Characterization of halloysite (North East Rif, Morocco): evaluation of its suitability for ceramic industry

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ABSTRACT: Halloysite from Nador (NE Morocco) has been studied to evaluate their suitability in ceramic industry. Cross-section involving all the Messinian facies was performed in the Melilla Neogene basin, at the foot of the Gourougou volcano, in order to understand the origin of the halloysite and appreciate its reserves. White layers of halloysite and red clays rich in
smectite occurred in contact with basal reef limestone, were characterized by mineralogical (XRD, IR), textural (SEM) and physico-chemical analyzes (grain-size, Atterberg limits, ATD/TG, XRF and specific surface area). Ceramic properties were evaluated for fired halloysite from 500 to 1100°C in order to appreciate technical processing for ceramic production.

The halloysite consists of fine particles with a high plasticity and a large specific surface area. XRD results revealed the presence of 7Å non-hydrated halloysite with the presence of gibbsite, alunite, K-feldspar plus other minor phases, and traces of smectite and illite.

Infrared spectroscopy confirms the occurrence of characteristic bands of halloysite at 3695 and 3618 cm⁻¹. SEM observations confirmed the predominance of tubular facies typical of halloysite. The chemical analysis revealed high aluminum content linked to the presence of some aluminous phases (gibbsite and alunite). ATD/TG and XRD results of fired clay sample evidenced halloysite dehydroxylation and a rearrangement of metakaolinite to form mullite and spinel from 975°C.

Moroccan halloysite has good properties for refractory ceramic application. However, quartz sand addition is required to avoid any cracks development at firing as well as to reduce the plastic behaviour of raw halloysite and minimize shrinkage during sintering.
Keywords: Halloysite, Morocco, Nador, Messinian, physico-chemical properties, ceramic, mullite.

INTRODUCTION

Halloysite is typically formed by hydrothermal alteration of alumino-silicate minerals. It occurs in association with dickite, kaolinite, montmorillonite and other clay minerals (El Amrani El Hassani & Sadic, 2016). According to Blanc et al., (2006), kaolinite would be the most stable clay ($\Delta H_f = -4115.30$ kJ/mol, $\Delta G_f = -3793.93$), followed by dickite ($\Delta H_f = -4099.80$ kJ/mol, $\Delta G_f = -3777.30$) and halloysite ($\Delta H_f = -4092.93$ kJ/mol, $\Delta G_f = -3771.95$); this might explain the scarcity of halloysite. Hollow tubular structure constitutes the predominant and chemically stable form of halloysite. Depending on humidity, halloysite occurs naturally in two different forms (Joussein et al., 2005): the hydrated form (n = 2), in which the sheets are separated by water molecules layer, with an equidistance (d001) close to 10 Å and meta-halloysite, which is the most common of the halloysite, with an interfoliar distance close to 7.15 Å similar to kaolinite. The latter is obtained by irreversible dehydration of the 10 Å halloysite between 60 and 100 °C (Ruiz-Hitzky et al., 2008). Decipher between kaolinite and halloysite forms based only on XRD spectra is challenging, and request some morphological observations (Singer et al., 2004; Joussein
et al., 2005). The halloysite has a tube-like shape, which is different from the hexagonal platelets of kaolinite, gives it the capability to retain water (Giese, 1988, Caillère et al., 1982, Pasbakhsh et al., 2013; Bain, 1971). The tubes have multi-layer walls with positively charged Al-OH on the inner surface and negatively charged Si-OH on the outer surface (Shchukin et al, 2005).

