MINERALOGICAL AND PHYSICOCHEMICAL INVESTIGATION OF Mg-SMECTITE FROM JBEL GHASSOUL, MOROCCO

Abdelaziz Benhammou[1],*, Boumediene Tanouti[2], Lahbib Nibou[1], Abdelrani Yaacoubi[2] and Jean-Pierre Bonnet[3]

[1] Ecole Nationale des Sciences Appliquées, Université Cadi Ayyad, Route Sidi Bouzid, BP 63, Safi, Morocco
[2] Faculté des Sciences Semlalia, Université Cadi Ayyad, Avenue My. Abdellah, BP 2390, Marrakech, Morocco
[3] Groupe d'Etude des Matériaux Hétérogènes, ENSCI, Avenue Albert Thomas, 87065, Limoges Cedex, France

Abstract—'Ghassoul' clay is a Mg-rich clay from Morocco which is of great industrial use and interest, but its characterization is still incomplete. The purpose of this study was to provide further details regarding the structure and characteristics of this important commercial clay mineral. Mineralogical and physicochemical characterizations of the raw form of 'Ghassoul' clay from Jbel Ghassoul in Morocco, and of its <2 μm size fraction, purified and Na$^+$-saturated, were carried out using X-ray diffraction (XRD), X-ray fluorescence (XRF), infrared spectroscopy (IR), and differential and thermogravimetric analysis (DTA/TG). The XRD data revealed that the raw Ghassoul clay consists mainly of a Mg-rich trioctahedral smectite, stevensite, together with quartz and dolomite. The IR spectra consisted of vibrations typical of trioctahedral smectites. The DTA/TG curves were also similar to those of trioctahedral smectites. Chemical analysis confirms that this Mg-rich trioctahedral smectite is a stevensite characterized by a limited isomorphic substitution of Si^{4+} by Al^{3+}. The thermal transformations examined by *in situ* XRD as a function of the firing temperature from 100 to 1200ºC indicated that stevensite was transformed to enstatite (MgSiO$_3$) at temperatures >800ºC and that quartz was transformed to cristobalite when the temperature exceeded 1100ºC. These transformations were irreversible. The specific surface area and cation exchange capacity (CEC) of the 'Ghassoul' clay are 133 m^2/g and 75 meq/100 g, respectively. The main exchangeable cation is Mg^{2+} (53 meq/100 g).

Key Words—Characterization, Ghassoul Clay, Smectite, Stevensite, Morocco.

INTRODUCTION

'Ghassoul' clay (also known as 'Rassoul' or 'Rhasoul') comes from a commercial Moroccan deposit, the only one located to the east of the Middle Atlas Mountains, in the Moulouya Valley, ~200 km from Fes (Figure 1). The deposit has been worked since ancient times, in underground mine galleries. For several centuries, 'Ghassoul' has been used in natural cosmetic products (soap, shampoo, skin conditioner). Currently, it is marketed for its detergent and grease-removing properties. 'Ghassoul' is used as a base ingredient in the fabrication of various dermatological products and anti-acne creams. Its etymology derives from the Arabic verb *Rassala* which means 'to wash.' The Ghassoul deposits are mainly exploited for the export market by the Sefrioui group of the Ghassoul company and its derivatives. According to the first article of the Moroccan Decree nº 2-73-370, dated March 5th, 1974, products can only be marketed under the name 'Ghassoul' if they contain at least 90% w/w of the clay mineral known as stevensite and contain Li (Hectorite). Stevensite belongs to the smectite group of clay minerals

which has a 2:1-type layer structure. The general chemical formula is Mg$_{3-x}$Si$_4$O$_{10}$(OH)$_2$-(M^{y+}.nH$_2$O), where M (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$) represents the interlayer cations which balance the negative charge generated by the isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral sheet.

