

## THERMAL BEHAVIOUR OF STEVENSITE AT TEMPERATURES UP TO 800°C

Christidis G.E<sup>1</sup> and Koutsopoulou E.<sup>2</sup>

<sup>1</sup> Technical University of Crete, Department Mineral Resources Engineering, 73100 Chania, Greece. christid@mred.tuc.gr

<sup>2</sup> University of Patras, Department Geology, 26500 Patras, Greece ekoutsop@upatras.gr

### Abstract

*Stevensite is a Mg-trioctahedral smectite with layer charge stemming from vacancies in the octahedral sheet. In the present work we studied the thermal behavior of Jbel Ghassoul stevensite from Morocco, known as Ghassoulite or Rhassoulite, free of talc layers. The clay fraction of the material was separated by sedimentation, it was subsequently heated from 250° to 800° C and the end products were examined with X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The influence of heating on the stevensite structure begins at 400°C and is completed at 500°C. It involves irreversible collapse of the layers at ~10Å, which do not re-expand in ethylene glycol (EG) vapors. In contrast, heating at lower temperatures does not affect the stevensite layers, which expand completely in EG. The FTIR spectra indicate the formation of talc-like (kerolite) layers after heating at temperatures exceeding 400°C. Within the current experimental setup, the transition to kerolite layers takes place without the formation of an intermediate mixed-layer stevensite/talc phase. Heating at higher temperatures does not change the transformation pattern, until 800°C where complete dehydroxylation of the 2:1 layer takes place, which is associated with the formation of enstatite. The results of this study clearly demonstrate that opposite to common trioctahedral and dioctahedral smectites, stevensite converts to another layer silicate prior to dehydroxylation.*

**Key words:** trioctahedral smectite, kerolite, XRD, Thermal treatment, transformation.

### Περίληψη

*Ο στιβενσίτης είναι μαγνησιούχος τριοκταεδρικός σμεκτίτης με φορτίο κρυσταλλικής δομής που προέρχεται από κενές οκταεδρικές θέσεις. Στην παρούσα εργασία μελετήθηκε η θερμική συμπεριφορά ενός καθαρού στιβενσίτη (χωρίς φύλλα τάλκη) από το Μαρόκο, γνωστού ως Ghassoulite ή Rhassoulite. Το αργιλικό κλάσμα του υλικού αποχωρίστηκε με καθίζηση, θερμάνθηκε σε θερμοκρασίες 250-600°C και εξετάστηκε με περιθλασιμετρία ακτίνων X (XRD) και φασματοσκοπία υπερύθρου (FTIR). Επίδραση της θέρμανσης στη δομή του στιβενσίτη ξεκινά στους 400°C και ολοκληρώνεται στους 500°C. Λαμβάνει χώρα μη αντιστρεπτή συρρίκνωση των φύλλων στα ~10Å, τα οποία δε διογκώνονται μετά από έκθεση σε αιθυλαινογλυκόλη. Αντίθετα έκθεση σε χαμηλότερες θερμοκρασίες δεν επηρεάζει τη συμπεριφορά των*

στιβενσιτικών φύλλων, τα οποία διογκώνονται πλήρως σε περιβάλλον αμιών αιθυλαινογλυκόλης. Τα φάσματα FTIR δείχνουν τη δημιουργία φύλλων τάλκη (κερολίτη) όταν οι θερμοκρασίες υπερβαίνουν τους 400°C. Με τις παρούσες πειραματικές συνθήκες η μετάβαση σε φύλλα τάλκη δεν έλαβε χώρα μέσω μικτής δομής στιβενσίτη/τάλη. Έκθεση σε υψηλότερες θερμοκρασίες δε μεταβάλλει την πορεία του μετασχηματισμού μέχρι τους 800 °C, όπου λαμβάνει χώρα αφυδροξυλίωση, η οποία συνδέεται με δημιουργία ενστατίτη. Η παρούσα μελέτη δείχνει σαφώς, ότι ο στιβενσίτης παρουσιάζει διαφορετική συμπεριφορά από τους υπόλοιπους διοκταεδρικούς και τριοκταεδρικούς σμεκτίτες, αφού μετατρέπεται σε άλλο φυλλοπυριτικό ορυκτό πριν την αφυδροξυλίωση.