Halloysite has several industrial applications (Zhou & Keeling, 2013, Schroeder & Erickson, 2014, Churchman et al., 2016), particularly in ceramics industry. A growing demand for this raw material is in general observed (Detellier & Schoonheydt, 2014, Pracejus et al., 2017). Recently, due to its specific morphology and properties, several studies have aimed to widen its application fields, to high technology application as support for catalysts and other functional materials (Lu et al., 2016). It is also capable of storing a large quantity of hydrogen molecules (Jin et al., 2014), drugs for medical purposes (Lvov et al., 2008, Tan et al., 2014, Yuan et al., 2012), to form antibacterial biological membranes (Chen et al., 2012; Zhang et al., 2013; Jin et al., 2014) and polymer-based composites (Abdullayev et al., 2013; Pan et al., 2011; Zhou et al., 2010). Halloysite is also a major absorber for cationic and anionic molecules (Zhao et al., 2010a, Abdullayev & Lvov, 2010, Luo et al., 2010, Zhao et al., 2010b). It also applied in nano-composites (Tan et al., 2014), like in other technological uses (Williams & Hillier, 2014).
In Morocco, the halloysite deposit is located only in the North Eastern in the Nador region (El Amrani El Hassani & Sadic, 2016). Within the Gourougou area, a large volcanic deposit dated from middle-Miocene to late Pliocene, is located the Maaza valley (Fig. 1). The halloysite occurs in thin layers (decimetric) in contact with the reefal limestone, cinerites and volcanic gravels. Despite the scientific and economic interest of this natural resource, in comparison with other countries, Moroccan’s halloysite investigations are still lacking. Several geological studies were undertaken in this region (Jeannette, 1958; Vivaldi & Vilchez, 1958; Vilchez, 1961; Azdimousa, 1991). In the point of view of sedimentology, Martin Vivaldi (1961) outlined that Maaza deposits is composed of a mixture of endellite, halloysite, gibbsite, montmorillonite and alunite, probably of hydrothermal origin.

The main aim of this study was to promote these halloysite deposits as well as to update the state of knowledge on its geological context, its mineralogical nature, and its physico-chemical and thermal properties. Furthermore, the various properties necessary to consider the valuation of halloysite in the field of ceramics were investigated.

**MATERIAL AND METHODS**

**Material**
The halloysite deposit is located in the southern part of the Neogene basin of Melilla (NE Morocco), at the foot of the Gourougou volcano, in the Maaza valley (N: 35°16’43.751” W: 3°01’20.865”’) (Fig. 1). The Melilla Basin genesis is related to the main orogenic movements of the Rif domain during the Middle Miocene (Choubert et al., 1968, Guillemin & Houzay, 1982). The opening of this basin is in relation with strike-slip faulting which marks the eastern limit of Alboran basin, following the tectonic directions established during the collision of internal zones of the Rif domain (García-Dueñas et al., 1992). The Melilla Basin is generally characterized by three major sedimentary cycles: (1) upper Tortonian marls, associated with volcanic events; (2) Messinian unconformably overlies the Tortonian deposits, reflecting an open sea environment with normal salinity; (3) early Pliocene corresponds to a shallow marine incursion during the late Messinian seawater evaporation.

The halloysite deposit belongs to the Neogene basin, located at the base of the Messinian series between marl which takes a reef-like appearance here, cinerite and red volcanic rounded gravel of millimetric-sized fragments from the Gourougou volcano (Guillemin & Houzay 1982). The halloysite is in the form of clusters or irregular lenses in contact with travertine situated at the base of the reef series, associated with a gray-colored alunite (Hilali & Jeannette, 1981). Halloysite lenses can reach one or two decimeters, intersecting the reef limestone at the base of the series (Figs. 2 and 3).
Cross-section involving all the facies described above was performed in the region (Fig. 3). Due the homogeneity of the halloysite deposit, a representative sample of 2 kg was sampled. Red clay, in contact with volcanic sandstone and reef formation, was also sampled.

**Experimental procedures**

*Mineralogical and chemical analysis*

The bulk sample was dried in an oven at 40 °C and then ground to < 250 μm size fraction. The mineralogical phases present in the shards were identified by X-ray diffraction using a powder Brucker D8-Advance diffractometer, with copper anticathode (University of Liege, Belgium). The angular range explored is located between 5° and 60° 2θ. The X-ray patterns were treated by the DIFFRACplus EVA software to remove the background noise and to calculate profile parameters such as line positions and intensity peaks. Minerals phases were determined semi-quantitatively (± 5%). Additional measurements were performed on oriented aggregates (Moore & Reynolds, 1989) prepared from the < 2 mm fraction obtained by suspension in distilled water of 1g of the bulk sample. The suspension was first sieved at 63 μm to limit particle settling during decantation and to reduce the amount of impurities within the clay aggregates. The < 2 μm fraction was taken from the suspension according to Stoke’s law, placed on a glass slide and the
XRD patterns recorded between 2° and 30° 2theta using the same step size
and time per step parameters mentioned before. These oriented aggregates
were subjected to three successive treatments, air drying, glycolation and
heating to 500°C for 4 h, to identify the minerals of the clay-size fraction.

