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Eprints ID: 3976

**To link to this article:** DOI: 10.1180/claymin.2008.043.3.05  
URL: <http://dx.doi.org/10.1180/claymin.2008.043.3.05>

To cite this version: RHOUTA, B. and KADDAMI, H. and ELBARQY, J. and AMJOURD, M. and DAOUDI, L. and Maury, Francis and Senocq, François and MAAZOUZ, A. and GERARD, J . - F . ( 2008) *Elucidating the crystal-chemistry of Jbel Rhassoul stevensite (Morocco) by advanced analytical techniques*. Clay Minerals, vol. 43. pp. 393-404. ISSN 1471-8030

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# Elucidating the crystal-chemistry of Jbel Rhassoul stevensite (Morocco) by advanced analytical techniques

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**ABSTRACT:** The composition of Rhassoul clay is controversial regarding the nature of the pure-mineral clay fraction which is claimed to be stevensite rather than saponite. In this study, the raw and mineral fractions were characterized using various techniques including Fourier transform infrared spectroscopy and magic angle spinning nuclear magnetic resonance (MAS NMR). The isolated fine clay mineral fraction contained a larger amount of Al (>1 wt.%) than that reported for other stevensite occurrences. The <sup>27</sup>Al MAS NMR technique confirmed that the mineral is stevensite in which the Al is equally split between the tetrahedral and octahedral coordination sites. The <sup>29</sup>Si NMR spectrum showed a single unresolved resonance indicating little or no short-range ordering of silicon. The chemical composition of the stevensite from Jbel Rhassoul was determined to be ((Na<sub>0.25</sub>K<sub>0.20</sub>)(Mg<sub>5.04</sub>Al<sub>0.37</sub>Fe<sub>0.20</sub>□<sub>0.21</sub>)<sub>5.61</sub>(Si<sub>7.76</sub>Al<sub>0.24</sub>)<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>). This formula differs from previous compositions described from this locality and shows it to be an Al-bearing lacustrine clay mineral.

**KEYWORDS:** Rhassoul, stevensite, structural characterization, structural composition, vacancies, short-range ordering, FTIR, MAS NMR.

The mined deposit of the Rhassoul clay, exploited in the Tertiary lacustrine basin of the Jbel Rhassoul in Morocco, is globally unique (Millot, 1954; Barrakad, 1981). It lies within a Miocene marly-dolomitic, gypsum-rich unit (Benammi & Jeager, 1995). The clay was first described by Dammour (1843) who also analysed its chemical composition. The dominant clay mineral was first named rhassoulite, in reference to the Rhassoul deposit

locality (Millot, 1954; Faust *et al.*, 1959). Further mineralogical study by Caillere & Henin (1956) and Fleischer (1955) subsequently identified the mineral as stevensite.

Most studies devoted to the Rhassoul clay deposit have dealt with its genesis and geological characteristics. Several mechanisms have been proposed to explain its origin. Some studies suggested that it originated from the alteration of the unstable volcanic ash dispersed in the lacustrine environment (Jeannette, 1952). Other authors favoured a neoformation mechanism in a confined environment (Trauth, 1977; Ais, 1984; Chahi, 1992; Durringer *et al.*, 1995). More recently, Chahi *et al.* (1999)

proposed that the stevensite resulted from diagenetic transformation of sedimentary lacustrine dolomite. During this transformation, the authors suggested that dissolution of Al-Fe-bearing minerals, namely illite, chlorite and palygorskite, released Al and Fe which were incorporated into the stevensite structure.

With respect to the typical well studied stevensite occurring elsewhere (Springfield, New Jersey, USA; Prócida Island, Italy), the composition of the stevensite from Jbel Rhassoul has been suggested to have a particularly large Al content as documented by Trauth (1974; wt.%  $\text{Al}_2\text{O}_3 = 2.1$ ), Chahi *et al.* (1993; wt.%  $\text{Al}_2\text{O}_3 = 1.7$ ) and Benhammou (2005) and Benhammou *et al.* (2005a,b) (wt.%  $\text{Al}_2\text{O}_3 = 2.24$ ). The Moroccan official bulletin (No. 3202; March 1974) defined Rhassoul clay as any product made up of 90% of stevensite and whose  $\text{Al}_2\text{O}_3$  percentage could reach 5 wt.%. These levels of Al exceed the amount that stevensite should contain by 1 wt.% (Capet, 1990).

According to Chahi *et al.* (1999), the abundance of associated Al-Fe-bearing accessory minerals aids the identification of the clay fraction composition as stevensite, Mg-saponite or Al-saponite, as proposed earlier by Trauth (1974). The stevensite and saponite clay minerals have characteristics so close that ambiguity might arise when identifying a sample taken from the Jbel Rhassoul. Moreover, several structural formulae have been proposed for the stevensite of the Jbel Rhassoul, which are different from the typical stevensite formula:  $\text{CEMg}_{\leq 3}\text{Si}_4\text{O}_{10}(\text{OH})_2$  (where CE designates cation exchange) (Velde, 1995; Caillère *et al.*, 1982). Chahi *et al.* (1999) proposed a formula in which Al simultaneously has a fourfold and octahedral coordination ( $\text{Si}_{3.95}\text{Al}_{0.05})(\text{Mg}_{2.74}\text{Al}_{0.07}\text{Fe}_{0.04}\text{Li}_{0.09})(\text{Ca}_{0.02}\text{Na}_{0.02}\text{K}_{0.03})\text{O}_{10}(\text{OH})_2$  whereas Benhamou *et al.* (2005, 2006) more recently reported a formula in which Al is only octahedrally coordinated ( $\text{Si}_{3.78}\text{Al}_{0.22}\text{Mg}_{2.92}\text{Fe}_{0.09}\text{Na}_{0.08}\text{K}_{0.08}\text{O}_{10}(\text{OH})_2$ ). Both these formulae were proposed without precisely knowing the Al coordination.