This Moroccan stevensite has been the subject of several recent studies in order to develop new industrial applications. Nibou *et al*. (2003) were interested in the development of cordierite ceramics from this stevensite and anadalusite. Benhammou *et al*. (2005a, 2005b, 2007) studied the adsorption of heavy metals in aqueous solution on raw and on organic- and inorganic-modified 'Ghassoul.' Lopez-Duran *et al*. (2003) studied the wettability of Ghassoul clay in humic acid. Elmchaouri and Mahboub (2005) studied the synthesis and characterization of Al-pillared stevensite. The geochemical characterization and the origin of the 'Ghassoul' formation were studied by Trauth (1974) and Chahi *et al*. (1993, 1997, 1999). In spite of these studies, this material still suffers from a lack of complete characterization, especially with respect to its behavior upon heating and cooling.

The aim of this work was to use X-ray powder diffraction (XRD), differential thermal and thermal gravimetric analysis (DTA/TG), X-ray fluorescence spectroscopy (XRF), and infrared spectroscopy (IR) to characterize 'Ghassoul' in greater detail, as well as to

* E-mail address of corresponding author:
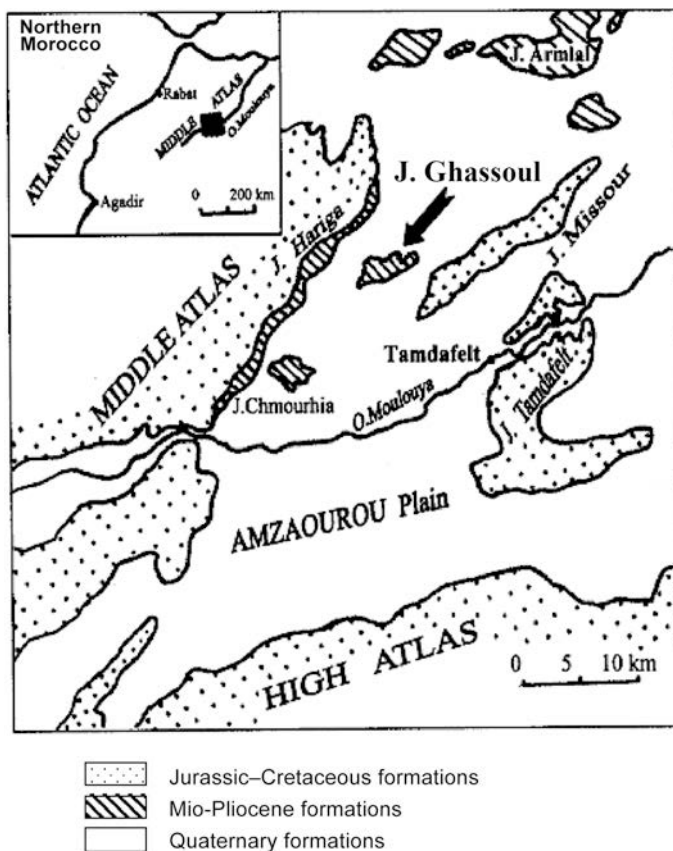Benhammou_ab@yahoo.fr

Figure 1. Location of Jbel Ghassoul in Morocco (Trauth, 1974)

determine its transformation during heating from 100 to 1200ºC and the reversibility after cooling to room temperature. Rehydration of 'Ghassoul' preheated to 250ºC was also investigated.

MATERIALS AND METHODS

The clay was obtained from Jbel Ghassoul in the Middle-Atlas Mountains of Morocco. The <2 μm size fraction was separated by sedimentation. The clay was saturated with Na^+ cations by washing l0 g of clay with 100 mL of 1 M NaCl solution. After centrifugation at 3600 rpm for 15 min (in a centrifuge with a rotor which has a 12 cm radius), the Na^+-saturated clay was washed with distilled water until a negative Cl^- test was obtained using $AgNO_3$. To dissolve carbonates, the Na^+-saturated clay was dispersed in 100 mL of 1 N sodium acetate-acetic acid buffer (pH = 4.8) and stirred. The Na^+-saturated clay was placed in suspension in a series of graduated cylinders and the <2 μm fraction was separated by sedimentation using the Stokes equation. Thereafter, the purified, Na-saturated clay was centrifuged and dried at 100ºC.