Chemical composition of major elements was carried out by X-Ray
Fluorescence spectroscopy (XRF) using a Panalytical Axios spectrometer
equipped with Rh-tube. The gas used is argon-methane and the data
program of treatment is IQ+ (University of Liege, Belgium).

Fourier transform infra-red (FTIR) were performed on the < 150 mm
fraction with a Fourier Transform Spectrometer Nicolet NEXUS type
(University of Liege, Belgium). The spectra were acquired on a mixture
containing 15% of the clay powder with oven-dried KBr. The spectra,
recorded from 4000 cm⁻¹ to 600 cm⁻¹ with a resolution of 4 cm⁻¹, were
obtained by accumulating 200 scans.

Thermal analysis ATG/DSC was carried out using an STA PT1600 (STA
Simultaneous Thermal Analysis - ATG/DSC) type under atmosphere
conditions (Mohammed V University of Rabat, Morocco). The sample was
heated from room temperature to 1000 °C with a rate of 10 °C/min.

Scanning electron microscopy (SEM) images were performed on clay
fraction and sintered clay by using a Philips microscope model XL30
(University of Liege, Belgium). Phase identification of the clay was also
determined by energy-dispersive X-ray spectroscopy (EDX). The images were obtained with a secondary electron detector at a voltage of 10 kV. The < 250 mm fraction was dispersed over a sample holder and gold-sputtered for (EDX) analysis.

Physical and textural analyses

The grain-size distribution is carried out on bulk sample using a particle analyzer by laser diffraction (Malvern Mastersizer 2000). The evaluation of the plasticity and the limits of Atterberg determination were carried out by the of Casagrande method (University of Liege, Belgium).

The blue methylene value (VBS) was determined in order to evaluate the capacity of clay to absorb cations from a solution, and thereby predict how the clay will react, based on the property of clays known as cation-exchange capacity. The number of ions available for this exchange values depends on the amount and characteristics of clays minerals, cation exchange capacity and specific surface area. (Mohamed 1er University of Oujda, Morocco)

Ceramic proprieties

Ceramic tests require the preparation of specimens (100 × 50 × 10 mm) using a 100 MP press. The drying shrinkage (up to 110°C) and firing shrinkage were obtained according to the relative variation in the length of
the specimen. They were thus defined: drying shrinkage = \(100(L_p-L_d)/L_p\) and firing shrinkage = \(100(L_m-L_f)/L_m\), where \(L_m\) is the length of the mould and \(L_p, L_d\) and \(L_f\) are the length of the pressed, dried and fired specimens respectively. The firing shrinkage and bending strength were determined using ASTM norm C326-03 and C674-88 respectively.

**RESULTS**

*Lithological description*

The Maaza Valley belongs to the Messinian sedimentary basin (Fig. 1). From lithological point of view, the cross-section performed in the region consists of reef limestone with gorgonians, Gastropods and Lamellibranchs. The later are surmounted by red clays with whitish horizons covered by coarse volcanic sands. Pyroclasts and clays with intercalations of gravel layers with rounded pebbles were then deposited (Fig. 2). At the top, a basaltic flow ends the series. The recorded observations (Figs. 2 and 3), display that the layer of halloysite thick from 25 cm to 130 cm, is not strictly interstratified between limestone reef and volcanic sand, but is wedge-shaped in contact with reef limestone and travertine.

*Halloysite characteristics*

The XRD results obtained on halloysite sample reveal that it is dominated by clay fraction (total clay, 74%) (Table 1). The raw clay also contains
gibbsite, k-feldspar (sanidine), alunite and some small amount of tridymite, fluorite and halite. The red clay sample is mainly composed of total clay fraction (60%), K-feldspar (18%), goethite (10%) and traces of quartz and hematite.

