

# Mineralogical, Physico-chemical and Geochemical Characterization of Three Kaolinitic Clays (Ne Algeria): Comparative Study

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# Abstract

Forteen clay samples collected from three kaolin deposits (Tamazert, Hadj Ali and Chekfa; NE Algeria) are characterized by several techniques in order to compare them to some kaolins used in industry especially that used in ceramics. All the samples were investigated by X-ray diffraction, Infrared absorption spectroscopy, thermal analysis (TG), plasticity, environmental scanning electron microscopy and chemical major elements analysis. The bulk mineralogical composition of all clays samples is dominated by kaolinite (21-75%), illite/ muscovite (33-76%) and quartz (7-21%). K-feldspar and plagioclase are only present in Chekfa and Hadj Ali clays with small amounts. Clay fraction (< 2µm) dominated by kaolinite and illite (98%). Chlorite and smectite are present in some samples of Chekfa and Hadj Ali clays with insignificant amount (1%). The particles-size distribution of all samples showed the abundance of sandy silt fraction (28-63%) and silty sand (39-64%) with moderate clayey fraction (2-7%). The chemical composition showed variable amounts of SiO<sub>2</sub> (59-68%), Al<sub>2</sub>O<sub>3</sub> (18-39%), Fe<sub>2</sub>O<sub>3</sub> (0.26-1.38%) and TiO<sub>2</sub> (0.34-0.69%) in accordance with the free quartz in all studied samples. Plasticity-index (7.5-7.9%), Specific surface (28-47m<sup>2</sup>) and Cation exchange (5-11meq/100g) values are moderate in all samples. Given these properties, these clays may be suitable in bricks and ceramic product.

## 1 Introduction

Clays are abundant raw materials on the surface of the Earth. They were widely used by ancient civilizations to store food, water (pottery), and to produce building materials (tiles, bricks) (Caillere et al., 1989). Currently, clay materials find place in many industrial, agricultural, civil, environmental and sanitary applications (Ciullo, 1996; Murray, 1999; Carretero et al., 2013; Awad et al., 2017b, 2018). They participate in economic (Kühnel, 1990; Ekosse, 1994; Murray, 2000) and technological development (Njopwouo, 1984; Martin, 1994, 2005; Harvey and Murray, 1997). Before the use of clay, knowledge of the mineralogical, physico-chemical and geotechnical properties is essential for a better use of this clay in the appropriate industrial field. However, the effective valorisation of monomineral clays as kaolin, talc, smectite for industrial applications (raw materials for ceramic, paint, paper...) often needs knowledge on the processes of the clay deposit genesis (Murray and Keller, 1993) and the mineral quality (Bloodworth et al., 1993; Mitchell, 1994; Merabet and Belkacemi, 2003; Martin, 2005; Nkalih, 2015, 2018; Laibi et al., 2017). Nowadays, with advances in scientific knowledge and technology clay minerals have made substantial contributions in various fields such as ceramics, catalysis, cosmetic (Mattioli et al., 2015), petrol and medicines. More recently clays are associated with development of geopolymers due to their physical and chemical properties before and after firing (Masigli & Dondi, 1997; Wilson, 1999; Punmia et al., 2003; Reeves et al., 2006; Murray, 2007; Mahmoudi et al., 2008; Lee & Yeh, 2008; Katte et al., 2019).

Kaolinite, with chemical formula  $Al_2 Si_2 O_5 (OH)_4$  is one of the most common minerals on Earth. The annual production of kaolin exceeds 25 million tons (Wilson, 2003). A rock is considered as "kaolin" when its amount of kaolinite is more than 50% (Dombrowski, 2000).

The grade and quality of economical kaolin deposits are mainly determined on the basis of kaolinite content and its degree of structural disorder, as well as quartz and Fe-Ti mineral impurities and heavy metals (Vie et al. , 2007; Teh et al., 2009; Gupta et al., 2011; Ptáček et al., 2013; Wardhana et al., 2014; Ndlovu et al., 2015).

The physical properties of kaolin such as color, opacity and whiteness, compactness, plasticity and rheology, and physicochemical properties, including sorption or cation exchange capacities are largely affected by chemistry and the mineralogy of the parent rock (Murray and Lyons, 1955, 1959; Vasilev et al., 1976; Cabrera and Eddleston, 1983; Lalglesia and Aznar, 1996; Fialips et al., 2000; Awad et al., 2017a).

Clayey materials are widespread in Algeria, important reserves of kaolin are presented in the Northern part of the country. This part is characterized by highland terranes with intense drainage and Mediterranean climate with a dense vegetal cover. This topographic and climate promote degradation of minerals and rocks with development of kaolin deposits associated with the Kabyle basement. Among the three main deposits (Tamazert, Chekfa and Hadj Ali), Tamazert and Chekfa deposits are under exploitation by the El Milia complex ceramic industry. However the quality of the finished ceramic products is insufficient for exportation. The third deposit of Haj Ali is used at an artisanal level for local pottery production. In this work we conduct a mineralogical and chemical characterization of the three northern Algerian kaolin deposits. Note the fourth kaolin deposits of economic potential from Djebel Debbagh (Guelma province) will not be treated in this study because of its different origin. The mineralogical composition has a major influence on uses of clays. Whiteness and quality decreases drastically with mineral mixture and/or chemical impurities in the kaolinite (Chandrasekhar and Ramaswamy, 2002; Gamiz et al., 2004).

## **2 General Setting**

### **2.1- Geographic condition**

The three kaolin deposits are located in the Kabylie of Collo and El Milia. this region is characterized by: a hot Mediterranean climate in summer (average 25 ° C) and a mild and rainy winter (average 1200mm / year); a very rugged mountainous relief where mountains occupy more than 80% of the region; a diversified plant cover (cork chain, maritime pines) and very dense and a highly developed hydrographic network which drains the region in a permanent regime (Oued El Kebir, Oued El Guebli, Oued Nile), and the abundance of sources which supply the villages drinking water. The Tamazert deposit is located about 17 km north of the town of El Milia (West of Jijel). Hadj Ali deposit is located at 14 km of the Ain Kechera town (West of Skikda) not far from Tamazert. Chekfa deposit is located about 23 km east of Jijel (Fig.1).

### **2.2- Geological condition**

The Kabyle massifs are traditionally considered as the substratum of the internal zones of the Tellian chain, an Algerian section of the Maghreb alpine chain (Fig. 1). The latter extends linearly along the Mediterranean coast over 1200 km from the Rif to Calabria. The massif of Less Kabylie is located in the northern position of the inner domain of the Tellian range (Fig. 2). It stretches along the Mediterranean

coast for more than 150 km between the region of Jijel in the West and the massif of Filfila (Skikda) in the East, with a NS extension of 50 km (Fig.1), it constitutes the outcrop of most important crystallophyllian lands of the Algerian coast. Previous work on Less Kabylie shows the existence of a major abnormal contact between the crystallophyllian Kabyle massif (basement layer) and the infra-Kabyle complex which is constituted by the Mauritanian, Massylian and Tellian units (Fig.1). (D-Delga, 1969; Bouillin, 1978; Vila, 1978). The studied deposits (Tamazert, Chekfa and Hadj Ali) are exactly located in Beni-Ferguene unit extending between the region of Sidi Abd El Aziz and Beni Bel Aid to the west and Kerkera region (south of Collo) to the east. This unit shows the superposition of three subunits that are from top to bottom: (i) the upper subunit paragneiss intruded by sills of amphibolites; (ii) the intermediate metapelitic subunit, where orthogneis interspersed with plurimetric blades eyed and granites sillimanites and (iii) the lower subunit formed by alternating light and dark metapelites, pyroxenite lenses, granites and leptynite (fine-grained gneissic type). This unit is overlapped by the upper south basement (base unit SS) and covered the north by the Nummudian formations, the Oligo-Miocène Kabyle (OMK) and Olistostromes of flyshs.

## **3 Materials And Methods**

### **3.1- Material and sampling**

The samples on which this study is based are collected from three kaolin deposits (Tamazert, Hadj Ali and Chekfa) according to N-S direction profiles. The clay materials of the three deposits present a similar organization. of the profile shows a succession of three vertical zone from top to bottom (Fig. 2): a strongly kaolinized zone (D); a moderately kaolinized zone (C1, C2, C3); a weakly kaolinized zone (B) and an intact zone (A) represent the parent rock. The passage between the parent rock and the weakly kaolinized level is not linear. Fourteen samples were taken (Table 1) from the different levels of the three profiles. Several preparation steps (grinding, sieving and washing) were carried out in order to obtain different information on the mineralogical composition of clay materials.