**Λέξεις κλειδιά:** Τριοκταεδρικός σμεκτίτης, κερολίτης, XRD, θερμική επίδραση, μετατροπή.

## 1. Introduction

The structural and crystal chemical characteristics of smectites have been studied extensively in the past by several independent analytical methods including X-ray diffraction (XRD), various spectroscopic methods including FTIR, Mössbauer and EPR spectroscopy, thermal analysis, chemical analysis (e.g. Lagaly & Weiss 1975; Talibudeen & Goulding 1983; Lim & Jackson 1986; Decarreau et al., 1987; Goodman et al., 1988; Iwasaki & Watanabe 1988; Lagaly 1994; Christidis & Dunham 1993; 1997; Christidis & Eberl, 2003; Christidis, 2006). Identification of smectite compositional characteristics is important for most industrial applications (Christidis, 2011). Hence several classification schemes of smectites have been proposed, based on their crystal chemical and thermal properties (Grim & Kulbicki, 1961; Schultz, 1969; Brigatti & Poppi, 1981; Newman & Brown, 1987; Alberti & Brigatti, 1985; Güven, 1988; Drits et al., 1998; Wolters et al., 2009).

X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy are powerful techniques used for the characterization of structural characteristics of smectites. Special tests have been proposed for fast distinction of the different smectite species such as the Hoffman-Klemmen effect, which provides a fast tool for distinction of beidellite from montmorillonite (Greene-Kelly, 1953). However, most previous work on the identification and characterization of smectites focus on the dioctahedral smectites. In contrast, characterization of the trioctahedral smectites by XRD methods is very basic and includes merely identification of the trioctahedral character, based on the position of the 060 diffraction maximum (e.g. Moore and Reynolds, 1997).

The main trioctahedral smectite species are saponite with predominantly tetrahedral charge and stevensite and hectorite mainly with octahedral charge. Stevensite is different from its counterparts because the layer charge stems from octahedral vacancies rather than substitutions in the structure (Brindley, 1984). The layer charge of stevensites is low and typically does not exceed 0.25 electrons per half unit cell (e/huc). Studies on the stevensite thermal properties are rather rare (Shimoda, 1971; Brindley, et al. 1977; Benhammou et al., 2009). Moreover, in several occurrences, stevensite occurs in the form of mixed layer stevensite/kerolite (e.g. Eberl, et al. 1982; Dekov et al. 2008). In contrast pure stevensites are rather rare. Recently Christidis & Mitsis (2006) described a new Ni-stevensite in Othrys mountain, Central Greece. The aim of this study was to describe the thermal characteristics of the Jbel Ghassoul stevensite from Morocco, and to display possible differences compared to the remaining trioctahedral smectites and a well characterized talc from Egypt. The particular stevensite was selected, because it is well characterized and it is well known that it does not contain traceable kerolite layers (Benhammou et al., 2009)

## 2. Materials and Methods

The stevensite sample from Jbel Ghassoul was supplied by Prof. K. El Ass, University of Rabat, Morocco. It is a gray-pink soft clay with a low grit content and soapy texture. The Egyptian talc was provided by IONIAN KALK SA (Kefalonia, Greece). Bulk mineralogy was determined by X-ray diffraction (XRD) with a Bruker D8 Advance XRD, equipped with a Lynx Eye strip silicon detector, using Ni filtered CuK $\alpha$  radiation (35kV, 35mA), 0.298° divergence and antiscatter slits, and a step size of 0.019 °2 $\theta$ , with 47.7 s count time per step. XRD analysis was performed from 4 to 70 °2 $\theta$ . The collected data were evaluated with the EVA® software provided by SOCABIM. 3 g of the bulk sample were heated at 800°C for 2 h and examined with the same diffractometer. Clay mineralogy was determined by dispersion of the sample in distilled water using an ultrasonic probe (20 seconds) and repeated washing until practically free of salts (electric conductivity < 25  $\mu$ S/cm). The <2  $\mu$ m fraction was separated by settling and dried on glass slides at room temperature. The glass slides with the calibration samples were heated at 250, 300, 400, 500, 550 and 600 °C for 90 min and were subsequently solvated with ethylene-glycol (EG) vapour at 60 °C overnight (min. 16 h) to ensure maximum saturation. XRD analysis was performed from 2 to 35°2 $\theta$  with the same diffractometer.