Mineralogical identification was performed by XRD using a Siemens D500 diffractometer employing CuKα radiation (λ = 1.5406 Å), with operating conditions of 40 kV and 20 mA. The XRD patterns of the air-dried <2 μm fraction, heated at 250ºC, and saturated with ethylene glycol were obtained over the range 5−60º2θ at a scanning rate of 0.5º2θ s^{-1}. The thermal transformations of clay were carried out by *in situ* XRD as a function of the firing temperature from 100 to 1200ºC in steps of 50ºC. Infrared spectra were recorded between 400 and 4000 cm^{-1} using a Nicolet 205 FTIR spectrometer by summing 32 scans at 2 cm^{-1} resolution. Pellets were prepared by dispersing 2 mg of sample into 198 mg of KBr.

The chemical analysis of 'Ghassoul' and its <2 μm fraction were studied by XRF using a Philips PW 1666 spectrometer using the $LiBO_2$ pellet technique and by GBC 904 flame atomic absorption spectroscopy (AAS). Differential thermal analysis (DTA) and thermo-gravimetric (TG) studies were obtained in air from ambient temperature to 1000ºC at a heating rate of 10ºC min^{-1}, using a STA 1500 microbalance.

The cation exchange capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined using the ammonium acetate method at pH 7 (Standard NFX 31130). The NH_4^+ ion fixed on stevensite was removed by percolation with l M NaCl solution at pH 3.
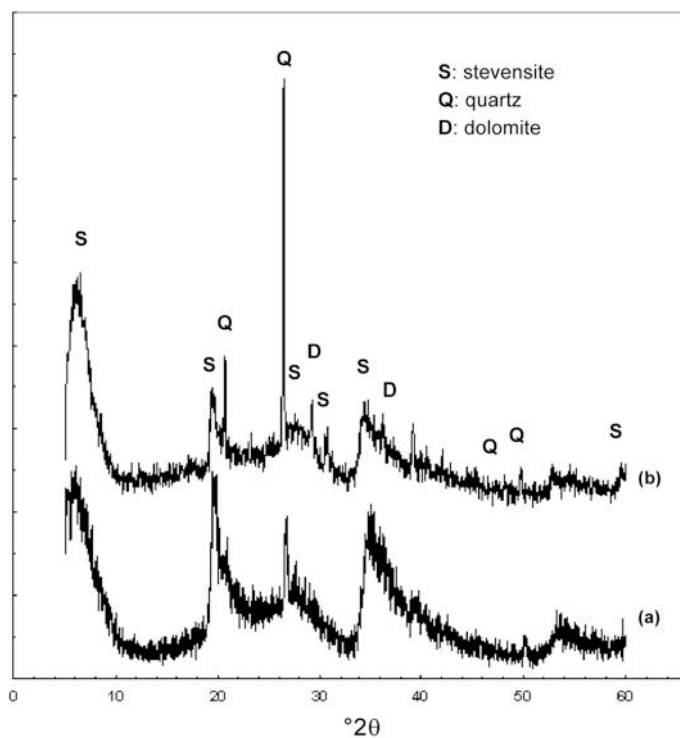
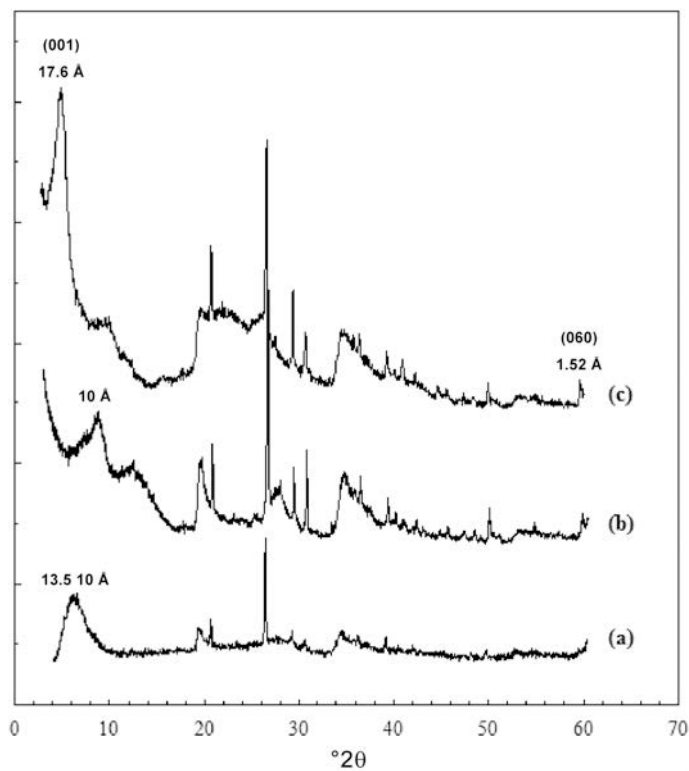Figure 2. XRD patterns of (a) the <2 μm fraction, and (b) of raw 'Ghassoul' clay.