### **3.2. Description of the profiles**

The profiles show identical morphologies and variable dimensions. Field observations and examination of thin sections in a polarizing microscope made it possible to follow the evolution of weathering from healthy rock to totally weathered rock. From bottom to top, there are three distinct sets: set of alterites, nodular set and clay-sandy loose set. This vertical succession characterized classic equatorial zones (Fig. 2).

### **3.2- Analytical methods**

#### **3.2.1 X-ray diffraction (XRD)**

Bulk minerals compositions were identified by X-ray diffraction (XRD) carried out with D8 Bruker Advance diffractometer using Cu K $\alpha$ 1 radiations ( $\lambda=1.5418$ ). All XRD bulk data were collected in same experimental conditions, in the angular range  $2\theta$  from 2 to 45°, 40 kV, 30mA, with step scan 0.020° and a step time 0.6s for all bulk samples. The clay fraction (< 2 $\mu$ m) is obtained by sedimentation according to the stocke's law

and centrifugation after removal of carbonate by HCl (10%). Oriented slides are analyzed under 3 treatments (natural, glycol and heated in 500°C for four hours). XRD data from clay fraction ( $< 2\mu\text{m}$ ) were carried in the range  $2-15^\circ 2\theta$  under the same conditions mentioned above.

### **3.2.2 Plasticity test**

The plasticity of a clay is a fundamental technological parameter which influences the characteristics of ceramic materials (Sadik *et al.*, 2012). It was carried out on the fraction less than  $63\mu\text{m}$ . In this study, we opted for the method known as "Atterberg limits". The Atterberg limits, were measured at the laboratory of Materials and Structures Mechanics at the University of Liege. Measurements have been done on the on raw samples using the method described by (Casagrande, 1947 and Andrade *et al.*, 2011). The plasticity index PI is calculated by the difference between LL and LP according to (Casagrande, 1947). The results of the tests carried out are presented in (Table 2).

### **3.2.3 Infrared spectroscopy (FTIR)**

Infrared spectra (FTIR) were recorded with a Nicolet NEXUS spectrometer at laboratory of mineralogy and crystallography at the University of Liege. For each sample, 32 scans were recorded with a resolution of  $1\text{ cm}^{-1}$  over an interval ranging between  $400$  and  $4000\text{ cm}^{-1}$  (corresponding to middle-infrared). Two mg of clays were mixed with 148 mg of KBr and then pressed up to 9 tones in order to obtain a homogeneous pellet. The pellet is then dried for several hours at  $120^\circ\text{C}$ . To avoid any water contamination the measurements were carried out under vacuum.

### **3.2.4 Thermal analysis**

Gravimetric analysis (TGA) was performed in the LCIS Green-Mat laboratory (Department of chemistry University of Liege using a NEZSCH STA 449 PC instrument. TGA analysis was performed on the clay and slit fraction ( $< 63\mu\text{m}$ ) over a temperature range at 2 to  $1000^\circ\text{C}$ .

### **3.2.5 Environmental scanning electron microscopy**

Morphological characteristics were performed using a Philips XL30 FEG Environmental Scanning Electron Microscope (ESEM) equipped with an Energy Dispersive X-ray Spectrometer EDS at the Laboratoire de Chimie Inorganique Structurale (LCIS) in University of Liege. The samples were examined with secondary electron detector at an acceleration of  $15\text{keV}$ .

### **3.2.6 Specific area and Cation exchange capacity**

Specific surface area (SSA) of natural samples was measured at the Laboratory of Chemical Engineering, Institute of Chemistry University of Liege by absorption of the methylene bleu method (Hang et Brindley, 1970; Chen et al., 1999). The "spot test" was used to determine surface area as prescribed by (Johnson 1957) and (Worall 1958). The Cation Exchange Capacity (CEC) was calculated by distillation. An amount of  $0.5\text{g}$  of the sample was mixed with  $2\text{ ml}$  of NaOH. Then titration is done with HCl and titrated by the

Kjeldahl method (Mackenzie et al., 1954). The exchangeable cations were measured using ammonium acetate method at the soil laboratory of Catholic University of Louvain.

### 3.2.8 Particles-size distribution

Particle-size analysis was performed at the Inorganic Chemistry Laboratory (LCIS) at the University of Liège, with a Laser particle size analyzer (Mastersize 2000, Malven). Equipped by Two dispersion units can be used: dry and wet. In the context of this work the wet process (HydroS) is used. The particle size fraction measurable by this instrument is between 0.02 and 2000microns.

### Chemical analysis

Chemical analyses were performed at the “Centre de Recherches Pétrographiques et Géochimiques” (CRPG -CNRS Nancy, France) by Atomic Emission Spectrometry using an Inductively Coupled Plasma source (ICP-AES) for major elements. The Loss on Ignition (LOI) was determined at 1000°C after fusion with  $\text{LiBO}_2$  and dissolution in  $\text{HNO}_3$ . The Limit of Determination (LOD) is calculated as 6 times the relative standard deviation of 100 measurements of blank. The measurement uncertainty is calculated for 200 mg of prepared samples. The analytical blank subtracted from the sample signal was a solution of  $\text{LiBO}_2$  (900 mg diluted in 100 ml of the  $\text{HNO}_3$ -  $\text{H}_2\text{O}_2$  - glycerol mixture).

## 4 Results And Discussion

### 4.1- Mineralogical composition

The X-ray patterns of bulk samples (Fig.3), showed the predominance of kaolinite, illite-muscovite and quartz in all samples of the three deposits clays. In Tamazert deposit, clay minerals (21-87%), quartz (7-25%), and muscovite-illite (8-60%). In Hadj Ali deposit, quartz (9-14%), clay minerals (30-44%), muscovite-illite (28-50%). In Chekfa deposit, quartz (9-13%), clay minerals (14-20%), muscovite-illite (34-47%), K-feldspar and plagioclase are more abundant than in the two previous deposits (25-43%). Kaolinite and muscovite-illite are identified by the (001) basal reflection and other secondary reflections respectively (7.12Å and 3.58Å) (9.98Å, 4.99Å and 3.32Å), quartz with their reflection (101) occur at (3.34Å) and the second reflection at (4.25Å). However K-feldspars at (3.18Å) and plagioclase at (3.22Å) are absent in Tamazert clays (TM), or rarely present together in the Hadj Ali (HA) and Chekfa (CH) clay samples. The X-ray patterns of the 3 clay deposits show a similar mineralogical composition of the raw samples with kaolinite, quartz, muscovite-illite. K-feldspars and plagioclase are only present in Hadj Ali and Chekfa deposits. This gives a first indication of the degree of alteration that affects each kaolinized deposit.

X-ray patterns of the clay fraction ( $\approx 2\mu\text{m}$ ) show dominance of kaolinite and illite, accessory minerals as chlorite and smectite are also present at small quantities ( $\leq 0.5\%$ ) in some samples of (CH and HA). Chlorite is identified by the persistence of the second reflection at (7Å) during heating. Smectite is evidenced by its characteristic peak at 14Å under natural condition that migrate to 16Å after glycolation and collapses to 10Å after heating. The semi-quantitative abundance of the minerals in all samples was

estimated from the height of a diagnostic peak multiplied by a corrective factor as reported (Table 3) by (Cook *et al.*,1975; (Boski *et al.*,1998 and Fagel *et al.*, 2003). The semi-quantitative data of the clay minerals of the TM, CH and HA deposits are shown in (Fig.4).These data show that, TM samples are enriched in clay minerals (57% on average) in regard with the samples of CH and HA (14% and 35% on average).

## 4.2 Plasticity test

Plasticity of clays is one of the most important parameters affecting the determination and process of clay production (Murray, 2007; Barış *et al.*, 2020). The Evaluation of the plasticity index (PI) is very important in determining the suitability of clays for the ceramic industry. The plasticity index of Tamazert and Hadj Ali clays was calculated from the arithmetic difference of LL and PL. these Clay materials are characterized by moderate plasticity index 9% and 8% respectively. we could not perform the plasticity test on the Chekfa samples because of the high quartz content. In the diagram of Holtz and Kovacs (1981) (Fig. 5), the clays of Tamazert and Hadj Ali are plotted in the zone of medium plasticity, the samples plot as kaolinitic clay. The PI of all samples clay is < 10%, samples were found unsuitable for building-related ceramics production due to the risk cracks during extrusion (Nyakairu *et al.*, 2002)

## 4.3 Infrared spectroscopy

Infrared spectra (Fig.6), show marked differences between the three studied samples. The first difference is marked in region of high absorption. Four bands at 3697, 3668, 3653 and 3621  $\text{cm}^{-1}$  are observed in the spectrum of the Tamazert sample whereas only three bands are present in the spectra of Chekfa and Hadj Ali samples 3698, 3652 and 3621  $\text{cm}^{-1}$ . These four bands are assigned to OH-stretching of kaolinite (Farmer 1974; Van Der Marel & Beutelspacher 1976). The second difference marked in the region of low absorption bands 1115-913  $\text{cm}^{-1}$  corresponding to the Si-O-Si and Si-O-Al stretching.