$^{27}\text{Al}$  and  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy constitutes an invaluable tool for distinguishing tetrahedral and octahedral Al environments, identifying short-range order and crystallographically detecting non-equivalent Si sites (Komarneni *et al.*, 1986). Furthermore, the Fourier transform infrared (FTIR) analysis carried out on heat-treated samples would help distinguish saponite

from stevensite (Parthasarathy, 2003). To our knowledge, neither MAS NMR nor FTIR analysis on heat-treatment samples have been used to study the clay fraction of the Rhassoul clay. Therefore, the aim of this work was to determine more precisely the crystal-chemistry of the principal clay mineral in the 2  $\mu\text{m}$  size fraction of this Moroccan clay deposit, using these advanced physicochemical characterization techniques.

## GEOLOGICAL SETTING AND CONTEXT

The Rhassoul deposit is located at the south-eastern border of the Tertiary basin of Missour. This basin constitutes the south-east extremity of the eastern Meseta, which is enclosed by the High Atlas mountains in the south, the Middle Atlas mountains to the west and north-west and the limestone plateau of Rekkane to the east (Fig. 1).

The basin development started at the superior Cretaceous formation and continued throughout the Cenozoic until it was halted by the thorough structural discrimination of units of the Atlas



FIG. 1. Geographic and geological map of Jbel Rhassoul, Morocco.

mountain chains (High and Middle ranges) and the limestone plateau of Rekkane (Jeannette, 1952). The rising of the Atlas ranges resulted in the creation of an intra-mountainous basin which collected continental sedimentation, of which mainly arose from the Jurassic-Cretaceous hinterland of the High and Middle Atlas ranges.

The Tertiary deposits are dominated by a very important conglomeratic formation along the basin margin; this facies passes within a few kilometres of marly-carbonate and marly-gypsiferous deposits. The Rhassoul deposit belongs to the marly carbonate facies. From a stratigraphic point of view, the most recent work on the Rhassoul formation assigned it to the Serravalian-Tortonian period of the Miocene (Benammi & Jeager, 1995), and indicated a sedimentation extent of almost 10 Ma.

The stevensite content varies independently of the dominance of laminated limestone, marl or gypsum. This general independence, combined with the apparent absence of any burial-depth control on stevensite abundance, suggests that the mineral formation and evolution are not noticeably controlled by post-sedimentary processes. Furthermore, because of the secondary gypsum which is omnipresent in the clay deposit, the Rhassoul has been previously considered to be an authigenic stevensite formed contemporaneously in a closed evaporitic gypsum-rich basin (Trauth, 1977; Duringer *et al.*, 1995).

## EXPERIMENTAL

The clay was crushed and sieved through a 50  $\mu\text{m}$  filter to obtain material of a uniform size. Thereafter, 20 g of clay powder was dispersed in 200 ml of de-ionised water and slowly mixed with 0.4 moles of NaCl dissolved in 200 ml of de-ionised water to exchange interlayer cations for  $\text{Na}^+$ . The saturation of the clay interlayer space by monovalent cations, especially  $\text{Na}^+$ , improved the aqueous dispersion of the clay after removal of the excess salt. According to the Hardy rule (Briant, 1989), the  $\text{Na}^+$  counter-ions form a thick diffuse layer around the negative surface of the clay platelets so that repulsion forces between particles are predominant and, according to DLVO theory, leads to the stabilization of argillaceous particles (Jolivet, 1994). These effects are considered to significantly aid separation of a purer <2  $\mu\text{m}$ -size clay mineral fraction (composed of Na-clay) by sedimentation. For ensuring effective cation-

exchange, the clay dispersion in electrolyte solution was stirred continuously for 24 h. Afterwards, the supernatant was discarded and the recovered solid added to a renewed salt electrolyte solution. The operation was repeated four times to attain complete Na-exchange. To remove excess salt and enhance dispersion of the clay, the clay slurry was repeatedly washed with deionized water and centrifuged at 2500 rpm for 3 min until the supernatant in the centrifuge vial appeared cloudy and free from chlorides (confirmed by  $\text{AgNO}_3$  test). To separate the fine fraction (particle size 2  $\mu\text{m}$ ), a suspension of 9 wt.%  $\text{Na}^+$  ion-exchanged washed clayey material was stirred and placed in a gradual glass tube to allow the 2  $\mu\text{m}$  particles to settle according to Stokes' law (Holtzapffel, 1985):

$$t = 190 \cdot x/d^2$$

where  $t$ : time (min),  $x$ : depth (cm),  $d$ : particle size ( $\mu\text{m}$ ).