Figure 3. XRD patterns of 'Ghassoul' clay: (a) air-dried; (b) heated at 250ºC; and (c) glycolated.

Table 1. Chemical analysis of the <2 μm fraction of Mg-smectite from Ghassoul, two stevensites, saponite, and hectorite.

	Mg-smectite (this study)	Stevensite — Faust and Murata (1953)	Stevensite — Faust and Murata (1953)	Saponite — Quakernaat (1970)	Hectorite — Faust (1959)
SiO_2	56.53	57.24	57.3	48.96	55.86
Al_2O_3	1.31	trace	trace	7.3	0.13
Fe_2O_3	0.82	1.14	1.14	11.93	0.03
CaO	0.14	0.38	0.97	2.42	trace
MgO	24.73	27.89	27.87	23.39	25.03
K_2O	0.32	—	0.03	0.06	0.10
Na_2O	1.35	—	0.03	0.04	2.68
Li_2O	—	—	—	—	1.05
F	—	—	—	—	5.96
LOI*	12.25	13.80	13.80	12.25	15.17
Total	97.49	100.19	100.19	97.49	102.98

*LOI: loss on ignition (1000ºC)

The exchangeable cations were analyzed by AAS. Nessler reagents were used to measure NH_4^+ with a GBC 911 UV-VIS spectrophotometer at 420 nm. The results were evaluated after two similar experiments and were compared to a blank test.

RESULTS AND DISCUSSION

The XRD patterns of raw 'Ghassoul' (Figure 2a) contained a strong peak at 14.73 Å (5.99º2θ), indicating that raw 'Ghassoul' consists mainly of phyllosilicates. The peaks at 3.37 Å (26.39º2θ) and 2.91 Å (30.65º2θ) also suggest the presence of quartz and dolomite, respectively. The XRD patterns of the <2 μm Na⁺-saturated fraction (Figure 2b) show a significant reduction in the character-istic peaks of the quartz and the characteristic peaks of the dolomite disappeared altogether.

Treatment with ethylene glycol and heating at 250ºC caused the basal (001) reflection to move from 13.5 to 17.6 Å and 10 Å, respectively, indicating that it is a swellable 2:1 clay, similar to that of the smectite group (Figure 3). The 060 reflection observed at 1.524 Å (60.7º2θ) places it in the trioctahedral smectite category. Given its large Mg content, insignificant Al, Li, Zn, and F contents, and absence of tetrahedral substitution, 'Ghassoul' is classified as stevensite rather than as saponite (Mg-rich, but beidellitic), hectorite (Li-rich, sometimes with F), or sauconite (Zn-rich) (Faust *et al*., 1953). This classification is further supported by compar-ing results obtained from chemical analysis of the <2 μm
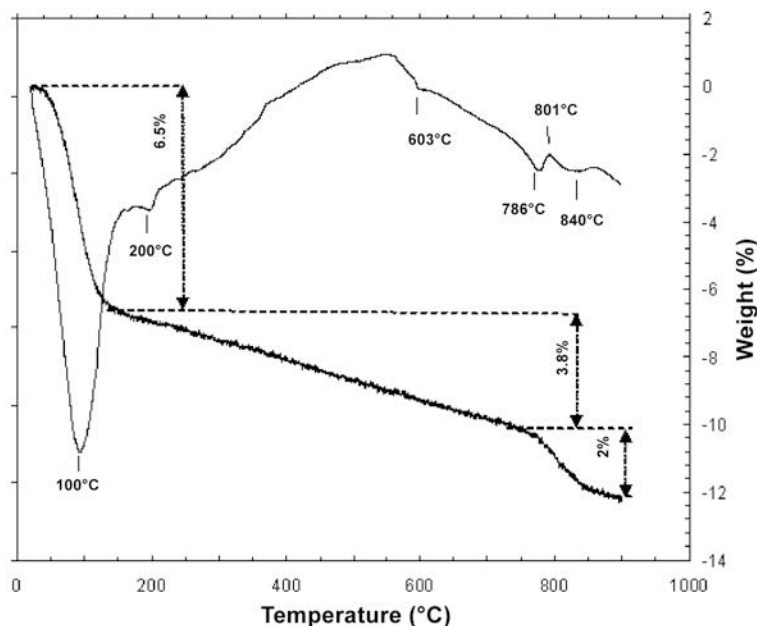