## 4.4 Thermal analysis

TGA curves (Fig.7) showing the samples mass loss (TM, CH, HA). A significant mass loss (4%) is observed above 400°C for the sample (TM) in comparison with loss of 1.5% for samples (CH and HA). This mass loss is attributed to the dehydroxylation structure (Nahdi *et al.*, 2002b) and dehydroxylation of kaolinite due to its transformation to metakaolinite (Wang *et al.*,2011). A slightly loss is observed around 180°C in all samples due to dehydroxylation of micaceous phase (Caillère *et al.*,1976), the mass loss below 180°C is due to the removal moisture water. In all t samples, values of loss mass is lower than the theoretical values of pure kaolin 1.5-4% (13.96 wt,%, Ptáček *et al.*,2010) reflecting the presence of impurities, especially free quartz.

## 4.5 Scanning electron microscopy

The micrographs (Fig. 8) obtained by the different samples showed the dominance of kaolinite pseudo-hexagonal particles organized as platelets or tight packages. EDS microanalyses reveal some small relics of feldspars and quartz in TM kaolinite whereas fresh or slightly altered K-feldspars minerals are

evidenced in both CH and HA kaolinites. The better crystallization of TM and HA samples evidenced by ESEM is consistent with X-ray diffraction and IR spectroscopy data.

#### 4.6 Physico-chemicals properties (SSA and CEC)

The CEC of Tamazert clay (11.58 meq/100g) is higher than for Chekfa and Hadj Ali (5.42 meq/100g and 6.46 meq/100g (Table.2). Such CEC are in the range of the values reported in literature for kaolin deposits (3 to 15 meq/100g, in Grim 1968). Specific surface areas of CH and HA kaolinites ( $\sim 45.5 \text{ m}^2/\text{g}$ ) are higher than that of TM kaolinite ( $28.7 \text{ m}^2/\text{g}$ ). This reflects the small grain size of Chekfa and Hadj Ali kaolinites compared to Tamazert kaolinite.

#### 4.7 Particles-size distribution

The suitability of clays for different industrial applications is based on their particle size distribution.

For ceramic products, the finer fraction ( $< 2 \mu\text{m}$ ) is of particular attention (Mahmoudi et al., 2008). The particle size distribution of the different samples shows that these clays are poor in fine fraction (2–7%), while the silty sands and sandy loam fractions are abundant (28 to 63% and 34 to 64%, respectively). The samples from Chekfa and Hadj Ali show low fine fraction contents ( $< 2 \mu\text{m}$ ) compared to those from Tamazert. In the ternary diagram widely used in the ceramic industry (Dondi et al., 1992), the clay samples studied were classified as silty sand (samples H1, H3 and C1) and sandy silt clay (sample T2, T3, T6, C1, C2 and H5, Fig. 9). On Winkler's (1954) ternary diagram (Fig.10), almost all of the samples show an aptitude for making construction products such as common bricks.

#### 4.8 Chemical analysis

The chemical composition of the clay samples are shown (Table 4). The clay show most abundant of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .  $\text{SiO}_2$  ranged from 49 to 64% for TM, 61 to 68% for HA and 64 to 69% for CH.  $\text{Al}_2\text{O}_3$  varies between 34 to 21% for Tamazert, 24 to 20% for Hadj Ali and 19 to 22% for Chekfa. The content in  $\text{Al}_2\text{O}_3$  within clays depends on the intensity of hydrolysis. More hydrolysis gives more kaolin minerals and, therefore higher  $\text{Al}_2\text{O}_3$  content (Yanik, 2011).  $\text{Fe}_2\text{O}_3$  is low for TM ( $< 1\%$ ) and ranges between 0.85 to 1.63% for HA and CH. CaO elements, MgO,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  are present in small quantities often lower than the detection limit, in all sites.  $\text{Na}_2\text{O}$  presents small variations from one site to another ( $< 1\%$  for TM and CH,  $> 2\%$  for most HA samples). In contrast,  $\text{K}_2\text{O}$  presents higher fluctuations, ranging between 1.8 and 5.1% for the 3 sites. LOI values from kaolin samples ranged from 5.7 to 7.0% for Chekfa, 4.2 to 5.0% for Hadj Ali and 6.6 to 13.8% for Tamazert. The low CaO, MgO,  $\text{Na}_2\text{O}$  values reflect an important leaching of calco-alcaline elements. It is probably due to their high mobility during kaolinization process and it is compatible with an advanced argillic alteration system close to hydrothermal kaolin deposits (Meyer and Hemley, 1967; Meunier et al., 1983. Inoue, 1995; Dill et al., 1997, 2000). However, the enrichment in  $\text{K}_2\text{O}$  observed in all samples is probably due to the release of the potassium content by feldspar dissolution.

## 5 Discussion And Perspective

#### 4.1. Weathering stage of the NE Algeria kaolinitic-rich deposits

Kaolinite, illite and quartz represent the main minerals in the 3 studied kaolin deposits from N Algeria. However the 3 sites are characterized by different properties that influence the quality of the kaolin ores. TM clays is more weathered than CH and HA as evidenced by the observed relics of K-feldspar and high crystallinity, high CEC (11,6 meq / 100 g) and Low SA (28,7 m<sup>2</sup>/g). In addition the presence of 2 bands at 3668 cm<sup>-1</sup> and 3653 cm<sup>-1</sup> on the IR spectrum of TM attests for a better crystallinity of its kaolinite (Cases *et al.*, 1982; Petit, 1994; Filiaps, 1999). The high SA in HA and CH reflects their low abundance of fine clay particle and the occurrence of impurities such as fresh feldspars. Likely the lower CEC in CH and HA may be explained by the presence of higher amount of illite (Tschapek et al., 1974; Yong et al., 1992) than in TM. The presence of large amount of free silica and fresh feldspars decrease the plasticity of clays (De Oliveira Modesto and Bernardin, 2008).

#### 4.2- Industrial use of NE Algeria kaolinitic deposits

The Algerian ceramics industry produces sanitary ceramics, ceramic tiles, crockery, earthenware, fertilizer, paint, pesticides, paper, plastic, rubber and porcelain. Major kaolin deposits are located in the northern Algerian who's Tamazert, Chekfa; Hadj Ali and Djebel Debbagh. Three categories of kaolin were produced from the TM site: KT3B (Kaolin bleached) to load and paper; KT2 for ceramics, plastics and rubber; KT1 for ceramics and insecticides. But these ranges of kaolin (KT3B, KT2 and KT1) produced in El Milia complex can not win the local market before the high quality of imported kaolin. Chekfa clay exploited by SARL Algeria Faiencerie for the manufacture of tiles, sanitary ceramics, floor, tiles and earthenware. In 2015, the operation of Chekfa deposit is stopped because the product quality became very poor and did not meet the requirements for industrial uses. Hadj Ali deposit is not yet exploited by SOALKA Company, but simples local's artisans using this kaolin in artisanal pottery. The current annual production reaches 50.000 tons for Tamazert and 30.000 tons for Chekfa (SOALKA, 2008) whereas Hadj Ali is not yet exploited. Tamazert, Chekfa and Hadj Ali deposits constitute the largest stocks of kaolin in Algeria estimated at 20 Million tons. Our study evidences that the Algerian Tamazert deposit of kaolin fit the local market of raw materials for high-quality ceramic industry. Technological developments (extraction and processes) can improve the productivity of the exploitation of the Tamazert ore.

#### 5- Comparison with other's kaolin

Kaolin deposits in northeastern Algérie (Tamazert, Chekfa and Hadj Ali) were compared with other deposits in the world. The genesis of, kaolin deposits in northeastern Algeria is identical to that found in Quebec (Canada). These kaolin deposits are the result of the meteoric or hydrothermal alteration of heterogeneous rocks with gneissic dominance constituting the Kabyle basement. These kaolin are compared with Cerro Rubio kaolin deposit in Patagonia (Argentina) and other kaolin exploited in nearby areas (Cravero, 2001); the Tetouan, Tanger and Fes kaolin kaolin deposits in Morocco (El Ouahabi, 2014), they show physico-chemical properties (CEC, SS), mineralogical and geotechnical characteristics (Atterberg limits) almost identical.

## 6 Conclusion

It is very rare to find pure kaolinite in nature, there are always impurities accompanying kaolinite. 100% pure kaolin is generally composed of approximately 46.5% SiO<sub>2</sub>, 39.5% Al<sub>2</sub>O<sub>3</sub> and 14% H<sub>2</sub>O.