This operation was repeated several times until the suspension was almost transparent. The remaining <2- $\mu\text{m}$  fine-clay mineral fraction (designated as Na-clay) was recovered by centrifugation at 3500 rpm for 40 min and then washed with distilled water before being air-dried.

The chemical composition of the untreated clay sample and the Na-clay separates was determined by inductively coupled plasma mass spectrometry (ICP-MS). The clay samples were heated to 800°C for one night prior to analysis to dehydrate the samples (Rautureau *et al.*, 2004). The cationic exchange capacity (CEC) of the separated Na-clay fraction was determined using a copper ethylenediamine complex according to the method described by Bergaya & Vayer (1997).

To identify the nature of mineral phases present, both raw clay as well and Na-clay separates were characterized by X-ray diffraction (XRD), measuring between 2° and 30°2 $\theta$  using a Philips diffractometer ( $\lambda = 1.5418 \text{ \AA}$ ). In order to maximize the intensity of the basal reflections ( $d_{001}$ ) of the main characteristic clay mineral, well-oriented samples were prepared by a wet-clay-cake method which involves repeated smearing of the clay film into the grooves of flat quartz plates to obtain a lamellar orientation (Holptzfell, 1985). Differential thermal analysis (DTA) and thermo-gravimetric (TG) studies were performed using Labsys apparatus (Setaram) with 60 mg of clay powder analysed at temperatures ranging from 300 K to 1273 K with a heating rate of 10 K/min. The FTIR

studies were performed using a Nicolet device under ambient conditions by scanning KBr pellets in the range 4000–400  $\text{cm}^{-1}$ . A JEOL scanning electron microscope (SEM) equipped with X-ray energy dispersion (EDX) was used for characterizing clay particles and performing local elemental analysis. Solid-state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra at room temperature were collected using a Bruker Advance 500 spectrometer equipped with a 4 mm cross polarization magic angle spinning (CPMAS) probe fitted with a standard spinning assembly.  $^{27}\text{Al}$  MAS NMR spectra were obtained at 130.32 MHz while  $^{29}\text{Si}$  MAS NMR spectra were

recorded at 99.36 MHz.  $^{27}\text{Al}$  chemical shifts were recorded with respect to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  as an external reference and  $^{29}\text{Si}$  chemical shifts were obtained with reference to tetramethylsilane (TMS) as an external standard ( $\delta_{\text{TMS}} = 0$  ppm).

## RESULTS AND DISCUSSION

### *XRD analysis*

The XRD patterns of untreated samples and the Na-saturated clay fractions prepared as textured smears are presented in Fig. 2a. The reflections of

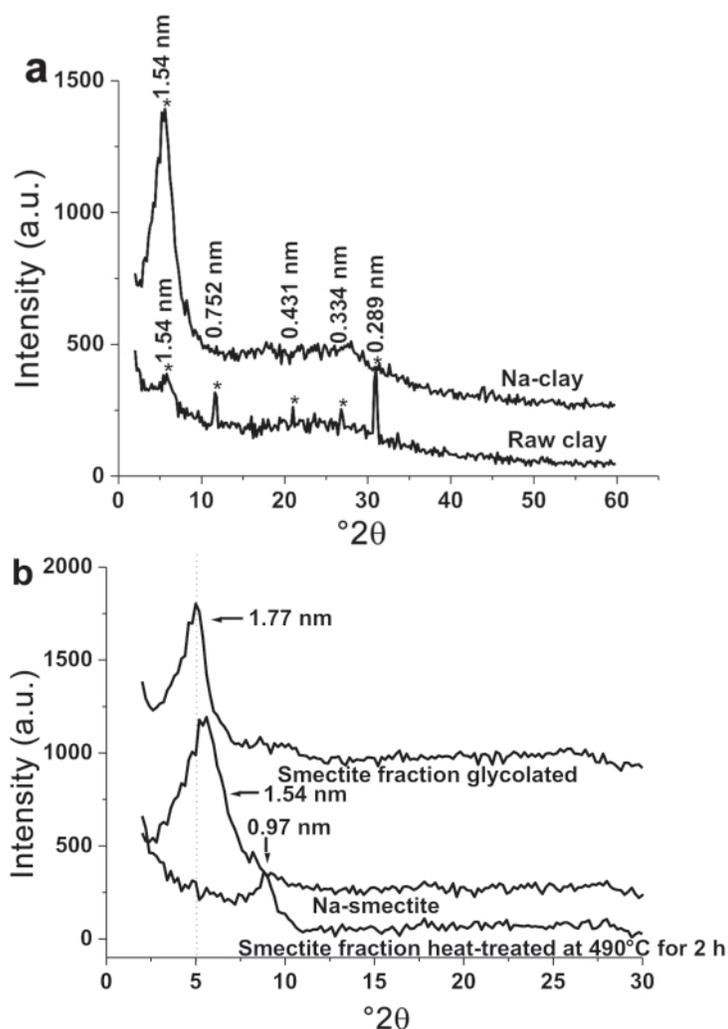


FIG. 2. XRD diagrams of (a) the raw clay sample and the separated fine clay fraction and (b) the effects of sample treatments on the interlamellar distance of the smectite mineral.

TABLE 1. Chemical composition of the Rhassoul clay and its fine mineral fraction.