Figure 4. DTA and TG curves of the <2 μm fraction of 'Ghassoul' clay.

Table 2. CEC of the <2 μm fraction of Mg-smectite from Ghassoul, stevensite, and hectorite.

Minerals	CEC (meq/100 g)
Mg-smectite, Ghassoul (this study)	75.1
Hectorite, California (Faust and Murata, 1953)	60.8
Stevensite, Patterson, New Jersey (Faust and Murata, 1953)	37.6
Exchangeable cations (this study)	
Ca^{2+}	7.10
Mg^{2+}	53.31
Na^+	12.14
K^+	1.56

Figure 5. Rate of hydration of 'Ghassoul' clay (dried at 250ºC) at RH of 60%.

fraction using XRF with selected analyses from the literature of the Mg-rich smectites (Table 1). The comparison confirmed that 'Ghassoul' is rich in Mg (25.03 wt.%) and has a smaller Al_2O_3 (1.31 wt.%) content than saponite. The chemical composition agrees closely with that of stevensite given by Faust and Murata (1953). Stevensite differs from saponite in that it contains less Al and from hectorite in that it contains less Li and F.

The specific surface area and particle density of the 'Ghassoul' clay are 133 m^2/g and 2.24 g/cm^3, respectively. The exchangeable cations observed were Ca^{2+}, Mg^{2+}, Na^+, and K^+ (Table 2) and the total CEC was 75.1 meq/100 g (Table 2). The CEC is a significantly large value compared to the values for natural stevensite, reported by Faust and Murata (1953) and Takahashi *et al.* (1997) to be 37.6 and 41 meq/l00 g, respectively. The most abundant exchangeable cation is Mg^{2+}
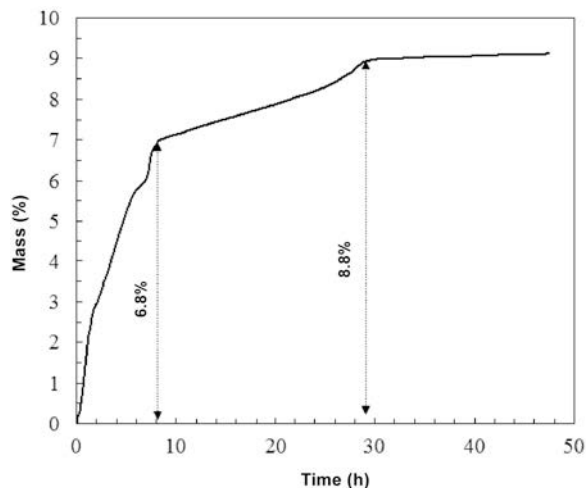
(53.3 meq/l00 g), in agreement with the results of Faust *et al.* (1959).