Regarding the clay fraction (< 2μm), the results (Table 1, Fig. 4) indicate that the clay minerals are essentially represented by dehydrated halloysite. It is characterized by a peak around 7.15Å under air dried (N) and ethylene glycol saturation conditions (EG) and disappears after heating to 500 °C. The (001) halloysite peak is sharp and symmetric suggesting its neoformed origin. The patterns reveal the presence in very small proportion of smectite and illite. Contrary to halloysite sample, illite and smectite are detrital due to the broad peaks at 14Å and 10Å, respectively. The red clay sample is mostly made by 60% of clay fraction, including smectite (96%) with traces of illite and kaolinite/halloysite. The sharp (001) peak at ~14 Å indicates the neoformed origin of smectite (Fig. 4).

Chemical composition of halloysite sample is dominated by SiO$_2$ (37.1%) and Al$_2$O$_3$ (37.4%), while red clay sample is enriched in SiO$_2$ (54.1%) with 16.6% of Al$_2$O$_3$ (Table 1). In addition, Fe$_2$O$_3$ content is higher for red clay (4.0%) than in halloysite sample (0.5%), which explains the white color of halloysite. K$_2$O, MgO, CaO, TiO$_2$ and SO$_3$ are also present in both samples but as small amount. It is noted that these elements are slightly higher in red clay than halloysite sample, except for SO$_3$ (1.6%) which is higher for
halloysite sample. The loss on ignition at 1000°C is relatively high (18%) in the halloysite sample, related to the high amount of halloysite (dehydroxylation) and the presence of aluminum hydroxide as gibbsite which loss its mass during heating.

The infrared analyzes (FTIR) of halloysite sample display several absorption bands which are reported in table 3. In the interval (between 400 and 4000 cm\(^{-1}\)), two types of characteristic vibrations are mainly observed: elongation vibrations and vibrations deformation. The obtained bands are slightly shifted compared to kaolinite ones, in addition to two others bands are recorded in the sample at 3695 and 3618 cm\(^{-1}\). The characteristic peaks of halloysite were observed at 1033 cm\(^{-1}\) for Si-O-Si vibration and at 3695 cm\(^{-1}\) for Al-OH vibration (Abdullah et al., 2015, Muthu et al., 2016). In good agreement with the dehydrated halloysite spectra published by Anton & Rouxhet (1977), studied halloysite presents two bands of vibration with almost equal intensities, located respectively at 3695 cm\(^{-1}\) (external hydroxyls) and 3618 cm\(^{-1}\) (internal hydroxyls).

The SEM images (Fig. 5) indicate that the white clay sample consists of tubular-facies, sometimes agglomerated, typical of halloysite having a diameter of 0.15 μm and a length of 600 μm in average. This result is in agreement with halloysite dimensions established by Bordepong et al., (2011) but higher than those found by Lvov & Abdullayev (2013). EDX
analysis displays that the sample contains in addition to silicon and aluminum, other elements as iron, sodium, potassium, chlorine and fluoride.

The physical properties of halloysite sample are reported in the Table 1. Halloysite sample is made by clayey silt with 62% and 38% of clay and silt fraction, respectively. The Atterberg limits indicate a high liquid limit (70%), plastic limit (38.5%) and plastic index (31.5%). According to Casagrande (1947), this sample has a plastic behavior indicated by a fairly high plasticity index. The halloysite sample has a fairly large specific surface area (55.48 m²/g) compared to that for kaolin clay (10-30 m²/g). This great value is explained by the dominance of the clay fraction and by the minority content of non-clay minerals. Halloysite has higher plastic limits (60-70) compared with those of kaolinite (40-60), due to the special tubular form and trough-like form of the clay mineral constitutes the main cause of the water retention properties of halloysite (Bain, 1971).

Differential thermogravimetric and thermal (ATD/TG) analysis indicate three endothermic and exothermic peaks (Table 3), which is typical of those of kaolinitic clays (Rollet & Bouaziz, 1972, Aliprandi, 1996, Jouenne, 1990). The endothermic peak at ~100 °C is due to the loss of water. For the endothermic peak that appears at ~304 °C, it was highlighted by Martin Vivaldi & Girela Vilchez (1958) on samples rich in gibbsite. The endothermic peak at 534 °C is characteristic of the kaolin group, and is attributed to the transformation of halloysite to metakaolinite (e.g., Minato &
Aoki, 1979; Caillere, 1982, Johnson, 1990, Prodanovic et al., 1997). The exothermic peak at 975 °C is due to the formation of mullite, pseudomullite, spinel, amorphous silica and γ-Al₂O₃ (Földvári, 2011).