Sample	Raw clay	— Na-clay —	
Oxides	Weight (wt.%)	Weight (wt.%)	Cations (22 O atoms)
SiO <sub>2</sub>	53.64	61.17	7.76
Al <sub>2</sub> O <sub>3</sub>	3.44	4.29	0.61
Fe <sub>2</sub> O <sub>3</sub>	1.64	2.18	0.20
Na <sub>2</sub> O	1.13	1.07	0.25
CaO	12.73	2.21	0
MgO	23.85	26.65	5.04
K <sub>2</sub> O	0.98	1.23	0.20
Total	97.41	98.8	14.42

the raw powder can be ascribed to the presence of a single smectite mineral phase (1.54 nm), quartz (0.431 nm and 0.334 nm) and dolomite (0.752 nm and 0.289 nm). The clay mineral reflection is notably broad, indicating a small crystallite size and/or a mixture of different water layer thicknesses where the two-water-layer structures appear to dominate. Dolomite appears to be the most abundant accessory phase (total carbonate amount assessed by Bertrand calcimetry method to be ~5%) but is not detectable in the purified Na-saturated clay fraction (no carbonate detected also by calcimetry). Saturation of the smectite with Na intensified the basal peak while its position remained unchanged. To identify the nature of the clay mineral, oriented flat plates were prepared from the fine fraction by being either glycolated or heated at 490°C for 2 h before XRD analysis. The corresponding XRD patterns presented in Fig. 2b show ethylene glycol treatment of the bulk clay material led to an increase of the basal interlayer spacing from 1.54 nm to 1.77 nm. Also, heat treatment of the Na-smectite separates induced significant interlayer collapse during dehydration, resulting in a shift of the interlayer space  $d_{001}$  from 1.54 to 0.97 nm. Similar values were reported by Holtzapffel (1985) for smectite in general and by Benhamou (2005) for the stevensite variety.

The degree of collapse (~0.57 nm) confirms the presence of the two water layers (Fripiat *et al.*, 1982), knowing that each water layer of Na<sup>+</sup> cations induces an interlayer-space increase space of ~0.26 nm (Velde, 1995). The XRD analysis of the randomly-oriented air-dried Na-clay sample has a  $d_{060}$  reflection at 0.1518 nm (Fig. 3), and thus

yields a  $b$  value of 0.9106 nm. This is indicative of a trioctahedral smectite (Güven, 1988) and is in good agreement with that reported for stevensite ( $b = 0.9108$  nm, Brindley and Brown, 1980). This reflection has a smaller  $d_{060}$  value than some other stevensite occurrences (0.1526 nm) or the ideal 2:1 talc structure (0.1527 nm) suggestive of a greater amount of octahedral vacancies (Jacobs *et al.*, 1996).

#### Thermal analysis

Figure 4 shows TG-DTA thermograms for both bulk and Na-saturated clay separates. In both cases, a clear endothermic effect is observed between 100 and 200°C associated with an interlayer weight loss of ~4% for the bulk clay and 6% for the pure Na-clay fraction. Two endothermic peaks recognised in the bulk sample at ~102°C and 140°C are associated with weight losses of approximately -2.6 wt.% and -1.4 wt.%, respectively. The higher temperature shoulder probably corresponds to the dehydration of divalent ions (Caillère & Hanin, 1982) and indicates the presence of various compensating cations (Caillère *et al.*, 1982). In contrast, the single lower temperature endothermic peak, observed at ~90°C in the case of Na-clay, reflects a very homogeneous monovalent state and confirms the complete saturation of the fine clay mineral fraction by Na<sup>+</sup>.

Another distinct endothermic peak occurs at 730°C, with a corresponding weight loss of ~10.3% for the bulk clay sample and 2.4% for the Na-clay fraction. In general, the endothermic effect registered in this temperature range can be attributed to the loss of crystalline water during dehydroxylation of the smectite (Mackenzie, 1972). However, the large weight loss value for the

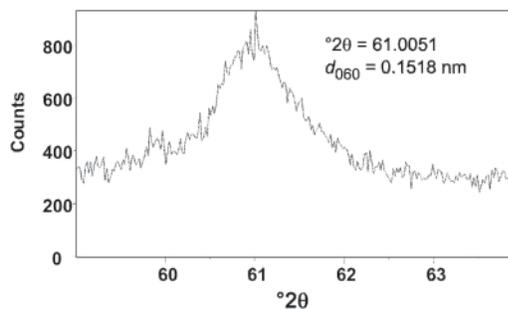


FIG. 3. Powder XRD diagram of Na-clay separates in the [59°–64°] 2θ range.