The clay fractions of the stevensite in the raw state and after heating at 500°C were examined with infrared (IR) spectroscopy using a Perkin Elmer 1000 Fourier Transform Infrared (FTIR) spectrometer in the range 400-4000cm<sup>-1</sup>. Each spectrum was the average of 50 scans collected at 4 cm<sup>-1</sup> resolution. 1.5 mg of the clay fractions was diluted in 200 mg KBr and pressed in 13mm KBr disks, which were subsequently dried at 150°C for 15 hours, prior to FTIR analysis (Russell 1987).

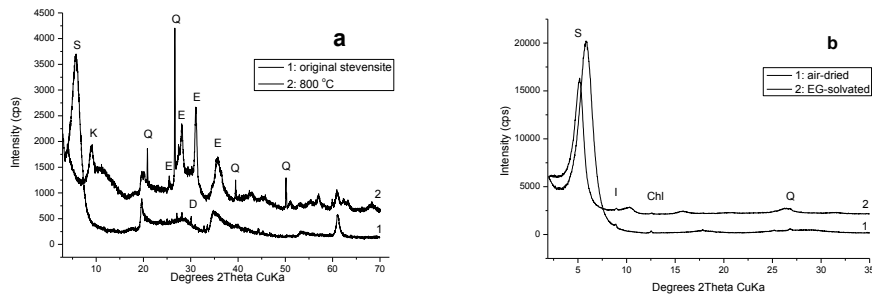
## 3. Results

### 3.1 X-Ray Diffraction

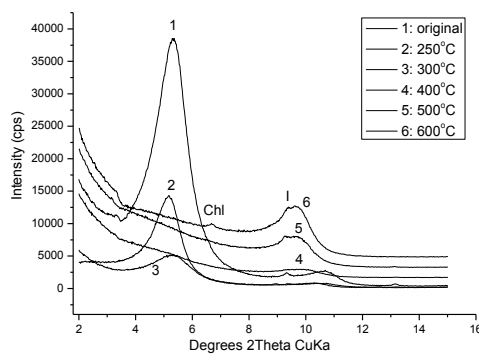
The XRD trace of the bulk stevensite sample is shown in (Fig. 1a). The material consists of stevensite, with minor illite, chlorite, quartz, dolomite, K-feldspar and albite. The hump at 10-18 ° 2 $\theta$  is due to instrumental artifact. The stevensite content exceeds 90%. The clay fraction contains >95% stevensite and traces of chlorite illite and quartz (Fig. 1b). The existence of a low angle shoulder in the 001 diffraction maximum of the EG solvated XRD trace might be indicative of random interstratification, possibly with kerolite layers. However the higher order diffraction maxima are rational suggesting that if kerolite layers are present, they should not exceed 5%. Therefore the smectite is considered to be pure stevensite. After heating at 800°C for 2 h a diffraction maximum at ~9° 2 $\theta$  (9.8 Å) is present, which corresponds to the collapsed stevensite layer (see below), and enstatite forms (Fig. 1a). These results are in full accordance with Benhammou et al. (2009). The coexistence of 9.8 Å (kerolite-like) layers and enstatite indicates that the onset of dehydroxylation occurs at lower temperatures. A small amount of kerolite-like layers still persists after heating at 950°C for 2 h, and simultaneously enstatite becomes more abundant (data not shown). As expected, chlorite, mica and dolomite also decomposed after heating. Therefore the first recrystallization product of Morocco stevensite *after* dehydroxylation is enstatite. The Ni-stevensite from Othrys mountain also collapsed at below 500°C, dehydroxylated at temperatures higher than 750°C and yielded enstatite at 800°C (Christidis & Mitsis 2006). Such behaviour is comparable to pure talc, which also recrystallizes to enstatite after dehydroxylation at higher temperature i.e. 900-1000°C (Brindley & Lemaitre, 1987).