Kaolinitic clays from the Tamazert, Hadj Ali and Chekfa deposits located in NE of Algeria were developed on a heterogeneous metamorphic basement with gneissic dominance from weathering from weathering (in situ). The main objective of the present study was the characterization and comparison between the three kaolins. To achieve this goal, we proceeded with two methods: field methods and laboratory methods. Fieldwork consists of collecting samples according to N-S direction profiles and their description. The laboratory methods consist of various analytical techniques performed on all the samples taken. Particle size analysis shows the presence of a small amount of the clay fraction (2–7%), the sandy silt fraction in proportions of (28–63%) and the sandy fraction in large proportions (39–64%). The Atterberg limits show that the clay materials of Tamazert and Hadj Ali are moderately plastic clays, with plasticity characteristics varying between (27–39%) and a plasticity index between (8–9%). Mineralogically, XRD reveals the presence of clay minerals such as kaolinite, illite, chlorite and smectite with relics of non-clay minerals such as feldspars and plagioclases. Geochemically, the oxides present are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> in large quantities, while Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are in small quantities. Alkalis (K<sub>2</sub>O and NaO), alkaline earth metals (MgO and CaO), MnO, P<sub>2</sub>O<sub>5</sub>, have very low to zero concentrations. The proportions of SiO<sub>2</sub> are abundant in all the samples. The clay in the areas studied are mainly impure kaolinitic clays. Based on the Winkler diagram we find that the studied clays are unsuitable for ceramic use.

The presence of clay minerals in the different samples was consolidated by the different analysis and characterization techniques. XRD and FTIR showed the presence of characteristic bands of kaolinite in most samples. In addition, the SEM micrographs obtained showed a characteristic morphology of kaolinite minerals in all samples.

From this study, we can conclude that the kaolinitic clay of Tamazert is the purest compared to the kaolinitic clays of Hadj Ali and Chekfa.

## Declarations

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## Tables

Table 1: Samples locations and descriptions

Site Name	Sample name	GPS coordinate	Level (m)	Colour
Tamazert	TA1	N 36°50'25.89" E 6°15'22.45"	555	White color with reddish spots
	TA2	N36°50'29.00" E 6°15'19.41"	560	
	TA3	N 36°50'26.78" E 6°15'18.93"	565	
	TA4	N 36°50'31.52" E 6°15'18.19"	570	
	TA5	N 36°50'29.95" E 6°15'18.24"	575	
	TA6	N 36°50'26.95" E 6°15'15.27"	580	
Hadj Ali	HA1	N 36°51'51.35" E 06°22'07.11"	550	White color with reddish spots
	HA2	N 36°51'49.37" E 06°22'08.40"	545	
	HA3	N 36°51'49.92" E 06°22'08.71"	540	
	HA4	N 36°51'49.41" E 06°22'08.30"	535	
	HA5	N 36°51'47.66" E 06°22'09.75"	530	
Chekfa	CH1	N 36°46'59.13" E 05°59'49.04"	435	White color with reddish spots
	CH2	N 36°46'56.28" E 05°59'45.05"	430	
	CH3	N36°46'55.49" E05°59'44.72"	425	

Table 2: physico-chemical properties of studied sites

		Tamazert	Chekfa	Hadj Ali
Cation exchange capacity (meq/100g)		11.5	5.42	6.46
Specific surface area (m <sup>2</sup> /g)		28.73	45.65	45.46
Exchangeable cation (meq/100g)	Ca <sup>+2</sup>	0.4	1.1	1.0
	K <sup>+</sup>	0.18	0.08	0.16
	Mg <sup>+2</sup>	0.79	0.95	2.07
	Na <sup>+2</sup>	0.1	0.2	0.2
Liquid limit (Wl)		34.8	39.2	-
Plastic limit (Wp)		26.9	31.7	-
Plasticity index (Ip)= Wl-Wp		7.9	7.5	-

Table 3: Mineralogical composition of bulk and clays fraction of all samples; diagnostic peak multiplied by a corrective factor

Samples	Minerals	Diagnostic peak (Å)	Correction factor	References				
Powder	Quartz	3.37-3.31	1.00	Cook <i>et al.</i> (1975)				
	K-feldspar	3.21-3.26	4.30					
	Plagioclase	3.18-3.21	-					
	Total clay	4.47	20					
Clay	Kaolinite (EG)	7.1-7.2	0.7	Boski <i>et al.</i> (1998)				
	Illite (EG)	10.00	1.00	Fagel <i>et al.</i> (2003)				
Mineralogical composition of bulk and clay fraction								
Bulk composition								
Clay composition (<2µm)								
Samples	Quartz	Muscovite	K-feldspar	Plagioclase	Total clay	Kaolinite (EG)	Illite (EG)	Smectite
T1	7	14	-	-	79	29	71	-
T2	14	56	2	-	28	46	46	-
T3	11	61	7	-	21	65	65	-
T4	23	13	-	-	64	33	33	-
T5	5	8	-	-	87	77	77	-
T6	10	11	-	1	78	23	23	-
H1	14	34	2	19	31	33	57	10
H2	9	44	-	18	29	30	67	3
H3	11	33	2	10	44	29	43	28
H4	11	29	3	18	39	40	7	53
H5	12	30	-	20	34	57	37	6
C1	9	34	18	25	14	21	74	5
C2	3	47	3	26	14	22	52	26
C3	10	47	9	16	15	60	40	-

Table 4: chemical composition in (%) of all samples

P <sub>2</sub> O <sub>5</sub>	Pf	Tot	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>
<i>Chemical compositions</i>											
<i>Tamazert</i>											
TA1 0.07	9.74	99.88	59.00	26.38	0.70	0.00	0.42	< l.d	0.04	2.96	0.56
TA2 0.04	6.62	99.32	64.55	21.39	0.77	0.00	0.46	0.16	0.56	4.35	0.48
TA3 0.06	6.57	99.46	63.28	22.50	0.57	0.00	0.33	0.05	0.23	5.49	0.37
TA4 0.05	9.76	99.49	61.07	25.60	0.26	0.00	0.23	0.05	0.09	1.90	0.50
TA5 0.04	13.86	99.49	48.72	34.02	0.26	<l.d	0.22	0.03	0.07	1.76	0.60
TA6 0.04	6.93	100.18	64.51	21.79	0.72	0.00	0.39	0.04	0.24	5.12	0.39
<i>Hadj Ali</i>											
HA1 <l.d	4.65	99.63	66.28	20.16	0.85	0.01	0.69	0.08	2.23	4.21	0.48
HA2 0.00	4.23	98.95	61.14	23.00	1.35	0.00	0.63	0.19	3.04	4.65	0.44
HA3 <l.d	6.39	100.06	64.57	22.38	0.90	0.00	0.63	0.09	0.37	4.37	0.36
HA4 0.00	4.98	99.32	61.25	23.60	1.25	0.00	0.72	0.39	2.46	4.19	0.45
HA5 0.04	4.32	100.27	65.74	20.72	0.94	0.01	0.62	0.16	2.91	4.34	0.47
<i>Chekfa</i>											
CH1 <l.d	6.39	100.06	64.57	22.38	0.90	0.00	0.63	0.09	0.37	4.37	0.36
CH2 0.06	5.70	99.30	68.77	18.60	1.63	0.00	0.35	0.04	0.33	3.47	0.34
CH3 0.04	7.02	100.92	68.40	20.11	1.38	0.00	0.34	0.03	0.12	3.09	0.39