**Ceramic properties**

The drying shrinkage is relatively low having about 0.5% of initial length of the halloysite bodies (Table 1). While, a high shrinkage of about 7.5% is recorded for specimen fired at 1100°C, that can be attributed to the loss of water and other volatile as well as to the sample melting. Linear shrinkage is a parameter which influences the reactivity of a material during firing. Generally, linear shrinkage increases as firing temperature increases. The increase in linear shrinkage means that a chemical transformation has taken place in the material. This change is associated with a flexural strength of 16.3 MPa. SEM analysis allows us to examine microstructure of the sintered bodies. Micrographs of heated halloysite bodies at 1100 °C do not evidence any tubular structure of halloysite (Fig. 8). The structure becomes more complex, with two forms of mullite: a cuboidal aspect, also called "primary mullite", and a needle-shaped mullite crystals or "secondary mullite". A heterogeneous microstructure is observed at 1100°C that arises from mixing and agglomeration of the original materials with more elongated tabular mullite in a glassy matrix than cuboidal form.
DISCUSSION

Genesis of halloysite

Fieldwork investigations indicate that fine white clay develops in contact with carbonate formations (reef limestone and travertine) and sandy layers (Figs. 2 and 3). This results from the gradual dissolution of calcite by acidic fluids rich in CO$_2$. The CO$_2$ comes from the atmosphere as well as derived from the leaching of the overlying sedimentary cover (karstification). The gradual dissolution of calcite generates a significant porosity in the reef limestone, improving the drainage and circulation of the weathering solution through the karst filling. The occurrence of lenticular shaped halloysite suggests its neoformed origin involving a transfer of silica and aluminum from volcanic ash from the Gourougou volcano. Mineralogical results obtained from red clay indicated the neoformed origin of smectite due to its (001) sharp peak. Likewise, the XRD spectra confirm that the halloysite is neoformed (Fig. 4). However, the occurrence of illite and smectite in white sample, and illite and kaolinite in red sample, suggest their inherited origin from parent rock, namely reef limestone and volcanic sandstone (Fig. 2). It is known that hydrothermal alteration of volcanic host rocks involves the replacement of primary igneous minerals and glass (e.g. plagioclase, orthoclase, quartz, biotite, muscovite, amphibole and pyroxene), other forms of silica (e.g. illite, smectite, chlorite, serpentine, albite, carbonates, talc,
kaolinite), sulfates (anhydrite, barite, alunite, jarosite) and oxides (magnetite, hematite, goethite) (Shanks et al., 2012). Consequently the presence of inherited illite, smectite and kaolinite as well as gibbsite and alunite allows us to confirm the volcanic origin of the halloysite through the hydrothermal circulation of fluid rich in sulphur. Ishikawa Alteration Index (AI) is 37 for red clay and 72 for halloysite sample indicates that both samples have experienced hydrothermal alteration (Ishikawa et al., 1976). Vivaldi & Vilchez (1958) have demonstrated the evolution of silico-aluminous amorphous phases (allophane) to well-crystallized minerals by release of silica and alumina, mainly (halloysite, gibbsite and alunite) as the following reaction: volcanic ash \(\rightarrow\) silico-aluminous amorphous minerals (allophane) \(\rightarrow\) halloysite, gibbsite and alunite.

Massive kaolin deposits are rare in North Africa, especially halloysite (Bechtel et al., 1999). In Algeria (Djebel Debbagh, north-eastern), western (Ain Khemouda) and northern (Tamra) Tunisia, halloysite is detrital occurred after the karst windows formed during Oligocene to Eocene times (Renac & Assassi, 2009, Mellouk et al., 2009; Moussi et al., 2011; Jemaï et al, 2015).

In Algeria, halloysite occur associated with minor alunite, absence of quartz, dominant kaolinite and illite. Halloysite occurrence has been interpreted as either hypogene, supergene or hydrothermal related to fluid circulation (Renac & Assassi 2009). In northern Tunisia, halloysite occurs in
association with kaolinite and Zn-aluminous hydrated halloysite (10 Å), its
genesis is driven by pedogenesis and hydrothermal alteration (Moussi et al.,
2011).