Heating of the clay fractions of stevensite up to 300°C and subsequent EG solvation did not affect the position of the 001 diffraction maximum. Only a progressive decrease of the diffraction intensity was observed instead (Fig. 2). At higher temperatures the 001 diffraction maximum collapsed to ~ 9.8 Å and did not re-expand after EG solvation. Moreover, the intensity of the new diffraction maximum increased with increasing heating temperature. The appearance of the new diffraction maximum strongly indicates the formation of a kerolite-like phase. The onset of

formation of this phase is observed at ~400°C, and it is fully developed at temperatures higher than 500 °C. The rational order of the higher order basal reflections attests to the lack of intermediate stevensite/kerolite mixed layer phase during progressive heating.



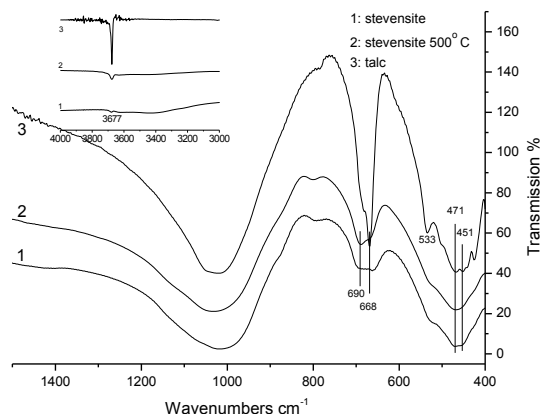
**Figure 1 – a) XRD traces of the Jbel Ghassoul stevensite (bulk sample) in raw state and after heating at 800°C. b) XRD traces of the oriented clay fractions of the original stevensite sample. Key to the symbols: S= stevensite, K= kerolite, Q= quartz, E= enstatite, D= dolomite, Chl= chlorite, I= illite. See text for discussion.**



**Figure 2– Oriented XRD traces of Jbel Ghassoul stevensite heated at 250-600°C and ethylene glycol solvated. Chl = chlorite, I = illite.**

### 3.2 FTIR Spectra

The FTIR spectra of the original and heated stevensite (500°C) are shown in Fig. 3. For terms of comparison the FTIR spectrum of a talc is also included. In the OH-stretching region all spectra display the characteristic band at 3677  $\text{cm}^{-1}$  attributed to  $\text{Mg}_3\text{OH}$  (Petit, 2005). The location of the band is identical in all three spectra, but the intensity in stevensite heated at 500°C is clearly higher compared the original stevensite and certainly lower than that of talc. In the region of lattice vibrations, the FTIR spectra of the original clay fractions are broader, while the bands of the heated sample seem to be more symmetric. The bands at 451  $\text{cm}^{-1}$ , 471  $\text{cm}^{-1}$  and 533  $\text{cm}^{-1}$  are attributed to Si-O-Mg vibration, Mg-O and/or translational OH-vibration and Mg-O vibration respectively. In the  $\text{Mg}_3\text{OH}$  bending region the stevensite and the heated stevensite display a doublet (668 and 690  $\text{cm}^{-1}$ ) but the intensity of the two bands is reversed after heating. Talc displays is single band (668  $\text{cm}^{-1}$ ). In conclusion, although heating caused structural differences in the structure of stevensite, the heated sample has clearly distinct structural features compared to well crystallized talc, being more typical to kerolite (Christidis & Mitsis, 2006).