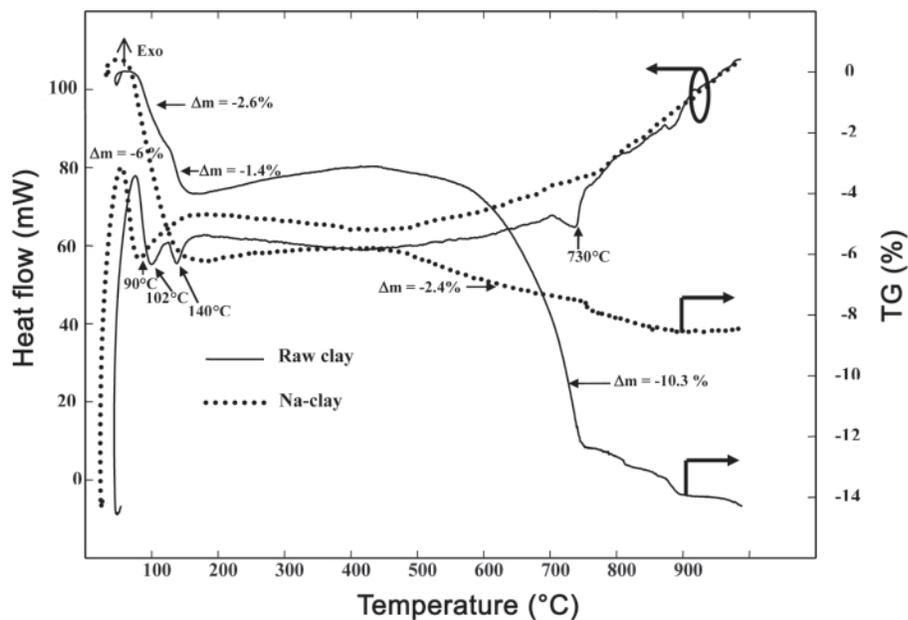


FIG. 4. TG-ATD thermograms of the raw clay and Na-clay samples.

untreated bulk material indicates some carbonate (dolomite) decomposition in this sample. The absence of a second clear endothermic peak below 1000°C is considered more characteristic of stevensite than saponite (Mackenzie, 1972; Capet, 1990). Mg-rich saponite, for example, is distinguished by the presence of a second endothermic peak at ~800–900°C (Capet, 1990).

#### Microstructural characterization

The SEM micrographs, as well as EDX analysis results for the bulk clay sample, are presented in Figs 5 and 6. In the natural clay sample the particles have an automorphous, petalloid-like microstructure typical of smectite clay (Chamely, 1989; Keller, 1985; Wilson & Pittman, 1977). Petals are either present in the form of planar flakes or exhibit folded edges to produce a flower-like structure (Figs 5a and b). The most salient feature is the occurrence of short bristled fibres occurring along the peripheries of flatter stevensite particles (Fig. 6). Owing to their rounded oval shapes, these elongated particles look like bacteria. Nevertheless, they also appear to have formed by substrate growth on the surfaces of stevensite particles and appear to be enriched in Mg (18.8 wt.%) compared to the bulk composition of

the petalloid structures (16.2 wt.%). This last hypothesis suggests a possible transition from stevensite to more Mg-rich varieties of fibrous clay minerals, such as sepiolite and/or palygorskite. This new phase wasn't observed in the XRD patterns (Fig. 3), probably because of the small amounts present are below the detection limit of XRD analysis. Such a transition is similar to that reported by several authors where sepiolite crystallizes on a stevensite substrate or palygorskite on magnesian smectite (Trauth, 1977; Chahi, 1996; Chahi *et al.*, 1993,1997; Daoudi, 1996).

Figure 7 shows examples of the shapes of the Na-saturated clay separates where the particles appear more irregular as a result of NaCl saturation. Likewise, the fibres seem to be fragile towards these treatments and are not observed in the fine Na-clay fraction (Pletsch, 1996; Daoudi, 2004) (Fig. 7). Conversely, by assuming these fibres to correspond to bacteria, their disappearance in Na-clay fraction, despite their small size, could be due to their inability to survive in the salt solution. So, as EDX analysis isn't a sufficiently reliable quantitative technique to accurately identify the nature of these fibres, more advanced characterizations should be carried out using, for instance, scanning transmission electron microscopy (STEM), especially in micro-diffraction mode.