## Figures

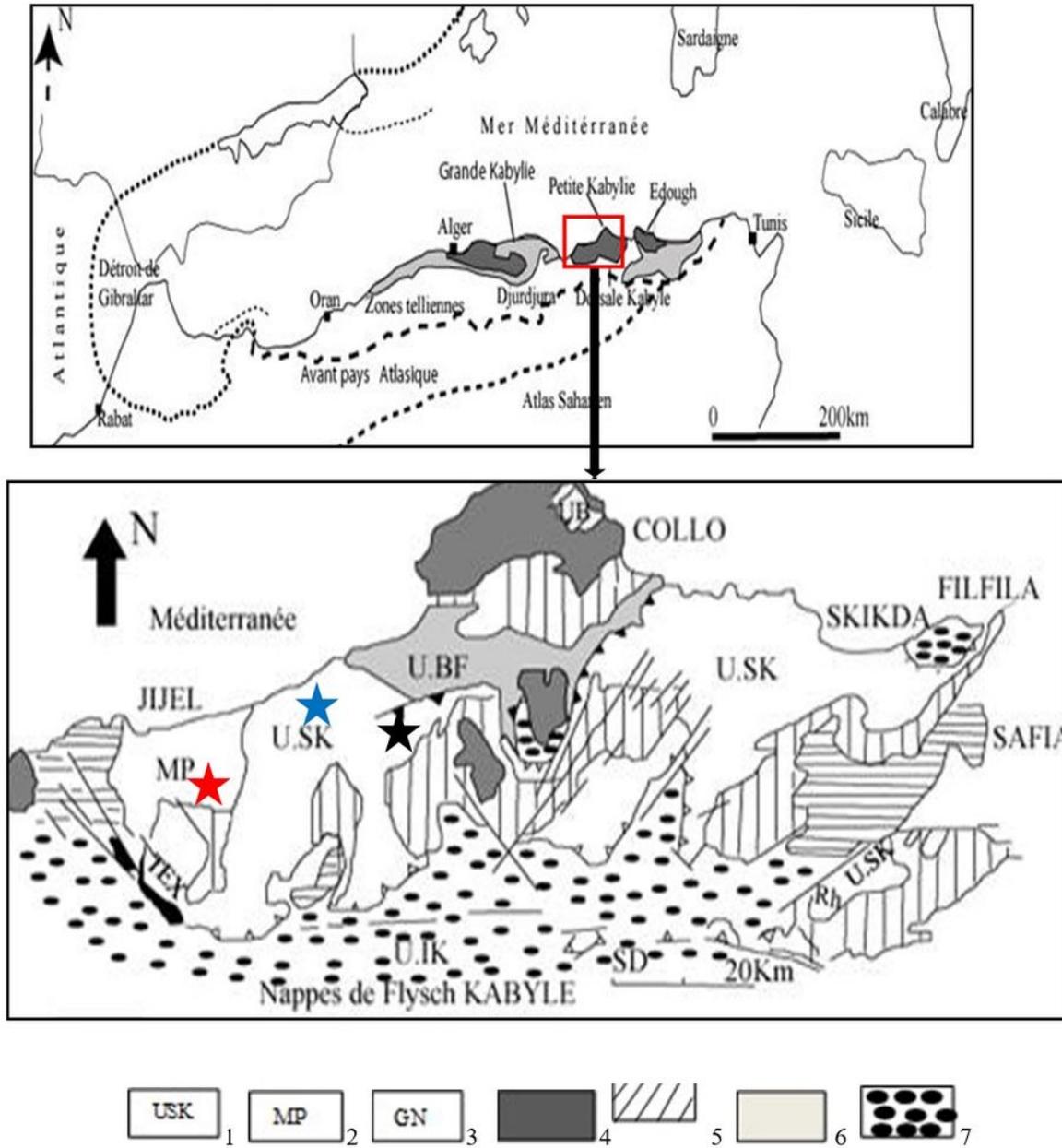
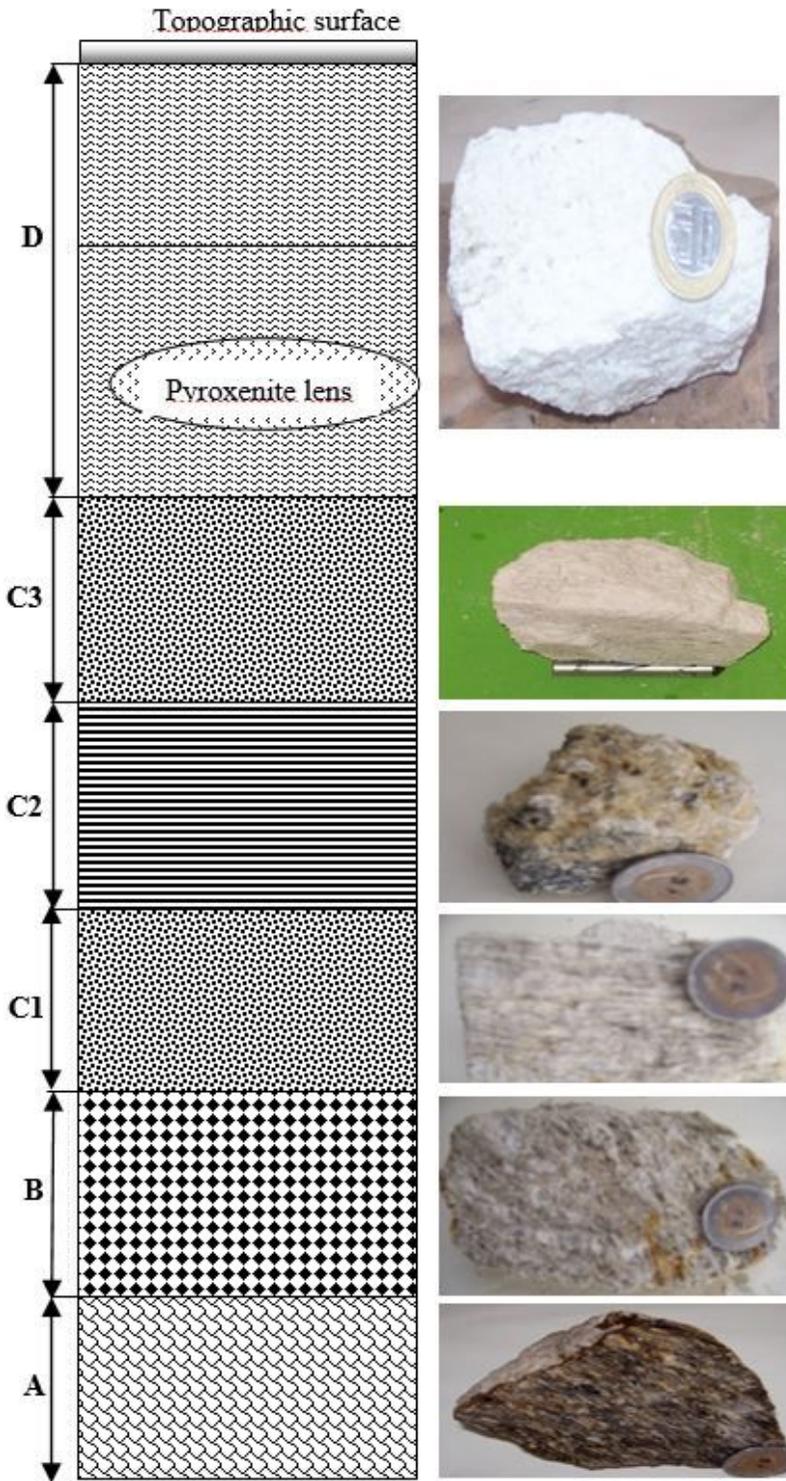