Algerian halloysite showed a tubular morphology with tube lengths of 2.5
μm and an outer diameter of 0.15 μm, while Moroccan halloysite displays
tube lengths of 600 μm in average with similar diameter. Tunisian halloysite
has tubular morphology of variable size in length and thickness and
sometimes spheroïdal (Chaari et al., 2015). Relatively low cation exchange
capacity value (18 meq/100 g) is showed for Tunisian halloysite, as
Algerian value (19 meq/100 g) indicating insufficient edge valences (Jemai
et al., 2015). Specific surface area of Algerian halloysite is 64 m²/g greater
than Moroccan value (56 m²/g). Similar value of ~57 m²/g was obtained for
halloysite from New Zealand (Levis and Deasy, 2002).

Characterization of halloysite

Al₂O₃ (37.4%) and SiO₂ (37%) are the main oxides in the sample, with a
SiO₂/Al₂O₃ ratio of 0.98, is close to 1 that is characteristic of the kaolin
group (Table 1). The absence of quartz and the presence of gibbsite Al(OH)₃
and alunite KAl₃(SO₄)₂(OH)₆ may explain the high concentration of
aluminum. The occurrence of small amount of TiO₂ and Fe₂O₃ (< 1.5%)
could not influence the color of the kilned product. The SO₃ (1.6%) and F₂O
(0.9%) contribution confirms the presence of alunite and fluorite, respectively as observed on XRD results. The low amount of alkali (K\textsubscript{2}O+Na\textsubscript{2}O) indicates the high degree of kaolinization, since halloysite is formed from the alteration of volcanic rocks.

Halloysite sample has higher clay fraction (74%) with greater plasticity and higher specific surface area than kaolinite clay. The high plasticity is confirmed by the high absorption of the methylene blue by the sample (VBS > 2). Methylene blue is absorbed preferentially by clay due to the fact that their sheet can easily be affixed water molecules. Furthermore, the measured specific surface area value is close to that determined for halloysite by Hofmann et al., (1966) (61 m\textsuperscript{2}/g). It noted that the studied halloysite from Morocco trends to exchange calcium and magnesium cations, which may explain the elevated amounts of these elements given by chemical results (Table 1). This fact also confirms the presence of tubular clay such as halloysite.

The halloysite displays a great plasticity that can be explained by the XRD results, indicating the predominance of phyllosilicate and the absence of a degreasing agent, especially quartz. The grain-size plays an important role for ceramic manufacturing, especially clay fraction which influences its plastic behaviour (El Ouahabi et al., 2014). Plasticity is one of the most important parameters for making clay products, which depends on the nature of their clay minerals (Allaoui et al., 2005, Guerraoui et al., 2008),
the presence of impurities (non-clay minerals) (Bergaya et al., 2006), and it is inversely proportional to grain size (ASTM C 326-03).

Suitability for ceramics

Halloysite has high plastic behaviour that has to be corrected by the addition of quartz to avoid any cracks development during drying. Furthermore, quartz plays the role of a filler to control deformation and shrinkage of the fired bodies, whereas K-feldspar, acting as a flux, is the main responsible for the formation of quasi-liquid phase during firing that affects the densification process (Toprak & Arslanbaba 2016). Moreover, flux interacts with halloysite, which confers to the plasticity for the bodies shaping and gives mullite and glass during firing (Carty et al., 1998; Iqbal & Lee 2000; Martín-Márquez et al., 2010). Therefore this influences the micro-structural features and physical properties of the fired bodies (Pagani et al., 2010).

Mineralogical evolution of fired bodies from 500 to 1100°C allows us to follow vitreous phase transformation and disappearance of initially existing phases (Fig. 6). Based on XRD results of fired bodies, disappearance of halloysite, gibbsite and tridymite occurred from 550°C, which therefore lead to neoformation of other stable silica–alumina phases. Crystalline phases (cristobalite, spinel, mullite, corundum and hematite) are neoformed from 900°C, which is also highlighted by thermal analysis (Table 3). Fluorite abundance decreases with intensity as increasing firing temperature until
1100°C. Fluoride improves the nucleation and growth of glass ceramics and decrease the aggregation extent of the glass network (Duan et al., 1999).