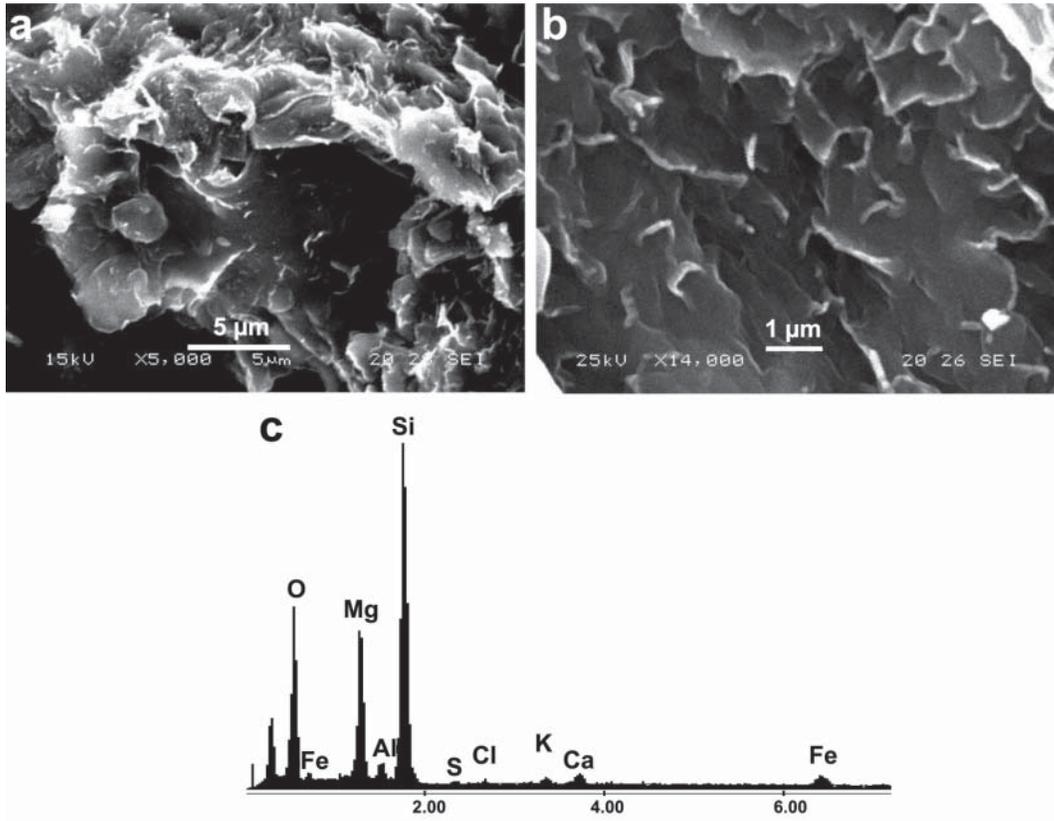


FIG. 5. SEM micrographs and EDX analysis of smectite particles in the raw-clay automorphous petalloid-like microstructure. (a) Folded edge petals forming flower like structure; (b) Petals gathered in the form of flakes; and (c) EDX analysis spectrum of the petals.

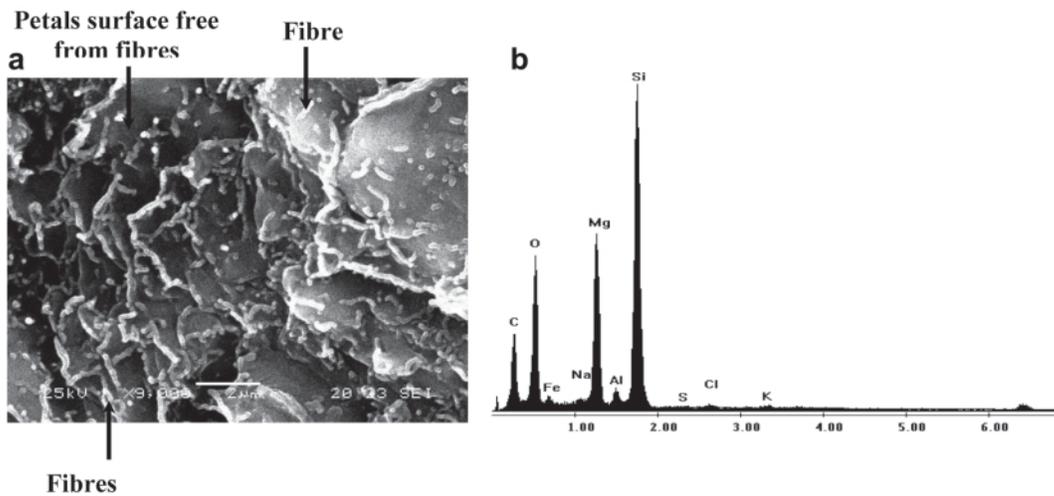


FIG. 6. (a) SEM micrographs and (b) EDX analysis of smectite particles in raw clay: evidence of bristled smectite-particle peripheries with short needles and an increase in the amount of Mg.

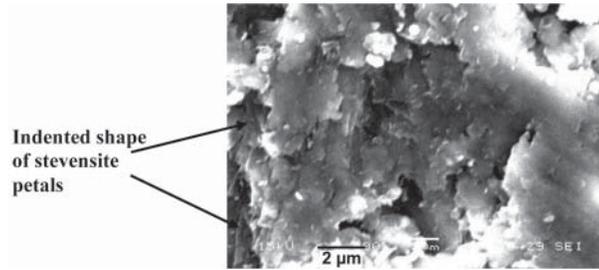


FIG. 7. SEM micrograph of the Na-clay.

### Chemical analysis

Chemical analyses of dehydrated bulk Rhassoul clay and Na-saturated clay separates are presented in Table 1, with the number of cations calculated on the basis of 22 oxygen (O) atoms (not taking into account  $\text{H}_2\text{O}^+$  and  $\text{H}_2\text{O}^-$  since samples are dehydrated) (Rautureau *et al.*, 2004).

These results show that the fine fractions are principally made up of  $\text{SiO}_2$  and  $\text{MgO}$ , constituting 77.5 wt.% and 87.8 wt.% of the total weight of bulk and separated fractions, respectively.  $\text{Al}_2\text{O}_3$  is notably concentrated in the fine clay mineral fraction. The large amount of  $\text{CaO}$  measured in the untreated clay may be ascribed partly to the dolomite recognized in XRD patterns (~5%), but particularly to gypsum in agreement with the geological setting (see section 2). Indeed, gypsum has been reported to be present in the Rhassoul clay deposit by several authors (Chahi, 1996; Chahi *et al.*, 1993; Chahi, 1997; Benhamou, 2005). The smaller concentration of Ca in the Na saturated clay (2.2 wt.%) suggests that the clay interlayer exchange was accomplished efficiently and that only small amounts of gypsum remain. Assuming that Ca is not contained in the clay mineral fraction but rather in the gypsum phase, the structural formula per unit cell of the Na-saturated clay calculated as  $(\text{Na}_{0.25}\text{K}_{0.20})(\text{Mg}_{5.04}\text{Al}_{0.37}\text{Fe}_{0.20}\square_{0.21})_{5.61}(\text{Si}_{7.76}\text{Al}_{0.24})_8\text{O}_{20}(\text{OH})_4$  confirms a trioctahedral Mg-rich smectite composition with a clear deficiency in octahedral cations. From this structural formula, the layer charge located in both the tetrahedral and octahedral sheets of the Na-clay can be estimated to be 0.45. The interlayer CEC corresponding to this interlayer charge ( $\xi$ ) can be calculated from the following equation proposed by Mermut & Lagaly (2001):