The DTA/TG patterns of the <2 μm fraction of the 'Ghassoul' clay consisted of four endothermic peaks (Figure 4). The first intense peak occurred at ~100ºC and is attributed to the dehydration of adsorbed water and hydrated cations such as Na^+ in the interlayer. The weight loss is ~6.5%. The second and the third endothermic peaks occurred at ~600ºC and 786ºC, respectively, and correspond to the dehydroxylation of structural OH. The weight loss observed between 200 and 800ºC is ~3.8%. The final endothermic peak appeared at ~840ºC with a corresponding weight loss of ~2%. The weak exothermic peaks at ~801ºC may be due to crystallization of Mg-smectite at high temperature. As reported by Shimoda (1971), the phase transformation of stevensite to enstatite
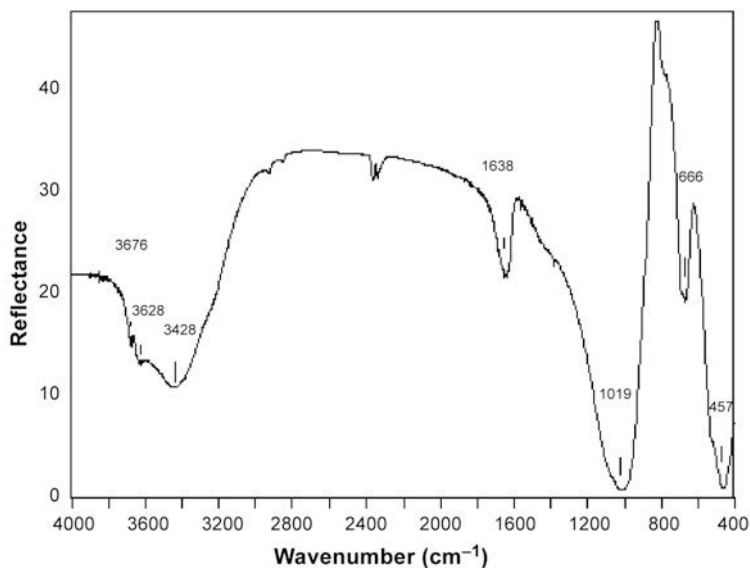

Figure 6. FTIR spectrum of the <2 μm fraction of 'Ghassoul' clay.

Table 3. IR absorption band positions of the <2 μm fraction of Mg-smectite from Ghassoul and of saponite, hectorite, and stevensite (Shimoda, 1971).

Frequency (cm^{-1})			
Saponite	Hectorite	Stevensite	This study
3680	3690	3685	3676
3630	3640	3630	3628
3400	3450	3435	3428
2355	—	—	2380
—	—	—	2342
1630	1645	1630	1638
1004	1010	1010	1019
655	665	670	666
463	463	450	457

(MgSiO$_3$) occurred at >800ºC. The results of thermal analyses are similar to those of the trioctahedral smectites: stevensite, saponite, or hectorite (Faust and Murata, 1953).

To control the reversibility of the dehydratation, a sample of 'Ghassoul' clay previously heated at 250ºC for 24 h was subjected to a hydration treatment at 25ºC under relative humidity (RH) of 60%. The evolution of sample weight *vs.* time (Figure 5) revealed a three-stage process: (1) a very fast increase in weight during the first

8 h (6.8% of the dried sample); (2) a second stage (8−30 h) during which the hydration rate was significantly slower and constant and the weight increase by the end of this stage represented 8.8% of the dried sample weight; and (3) a very slow hydration.