The behaviour of halloysite fired at 1100°C displays a high flexural strength (16.3 MPa) associated with shrinkage of 7.5% indicating some melting and development of vitreous phases. However, this change involved cracks development (Fig. 7) due to the absence of filler as quartz (Souza et al., 2006). Flexural strength is mainly influenced by the mullite development and the formation of a vitreous phase which likely improves the mechanical strength. Regarding the microstructure from 1100°C based on SEM observations, the occurrence of two mullite crystals forms is related to feldspar and its interaction with halloysite. In general, mullite crystals grow in a viscous aluminosilicate liquid, as primary mullite in pure clays and secondary mullite in the presence of alkali fluxes (Na₂O + K₂O) (Lee et al., 2008), which is in agreement with chemical and mineralogical results obtained from halloysite sample. It should be noted, however, that other variables influence mullite formation by affecting the composition and viscosity of the liquid in which it grows. Since is difficult of determine the stoichiometry of mullite formed in vitreous systems due to the heterogeneity of the microstructure.

In the light of the obtained results, studied halloysite is suitable for light vitrified raw materials for ceramic from 900°C, but appropriate formulations need to be done in order to prevent manufacturing defaults.
CONCLUSION

In this work, halloysite deposit from the Neogene basin (Nador region), located at the foot of the Gourougou volcano in the Maaza Valley have been investigated. White layer of halloysite, of 25 to 130 cm thick, occurred in wedge-shaped form in contact with lower reef limestone and upper volcanic sand. The clayey material consists of fine particles (68%) with a high plasticity (31.5%) and a fairly large specific surface area (55.48 m²/g).

XRD results revealed the presence of 7Å non-hydrated halloysite (metahalloysite) and traces of smectite and illite, which is confirmed by SEM observations. The halloysite occurs in association with gibbsite, alunite, K-feldspar and other minor phases (tridymite, fluorite and halite). This halloysite has characteristics infrared bands at 3695 and 3618 cm⁻¹.

Thermal and thermogravimetric analysis revealed halloysite dehydroxylation in metakaolinite followed by the rearrangement of metakaolinite to form mullite and spinel from 900°C. The chemical analysis revealed a high aluminum content (Al₂O₃ = 37.4%) linked to the presence of some aluminous phases (gibbsite and alunite), which reduces slightly the SiO₂/Al₂O₃ ratio.

Regarding to ceramic proprieties, specimens were produced and fired from 500-1100°C in order to appreciate the processing technique in ceramic products from raw halloysite material. An increase in linear shrinkage with great flexural strength was recognized. Given these results, Moroccan
halloysite has good properties for application in the refractory ceramic industry. However, addition of quartz sand fraction is required for avoiding cracks development at firing as well as to reduce the high plastic behaviour of halloysite and minimize its shrinkage during sintering.

REFERENCES


ASTM C326-03, Standard test method for drying and firing shrinkages of ceramic whiteware clays, 15–02, Verre et céramique.


**Figure captions**

FIG. 1. Geographical localization (A) and geological map of the study area indicating the prospected area (B).

FIG. 2. Geological cross-section (A) performed in the Maaza region based on the stratigraphy and lithological description in the field. Cross-section (B) showing sharp lateral and vertical changes in lithology within the area (modified after Hilali & Jeannette (1981)).

FIG. 3. Images illustrate the beveled shape of the various outcrops of studied white clay (halloysite).

FIG. 4. X-ray diffractograms of the studied clay fractions (<2µm) with the three different treatments (N: air dried run; EG: Saturated with ethylene glycol, H: Heated at 500 °C for 4h). A: white clay sample (halloysite); B: red clay sample.
FIG. 5. SEM images of white clay sample showing tubular morphology of halloysite associated with detrital illite. Ilt: illite; Hls: halloysite.

FIG. 6. XRD patterns of white sample in terms of heating temperature evolution up to 1100°C. Ha: halloysite; Aln: alunite; Gbs: gibbsite; Tclay: total clay; Trd: tridymite; Hl: halite; Sa: sanidine; Fl: fluorite; Mul: mullite; Crs: cristobalite; Crn: corundum; Spl: spinel; Hem: hematite. Mineral abbreviations are according to Whitney & Evans (2010).

FIG. 7. Aspect of the halloysite fired product at 1100°C showing some deep cracking features.

FIG. 8. SEM images of halloysite sample showing primary (Mul1) and secondary (Mul2) mullite microstructural features of fired sample after 1100°C.