$$\text{Interlayer CEC (cmol}_c\text{Kg}^{-1}) = 10^5 \times \xi/M$$

where M designates the molecular mass. For the Na-saturated smectite fraction the interlayer CEC is ~58 mEq/g, which is slightly less than the measured value (~60 mEq/100 g calcined clay). The difference between both values is probably due to edge charges which probably represent 5% of the total CEC for this sample.

The calculated structural formula could represent that of hectorite, stevensite or saponite. However, the absence of Li in the mineral composition can be used to exclude hectorite (Caillère *et al.*, 1982; Singhal, 2003). The fact the amount of  $\text{Al}_2\text{O}_3$  in the mineral is >1 wt.% could be taken as an indication of stevensite (Capet, 1990), but the above formula differs from that corresponding to the stevensite end-member  $(M^{0,II}(\text{Mg})_{<3}(\text{Si})_4\text{O}_{10}(\text{OH})_2)$  in which tetrahedral substitutions cannot occur (Velde, 1995). The chemical composition of the studied smectite also appears to be similar to compositions reported for saponite (Velde, 1995; Parthasarathy *et al.*, 2003), which led Trauth (1977) and Chahi *et al.* (1999) to suggest that the Rhassoul clay could be saponite. Clearly, to distinguish between stevensite and saponite, further analytical characterizations are required.

### $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS NMR

$^{27}\text{Al}$  MAS NMR spectra of the Rhassoul and Na-stevensite are presented in Fig. 8. In both cases two resonances are observed, one at the chemical shift of 68 ppm and another at 5 ppm, which represent tetrahedral and octahedral coordination of Al, respectively (Komarneni, 1986). This is in agreement with the above structural formula, in which Al is shared by tetrahedral and octahedral sites.

Figure 9 exhibits the  $^{29}\text{Si}$  MAS NMR spectra recorded for the bulk Rhassoul clay sample and Na-saturated smectite separates. Only a single unresolved peak is observed at the chemical shift of

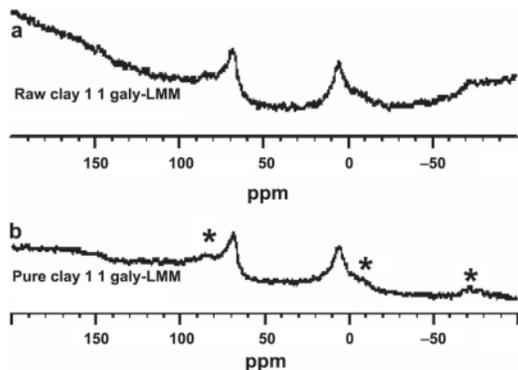


FIG. 8.  $^{27}\text{Al}$  MAS NMR of (a) bulk Rhassoul clay and (b) Na-stevensite (\* = rotating bands).

−95.1 ppm from tetramethylsilane (TMS) corresponding to the tetrahedral coordination of Si. This unresolved resonance is probably associated with the component  $\text{Q}^3$  (0 Al or Si(3Si)) without any Al substitution, such as in talc (Komarneni, 1986). Otherwise, this indicates that, in contrast to structural formula, the  $\text{SiO}_4$  tetrahedra studied is only attached to three  $\text{SiO}_4$  tetrahedra. Furthermore, the peak appears broad in both cases since it is extended over a width of ~10 ppm. This confirms the poor crystallinity and thereby indicates there is little or no short-range ordering of silicon chemical environments in the Rhassoul smectite (Komarneni, 1986; Reinholdt, 2001). This discordance could be explained by the small amount of Al in the fourfold

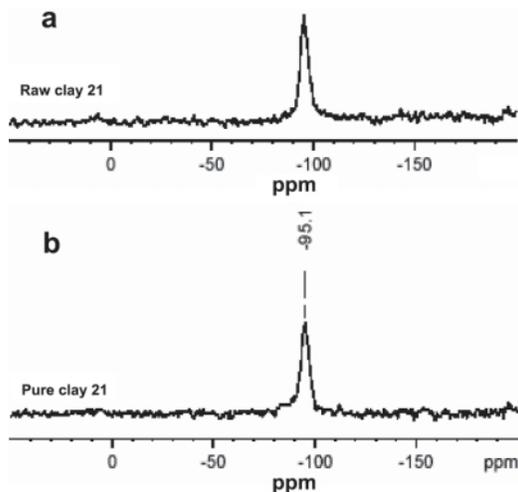


FIG. 9.  $^{29}\text{Si}$  MAS NMR of (a) bulk Rhassoul clay and (b) Na-clay separates.

coordination. Conversely, the absence of any shoulder peak at the chemical shifts of −97 ppm and −90 ppm, a reflection which is taken to be diagnostic of saponite (Komarneni, 1986), allows us to positively identify the smectite mineral of the Rhassoul clay deposit as stevensite.