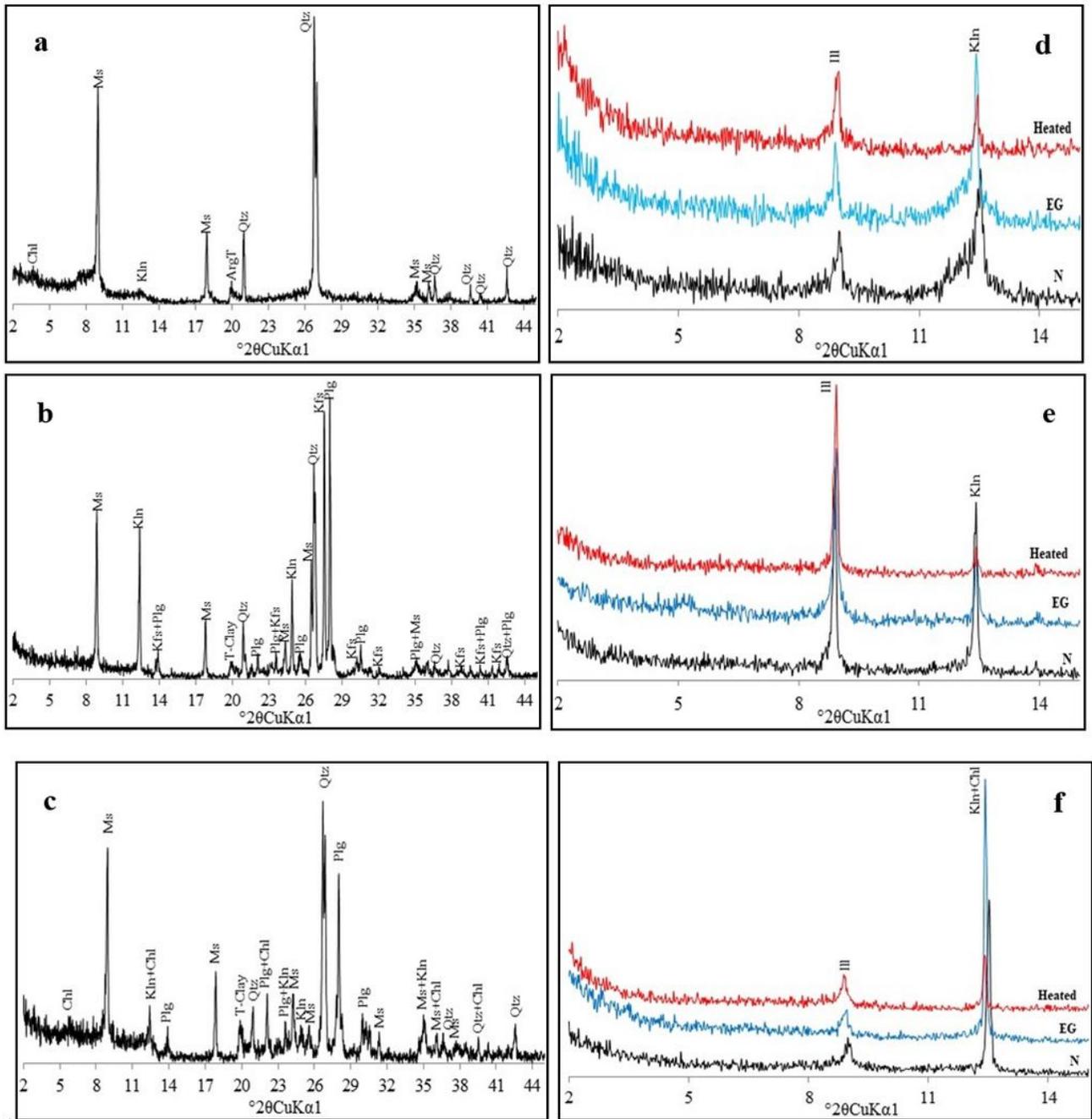
Figure 1

please see the manuscript file for the full caption



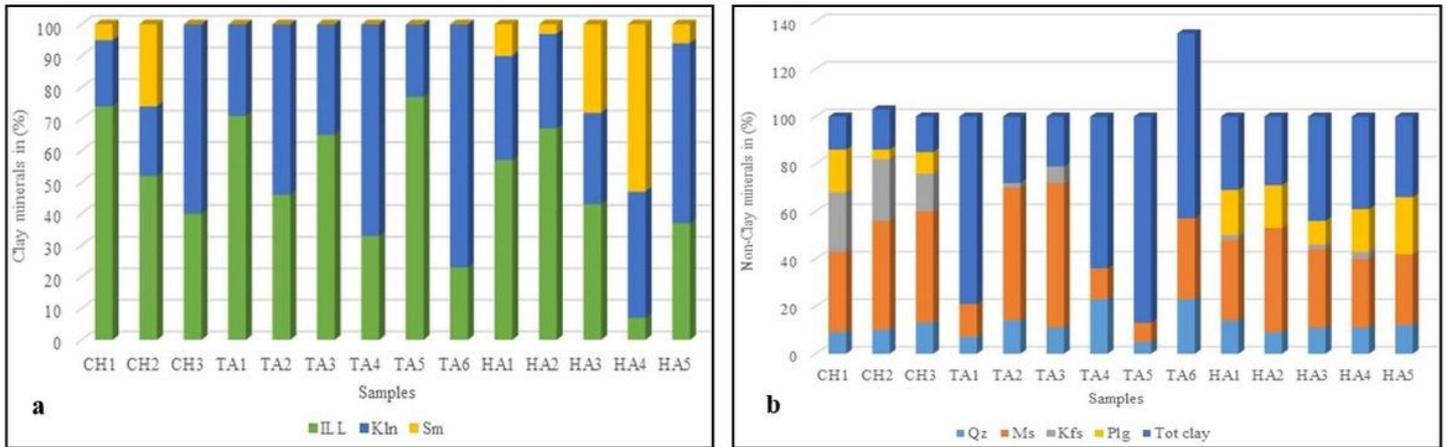
**Figure 2**

Vertical succession of the different levels forming the kaolin deposits (TM, Ch and HA), from the bottom to top: A, Parent rock; B, compact layer little affected by weathering (transition zone); C1, C2 and C3, slightly kaolinized layer; D, strongly kaolinized layer



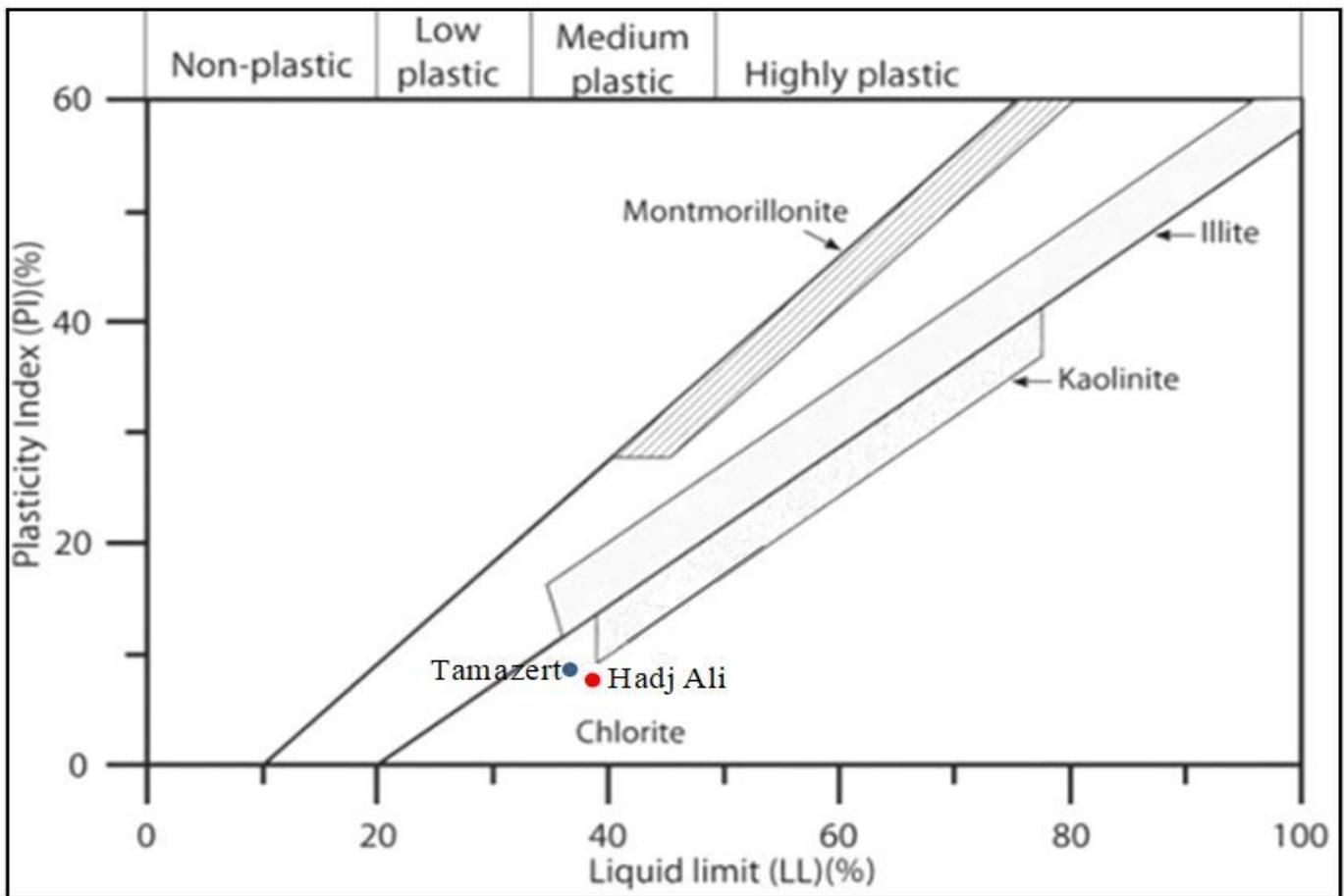
**Figure 3**

X-ray diffraction patterns: (A, B and C) bulk mineralogical of (T, C and H); (D, E and F) mineralogical of oriented clay fraction (<2µm) (T, C and H). Qtz: Quartz, Kln: kaolinite, Ms: Muscovite-illite, T-Clay: Total clay, Kfs: K-feldspar



**Figure 4**

Graphics show mineralogical composition: (a) composition of clay minerals; (b) Composition of non-clay minerals.



