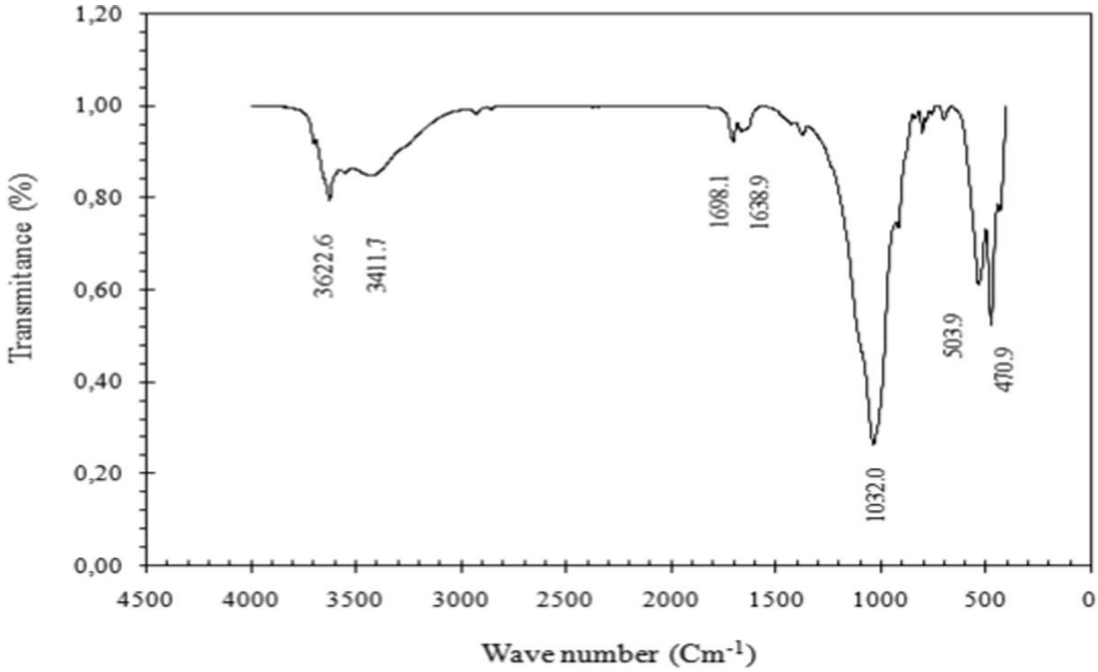

Figure 7: Infrared spectrum of the fraction <2µm of PC.

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^+ and K^+ [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.

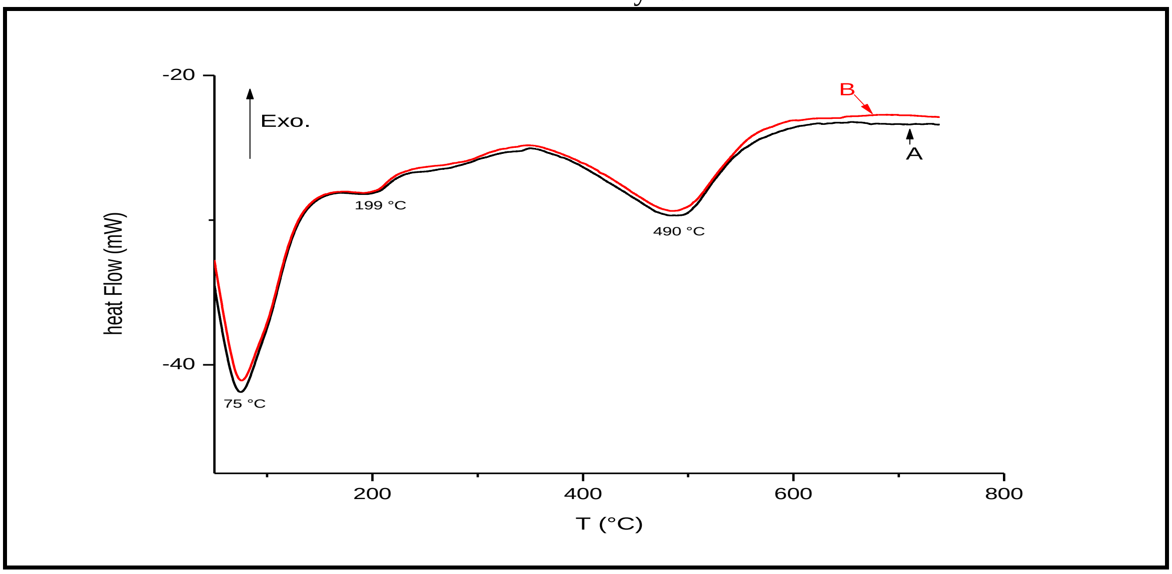

Figure 8: Typical DSC thermogram of the fraction <2µm of Miocene sample (A) and Pliocene sample (B).

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^{-3}ppm)	**Ca**	9.7	12.7
	Mg	6.85	6.3
	K	4.25	1.6
	Na	4.75	4.65
Concentrations (IN 10^{-3}ppm	**CaO**	135.8	178.5
	MgO	10.96	10.08
	Na_2O	12.92	12.65
	K_2O	10.24	3.85
Weight percent (IN %)	**CaO**	13.58	17.85
	MgO	1.09	1.00
	Na_2O	1.29	1.26
	K_2O	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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