#### FTIR spectroscopy

The FTIR spectra of the natural bulk Rhassoul clay and the Na-saturated smectite separates shown in Fig. 10 does not reveal appreciable differences between the two sample fractions. They show, in the range of 2500 to 4000  $\text{cm}^{-1}$ , absorption peaks at 3620 and 3434 that could be attributed to the OH-stretching mode and reflect the trioctahedral character of the isolated smectite fraction. The breadth of these bands confirm a small crystallite size. In the wavenumber range 400–2000  $\text{cm}^{-1}$ , the bands at 663 and 1637  $\text{cm}^{-1}$  are known to arise from trioctahedral smectite and correspond to OH-deformation (Al-Fe-Mg OH). The intense and sharp peaks observed at 1017 and 470  $\text{cm}^{-1}$  are ascribed to SiO stretching and deformation, respectively. In agreement with thermal analysis results, the peaks at 1451 and 1378  $\text{cm}^{-1}$  correspond to traces of dolomite. The weight percentage of the carbonate phase remaining is <5%, which represents the threshold of detection by XRD analysis (Eberhart, 1989). To distinguish between the different trioctahedral smectites, especially saponite and stevensite, Russell and Fraser (1994) suggested

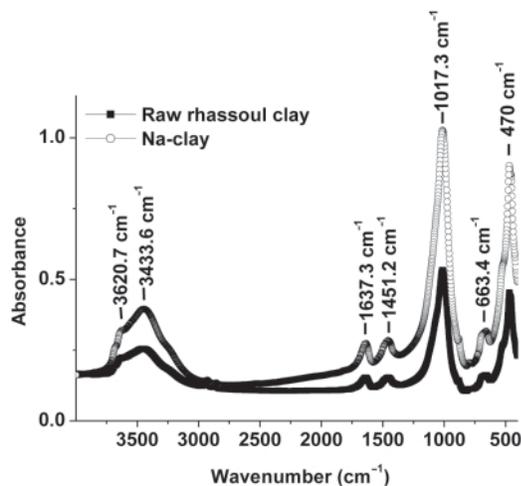


FIG. 10. FTIR absorption spectra of bulk Rhassoul clay and its fine clay mineral fraction (Na-clay).

that FTIR spectra should be collected after heat-treatment of the KBr-pressed samples. Figure 11 shows the FTIR spectra of Na saturated clay heated at 150°C overnight. The spectrum of the heat-treated sample exhibited similar absorption bands to those of the OH-stretching mode observed before annealing, but with a collapsed intensity due to dehydration. No additional high-frequency satellite band at  $\sim 3722\text{ cm}^{-1}$ , occurring in saponite (Russell and Fraser, 1994), was detected.

### CONCLUSION

The crystal chemistry of raw Rhassoul clay and its isolated fine clay mineral fraction were characterized using several advanced analytical techniques. X-ray diffraction as well as TA confirmed the smectite character of the clay mineral. Despite there being a larger amount of Al (>1 wt.%) than that reported for other stevensite occurrences,  $^{27}\text{Al}$  MAS NMR analyses of the bulk and clay-sized fraction of the Jbel Rhassoul deposit confirmed the smectite to be stevensite rather than saponite. This Mg-rich trioctahedral smectite contains significant amounts of Al (wt.%  $\text{Al}_2\text{O}_3 = 4\%$ ) and has a CEC of  $\sim 60$  mEq/100 g calcined clay. Despite minor contamination by dolomite and/or gypsum, the near-pure Na-saturated clay fraction was determined to have the following chemical formula:  $(\text{Na}_{0.25}\text{K}_{0.20})(\text{Mg}_{5.04}\text{Al}_{0.37}\text{Fe}_{0.20}\square_{0.21})_{5.61}(\text{Si}_{7.76}\text{Al}_{0.24})_8\text{O}_{20}(\text{OH})_4$ .

Combined FTIR and MAS NMR measurements show little or no short-range ordering of Si in an Al-rich smectite deficient in octahedral cations.

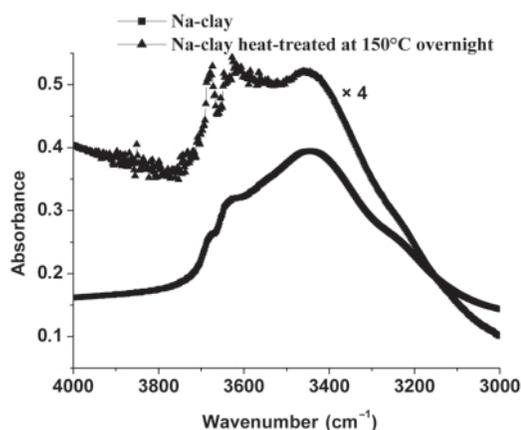


FIG. 11. FTIR absorption spectra of Na-clay before and after Na heat-treatment up to 150°C.

### ACKNOWLEDGMENTS

Financial support from the 'Convention de coopération CNRST – Maroc/CNRS – France' within the framework of project chimie 04/08 is gratefully acknowledged. The authors thank REMINEX for facilities to perform the ICP chemical analysis and Professor Abdellatif Boussaid for his help in revising the paper.

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