**Figure 5**

Position of clay samples on the Holtz and Kovacs diagram (Holtz & Kovacs, 1981)

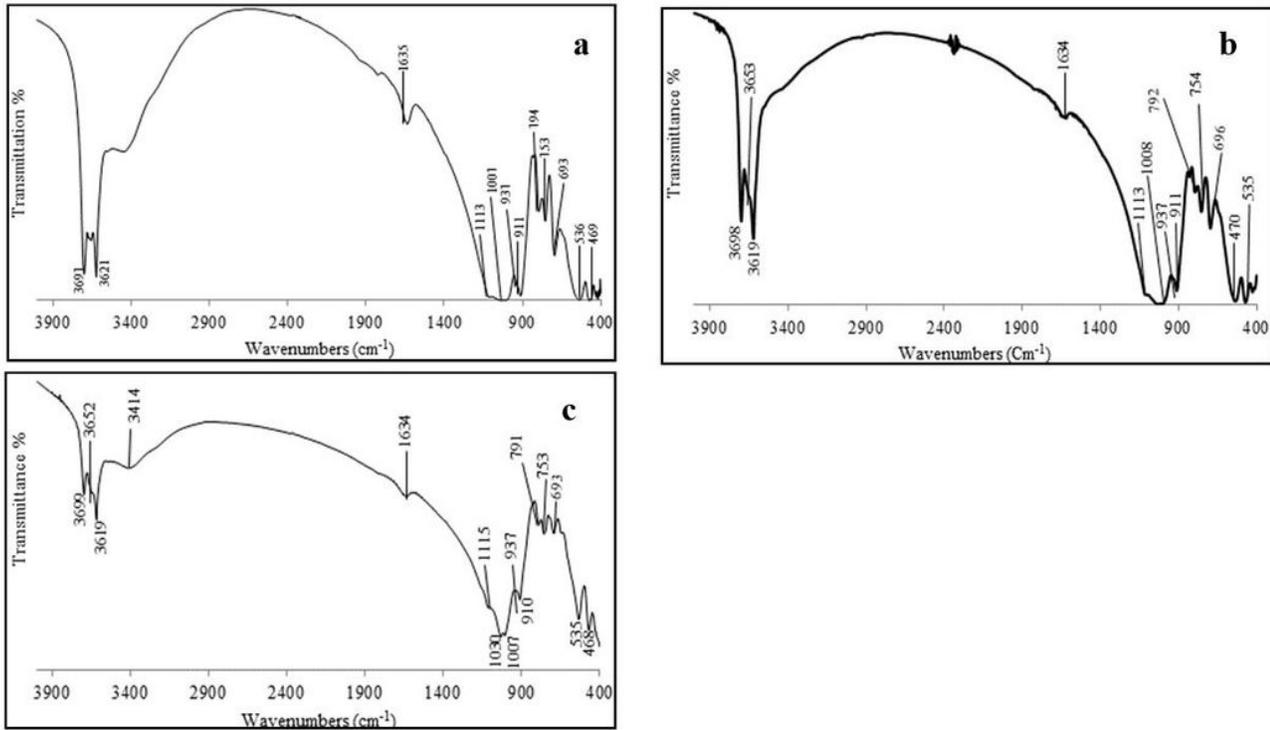


Figure 6

IR spectra of clays samples: (a) Tamazert; (b) Chekfa and (c) Hadj Ali

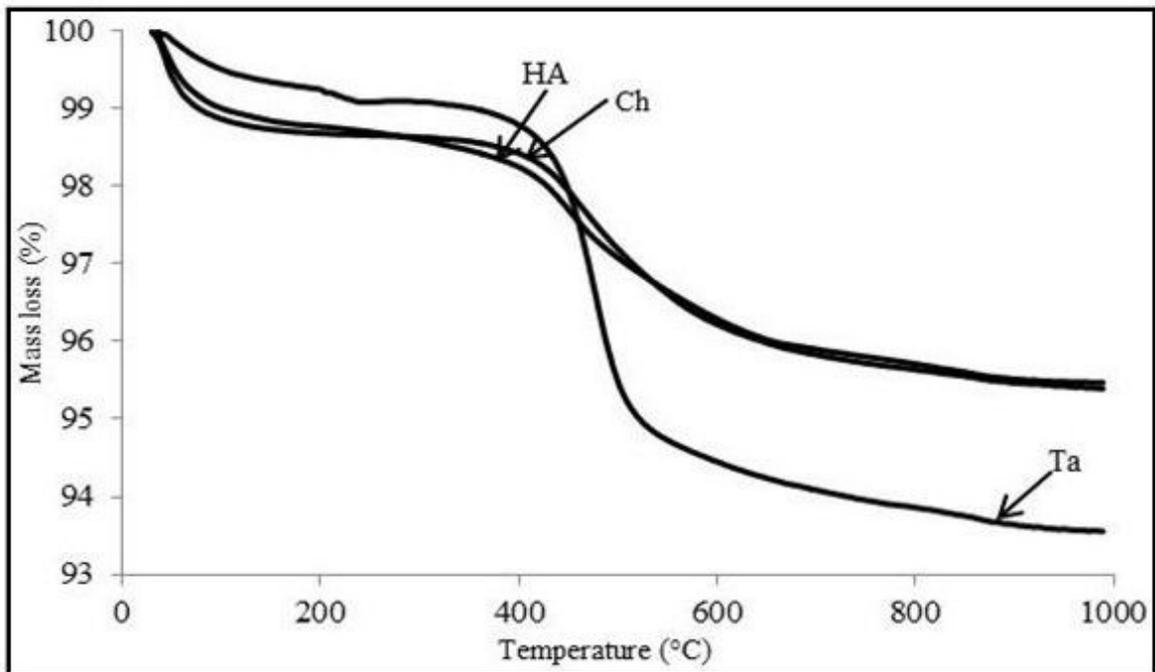


Figure 7

TGA Thermograms of Tamazert (TM), Chekfa (CH) and Hadj Ali (HA) clays samples.