**Figure 3 – Mid FTIR spectra of the Jbel Ghassoul stevensite in raw state and after heating at 500°C. The IR spectrum of talc is shown for comparison. See text for discussion.**

#### 4 Discussion

This work has clearly shown that stevensite is different than the remaining trioctahedral smectites not only due to the origin of layer charge (octahedral vacancies *vs* ionic substitution in the structure) but also because although it has comparable dehydroxylation temperature with saponite and hectorite (Paterson and Swaffield, 1987), the swelling properties are lost after heating well below the dehydroxylation temperature. This difference in thermal behaviour has been used recently as part of a new approach to identify the trioctahedral smectites (Christidis and Koutsopoulou, 2013). The loss of swelling is associated with the solid state transformation of stevensite to kerolite-like layers. Kerolite is disordered talc with similar XRD characteristics as smectites, which does not swell in EG vapours (Brindley 1984). It often forms random mixed layer phases with stevensite in nature (Eberl et al., 1982; Dekov et al., 2008). The lack of intermediate mixed layer stevensite/kerolite indicates the presence of homogeneous stevensite domains in the original clay. If minor kerolite domains were present in the original clay, then they should form distinct areas and should not be mixed with stevensite domains (Christidis and Mitsis, 2006). Such a hypothesis explains the XRD traces after EG solvation, which are not compatible with the existence of mixed layer phases. In this scenario, any trace distinct kerolite domains would possibly be masked by the 002 diffraction maximum of stevensite, due to their low abundance.

Heating at 800°C shed additional light on the structural characteristics of stevensite. The coexistence of abundant kerolite-like layers and neofomed enstatite crystals is in accordance with the widely accepted influence of kinetics on the transformation of kerolite to enstatite (Brindley & Lemaitre, 1987). What is not known with certainty is if this kinetic influence on the transformation, is due to existence of energy barriers, or due to structural heterogeneity of the original stevensite. This study has shown that the stevensite layers are relatively homogeneous, due to the apparent lack of kerolite domains. However, the Jbel Ghassoul stevensite contains 1.31% Al<sub>2</sub>O<sub>3</sub> (Benhammou et al., 2009), suggesting the presence of saponite layers, although part of this Al<sub>2</sub>O<sub>3</sub> is due to the presence of traces of chlorite and illite. It is thus suggested that the presence of saponite layers, which also yield enstatite at temperatures higher than 800°C (Brindley and Lemaitre, 1987), may also affect the kinetics of transformation of stevensite.

Due to their high dehydroxylation temperatures trioctahedral smectites in general have good potential for application in the foundry industry (iron ore pelletization and foundry sand binders) and as fire retardants (Christidis, 2011). However it is clear that stevensite does not follow this trend, because it converts to a kerolite-like phase at least 400°C lower than the dehydroxylation temperature. Therefore, the swelling properties which are of vital importance for foundry applications deteriorate at temperatures lower than the *trans*-vacant smectites, which

dehydroxylate at 500-550°C (Drits et al. 1998; Guggenheim & Koster van Groos, 2001). It is well known that *trans*-vacant smectites are not suitable for foundry applications (Christidis, 2011). This underlines the significance of identification of stevensite layers during assessment of bentonite deposits, in areas where it occurs in close association with saponite, such as the Vicalvaro Basin, Spain (Cuevas et al. 2003). In contrast, due to its fine grain size and swelling properties, coupled with the chemical composition, stevensite is used as a gelling agent, especially after modification with organic compounds, and in the formulation of cordierite ceramics (Benhammou et al. 2009).

## 5. Conclusions

The Jbel Ghassoul stevensite was heated in the temperature range 250-800°C. Heating above 400°C resulted to collapse of the stevensite layers and to formation of non-swelling kerolite-type layers. This transformation occurs well below the dehydroxylation temperature of stevensite. At 800°C enstatite forms but the transformation of the kerolite layers is not complete. Identification of stevensite layers is a vital importance during assessment of bentonites containing trioctahedral smectites, especially for high temperature applications such as the foundry industry.

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