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STUDY OF RAW AND THERMALLY TREATED SEPIOLITE FROM THE MANTOUDI AREA, EUBOEA, GREECE
X-ray diffraction, TG/DTG/DTA and FTIR investigations

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Raw and thermally treated sepiolites from the Mantoudi area, Euboea, Greece, were investigated by means of X-ray diffraction (XRD) in combination with thermo-gravimetric analysis (TG/DTG) and differential thermal analysis (DTA), as well as Fourier transform (FTIR) spectroscopy, in order to study the collapse of the sepiolite structure with increasing temperature. The main mineral constituent (>95%) is a well crystallized sepiolite. Quartz and dolomite occur in minor amounts. Calcination of the samples was carried out up to 350, 720 and 820°C, for 2 h, and 'sepiolite dihydrite', 'sepiolite anhydrite' and 'enstatite' were formed, respectively, as magnesium co-ordinated water and octahedrically co-ordinated hydroxyl groups, are removed and the dehydroxylated phase recrystallize to enstatite ($MgSiO_3$). These structural and textural changes play an important role to the properties and uses of the studied sepiolites.

Keywords: *calcination, FTIR, sepiolite, TG-DTG-DTA, XRD*

Introduction

Sepiolite [$Mg_8Si_{12}O_{30}(OH)_4{\cdot}4(H_2O){\cdot}nH_2O$] is a microfibrous 2:1 tri-octahedral sheet silicate mineral. Structurally it is formed of blocks and channels extending in the fiber direction (*c*-axis). Each structural block is composed of two tetrahedral silica sheets and a central octahedral sheet containing Mg. Isomorphic substitutions of Si^{4+} in the tetrahedral sheet of the mineral lattice with Al^{3+} form negatively charged adsorption sites. These sites are occupied by exchangeable cations, which compensate the electrical charge. The pre- dominant exchangeable cation is Mg^{2+}. Due to the discontinuity of the external silicate sheets, a significant number of silanol groups (Si–OH) are situated at the surface of this mineral. The sepiolite mineral includes three types of water: zeolitic or channel water (nH_2O), magnesium co-ordinated water ($4H_2O$) and octahedrically co-ordinated hydroxyl groups (Fig. 1). The difference from the others sheet silicate minerals is the inversion of the tetrahedral sheets, every six tetrahedral units, creating 5.6·11.0 Å channels, which grow up in the c-axis di-

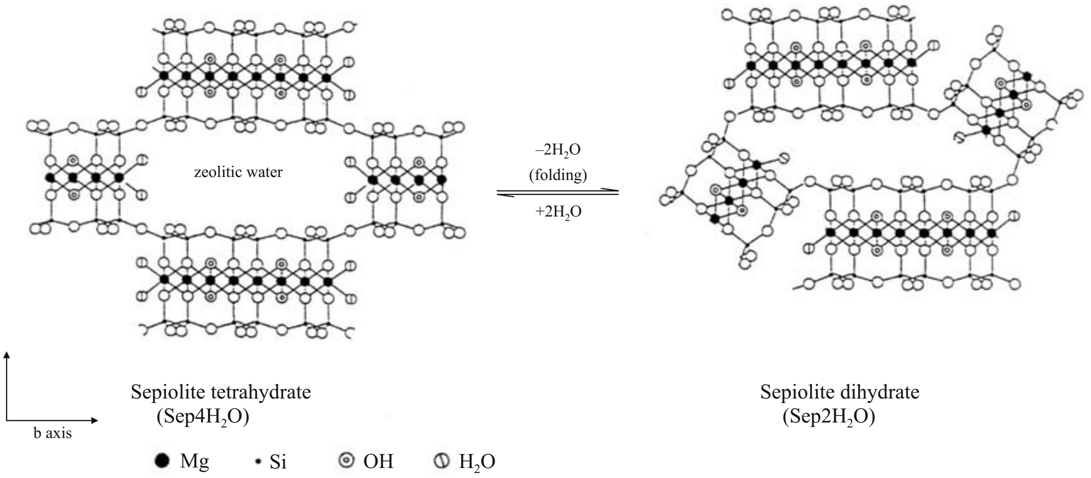

Fig. 1 Structure of sepiolite tetrahydrate ($Sep4H_2O$) and sepiolite dihydrate ($Sep2H_2O$)

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rection. These channels may be filled with water, organic molecules, etc. [1–5].

The interest in this mineral lies in its special sorptive, colloidal–rheological and catalytic properties, which are the basis for many technological applications [6]. Owing to its structural characteristics, sepiolite has specific physical-chemical properties such as high porosity and surface area, strong adsorptive power and strong capacity to form stable suspensions at low concentrations. Because of the above properties it is used as industrial raw material in numerous applications such as molecular sieving, filtering, decolorization, feed additive (E-562) as it reduces the detrimental effects of mycotoxin-contaminated diets in animals etc. [7].