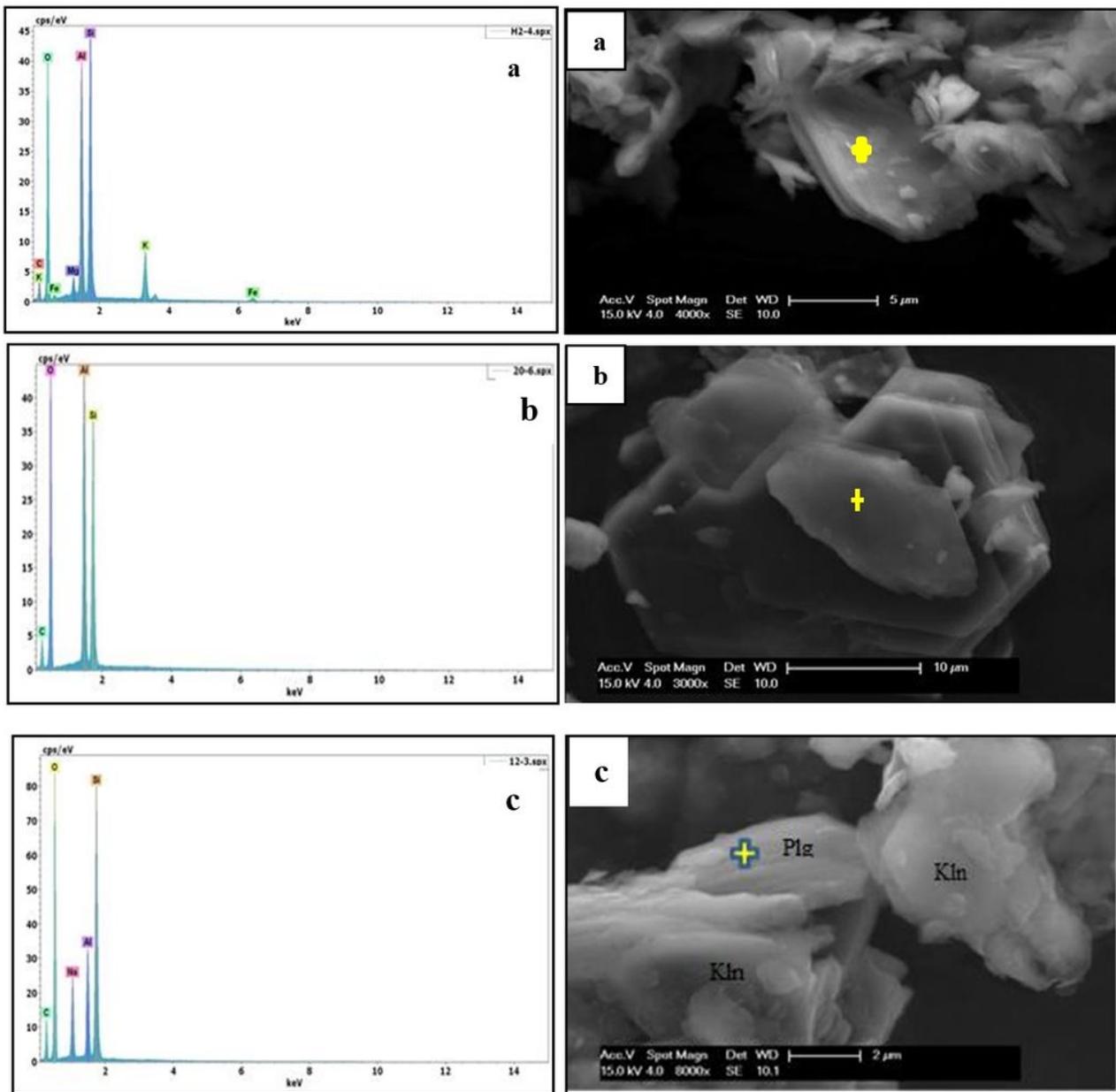
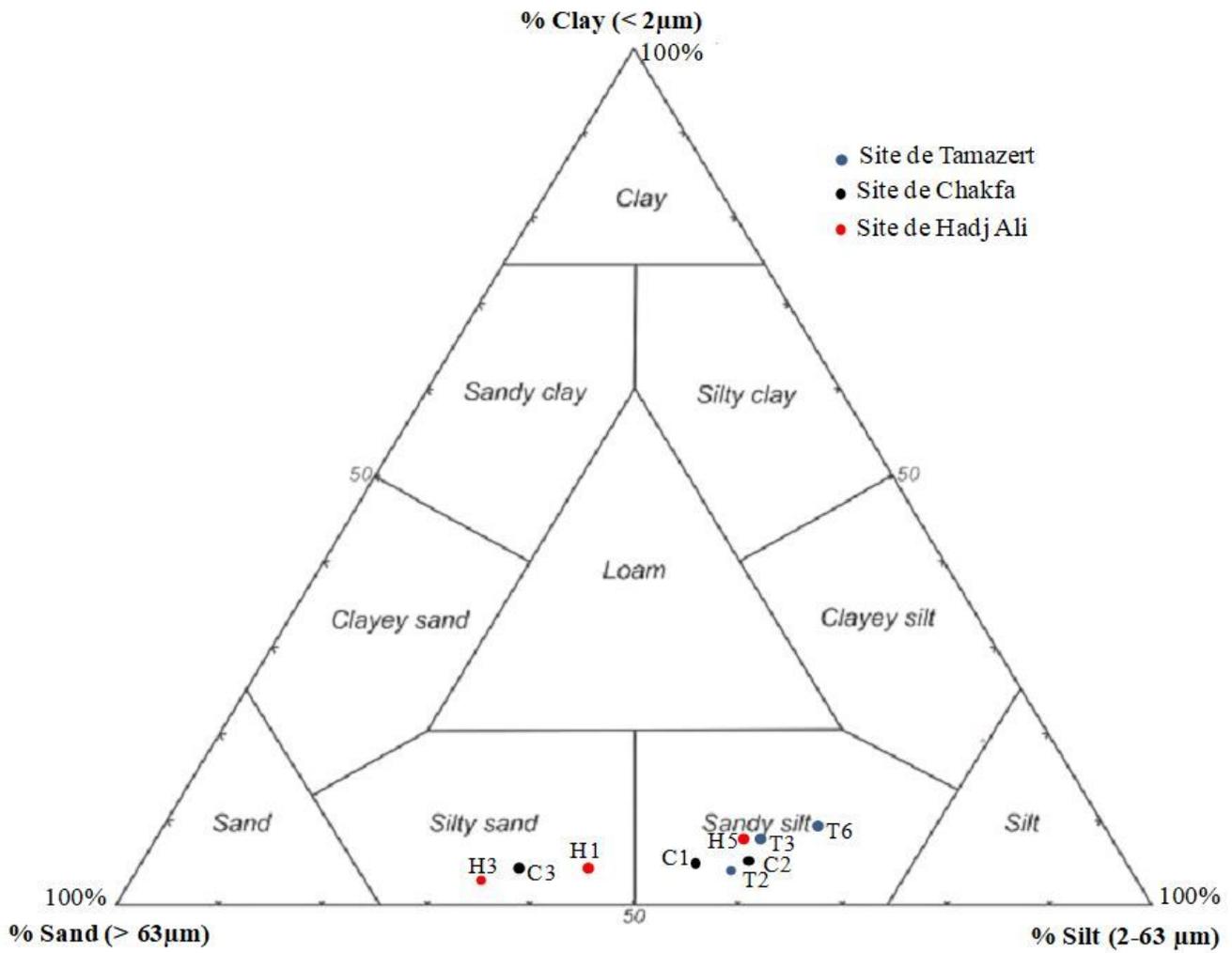


Figure 8

ESEM/EDX Photograph: (c) showing semi-hexagonal kaolinite particles (Kln) and unaltered plagioclase (Plg) (Tamazert); (b): showing hexagonal and semi-hexagonal kaolinite particles (Hadj Ali); (a): showing hexagonal kaolinite particles (Chekfa)



**Figure 9**

Ternary classification of clay materials based on sand-silt-clay ratios (after Dondi et al., 1992)

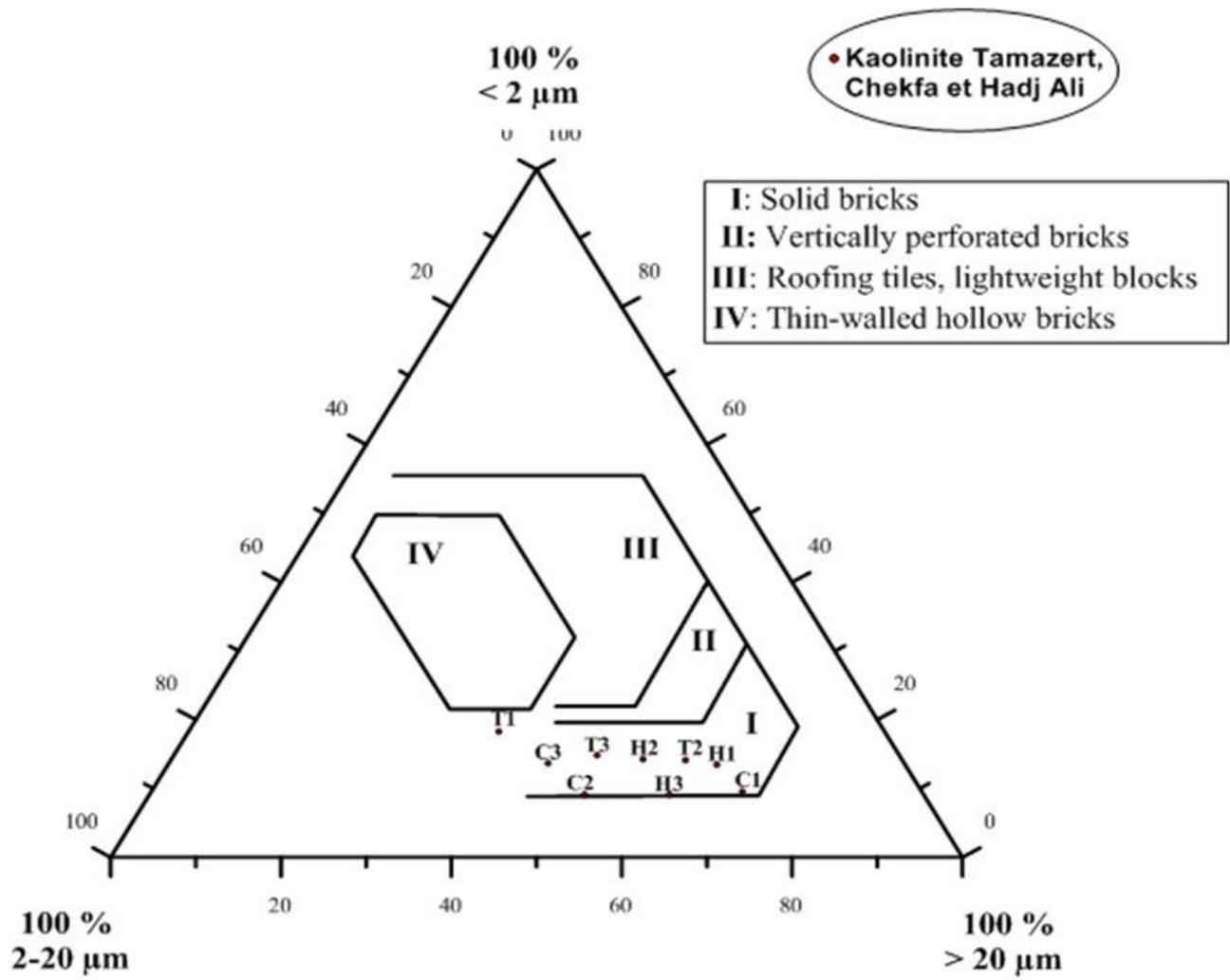


Figure 10

grain-size distribution of clay samples according to Winkler's diagram (1954)