The IR spectra of the <2 μm fraction of the 'Ghassoul' clay in the range 400−4000 cm^{-1} (Figure 6) were compared (Table 3) with the absorption bands of stevensite, saponite, and hectorite (Shimoda, 1971). The IR data show intense OH-stretching bands due to hydroxyl groups and adsorbed H$_2$O molecules, indicating a large amount of H$_2$O associated with the structure, as is typical for minerals of the smectite group. The absorption band at ~3676 cm^{-1} is attributed to vibrations of structural OH groups in a trioctahedral (Mg)$_3$OH (Brindley *et al.*, 1979). The bands at 3628 and 3428 cm^{-1} are attributed to the OH-stretching vibrations of interlayer and hygroscopic H$_2$O, respectively. The strong band near 1638 cm^{-1} corresponds to the bending vibration of adsorbed atmospheric H$_2$O molecules. Brindley *et al.* (1979) observed that the intensity of this band decreased for kerolite heated at 500ºC, indicating that the molecules of water from the interlayer spaces were removed. In the lower-frequency region from 400 to 1200ºC, the intense bands near 1020 cm^{-1} are probably due to Si−O stretching bands in the
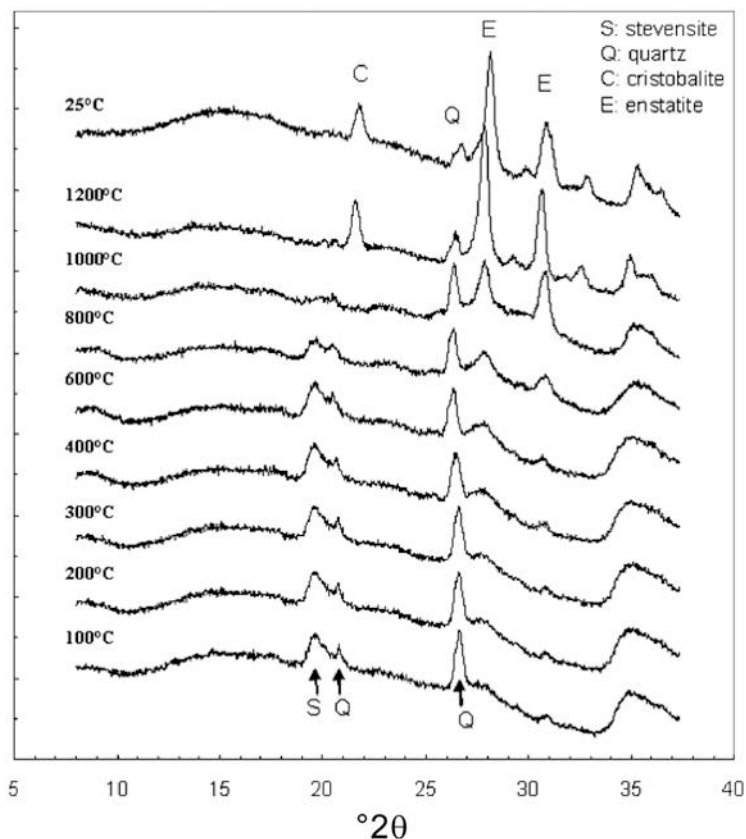

Figure 7. *In situ* XRD patterns of 'Ghassoul' clay heated at different temperatures.

tetrahedral sheet. The absorption bands at 457 and 666 cm^{-1}, corresponding to a vibrational frequency of Si-O-Mg, are related to Mg in the octahedral sheet. The band at 666 cm^{-1} is characteristic of the trioctahedral smectites (Brindley *et al.*, 1979). The bands in the frequency range (600–700 cm^{-1}) are characteristic of the trioctahedral smectites (Parthasarathy *et al.*, 2003).

In situ XRD experiments of the 'Ghassoul' clay dehydrated at 250ºC were investigated at temperatures between 100 and 1200ºC to provide information on the transformation phases that develop during firing (Figure 7). During heating, stevensite disappeared and enstatite (MgSiO$_3$) and cristobalite were formed. The cooling from 1200ºC to room temperature failed to modify the XRD patterns, implying that the structural transformations were irreversible. The first peak characteristic of enstatite (28º2θ) appeared at 400ºC. This intensity increased continuously during the heat treatment. The second peak (at 31º2θ) was detected at 900ºC. The transformation phase of the stevensite to the enstatite can be explained by the exothermic peak, observed by differential thermal analysis, at 840ºC which was attributed to the crystallization of anhydrous silicate. This transformation can be represented by the following reaction (Khassin *et al.*, 2001):

$$Mg_3Si_4O_{10}(OH)_2.n(H_2O) \xrightarrow{\text{Exothermic}}$$
$$\tfrac{3}{2}(MgSiO_2 + MgO) + \tfrac{5}{2}SiO_2 + (n+l)H_2O$$
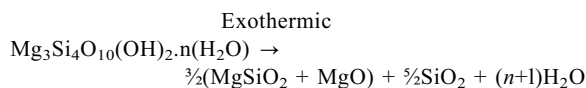
CONCLUSION

Characterization of 'Ghassoul' clay from the Jbel Ghassoul Mountains was achieved by means of several analytical techniques. X-ray diffraction indicated that the natural 'Ghassoul' clay consists mainly of Mg-rich trioctahedral smectite with the presence of impurities such as quartz and dolomite. Given the small amount of Al$_2$O$_3$ (1.31 wt.%), the chemical composition of the <2 μm fraction agrees with that of stevensite, characterized by a weak isomorphous substitution of Si^{4+} by Al^{3+}.

The exothermic peak observed at 801ºC by DTA can be explained by crystallization of the stevensite and this was confirmed by *in situ* XRD which showed the irreversible transformation of the stevensite to enstatite (MgSiO$_3$) at >800ºC. The study of hydration of stevensite previously heated at 250ºC showed that the dehydration determined by TG is reversible. The CEC and the specific surface area are 75 meq/100 g and 133 m^2/g, respectively, and the main exchangeable cation is Mg^{2+} (53 meq/100 g).

ACKNOWLEDGMENTS

REFERENCES

Benhammou, A., Yaacoubi, A., Nibou, L., and Tanouti, B. (2005a) Adsorption of metal ions onto Moroccan stevensite: kinetics and isotherm studies. *Journal of Colloid and Interface Science*, **282**, 320–326.

Benhammou, A., Yaacoubi, A., Nibou, L., and Tanouti, B. (2005b) Study of the removal of mercury(II) and chromium(VI) from aqueous solutions by Moroccan stevensite. *Hazardous Materials*, **B117**, 243–249.

Benhammou, A., Yaacoubi, A., Nibou, L., and Tanouti, B. (2007) Chromium(VI) adsorption from aqueous solution onto Moroccan Al-pillared and cationic surfactant stevensite. *Hazardous Materials*, **140**, 104–109.

Brindley, G.W. (1955) Stevensite, a montmorillonite-type mineral showing mixed-layer characteristics. *American Mineralogist*, **40**, 239–247.

Brindley, G.W., Bish, D.L., and Wan, H.M. (1979) Compositions, structures, and properties of nickel-containing minerals in kerolite-pimelite series. *American Mineralogist*, **64**, 615–625.

Chahi, A., Duplay, J., and Lucas, J. (1993) Analyses of palygorskites and associated clays from the Jbel Rhassoul (Morocco): chemical characteristics and origin of formation. *Clays and Clay Minerals*, **41**, 401–411.

Chahi, A., Fritz, B., Duplay, J., Weber, F., and Lucas, J. (1997) Textural transition and genetic relationship between precursor stevensite and sepiolite in lacustrine sediments of the Jbel Rhassoul (Morocco). *Clays and Clay Minerals*, **45**, 378–389.

Chahi, A., Duringer, Ph., Ais, M., Bouabdelli, M., Guathier, F., and Fritz, B. (1999) Diagenetic transformation of dolomite into stevensite in lacustrine sediments from Jbel Rhassoul, Morocco. *Sedimentary Research*, **69** 1125–1135.

Elmchaouri, A. and Mahboub, R. (2005) Effects of preadsorption of organic amine on Al-PILCs structures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **259,** 135–141.

Faust, G.T. and Murata, K.J. (1953) Stevensite, redefined as a member of the montmorillonite group. *American Mineralogist*, **38**, 973–987

Lopez-Duran, J.D.G., Khaldoun, A., Kerkeb, M.L., Ramos-Tejada, M., and González-Caballero, F. (2003) Wettability of montmorillonite clays in humic acid solutions. *Clays and Clay Minerals*, **51**, 65–74.

Nibou, L., Benhammou, A., Yaacoubi, A., Bonnet, J-P., and Tanouti, B. (2003) Synthèse et caractérisation de céramiques de cordiérite obtenues à partir du Rhassoul. *Annales de Chimie Science des Matériaux*, **28**, 83–90.

Parthasarathy, G., Choudary, B.M., Sreedhar, B., Kunwar, A.C., and Srinivasan, R. (2003) Ferrous saponite from the Deccan Trap, India, and its application in adsorption and reduction of hexavalent chromium. *American Mineralogist*, **88**, 1983–1988.

Quakernaat, J. (1970) A new occurrence of a macrocrystalline form of saponite. *Clay Minerals*, **8**, 491–493.

Shimoda, S. (1971) Mineralogical studies of a species of stevensite from the Obori mine, Yamagata prefecture, Japan. *Clay Minerals*, **9**, 185–192

Trauth, N. (1974) Argiles évaporitiques dans la sédimentation carbonatée continentale tertiaire, Bassin de Paris, de Mormoiron et de Salinelles (France), Jbel Ghassoul (Maroc). Thesis, Univ. Strasbourg, France, 309 pp.