In this paper high purity sepiolites were studied in order to investigate the structural changes caused by their thermal treatment [8]. The raw sepiolite samples are from the underground magnesite mine of ‘Gerorema’ (Prokopi area, N. Euboea, Greece) and are products of alteration of peridotites. They were found in the contact between magnesite and serpentinite. The thickness of the sepiolite lenses/layers ranges from 20 to 50 cm. Although these modifications play an important role to sepiolite properties and uses no systematic study has been carried out up to now.

Experimental

Techniques

The raw and thermally treated sepiolite samples from the Mantoudi area, Euboea, Greece, were studied by X-ray diffraction (XRD), Fourier transform (FTIR) spectroscopy, as well as thermogravimetric analysis (TG/DTG) and differential thermal analysis (DTA).

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, with Ni-filtered CuK$_{\alpha_1}$ radiation (λ=1.5405 Å), operating at 40 kV, 30 mA.

The IR measurements were carried out using a Fourier transform IR (FTIR) spectrophotometer (Perkin Elmer 880). The FTIR spectra, in the wavenumber range from 400 to 4000 cm^{-1}, were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample: KBr approximately 1:200), at 8 tons cm^{-2}.

DTA and TG/DTG were obtained simultaneously using a Mettler Toledo 851 instrument. The samples were heated from 20 to 1200°C at a constant rate of 10°C min^{-1}.

Results and discussion

Study of sepiolites by XRD method

XRD study showed that the main mineral constituent of the raw material (>95%) is a well crystallized sepiolite, as indicated by the characteristic narrow and intense diffraction peak at d_{110}=12.05 Å (Fig. 2). Quartz (d_{101}=3.34 Å) and dolomite (d_{104}=2.89 Å) are present in minor amounts (Fig. 2). The other peaks in same pattern belong to the sepiolite.

Sepiolite heating causes structural and textural changes connected to the dehydration and dehydroxylation processes. So,

- After heating of the raw material up to 350°C for 2 h (Fig. 3a), the intensity of the peak at 12.05 Å is slightly decreased and new peaks at d=10.2 and 8.08 Å appear, due to the formation of sepiolite dihydrite (Sep2H$_2$O), according to the reaction:

$$\mathrm{Sep4H_2O{\cdot}\mathit{n}H_2O} \xrightarrow{-n\mathrm{H_2O},\ \sim100^\circ\mathrm{C}} \underset{\text{sepiolite tetrahydrite}}{\mathrm{Sep4H_2O}} \xrightarrow{-2\mathrm{H_2O},\ \sim300^\circ\mathrm{C}}$$

$$\underset{\text{sepiolite dihydrite}}{\mathrm{Sep2H_2O}} \xrightarrow{-2\mathrm{H_2O},\ \sim650^\circ\mathrm{C}} \underset{\text{sepiolite anhydrite}}{\mathrm{Sep}}$$

- When the sample is heated up to 720°C, the peak at 12.05 Å is totally disappeared, indicating the total destruction of sepiolite dihydrite. The slight increase in the peaks at ~10 and ~8 Å (Fig. 3b) indicates that the formation of sepiolite anhydrite is not followed by any deformation of the crystal lattice of the sepiolite dihydrite. The decrease in intensity of the 2.88 Å peak and the appearance of the 3.04 Å peak represent the first step of calcinations of the dolomite to give calcite.
- After heating of the sample up to 820°C (Fig. 3c), peaks at ~10 and ~8 Å disappear, indicating the complete destruction of the crystal lattice. New peaks at 2.88, 3.18 and 2.54 Å suggest the formation of enstatite (MgSiO$_3$) as a new crystalline phase [9, 10].

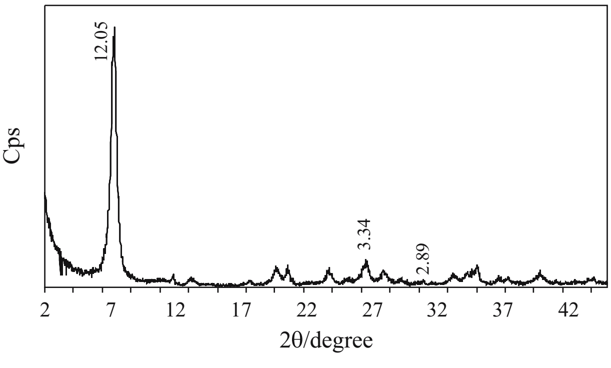

Fig. 2 XRD diagram of a representative sepiolite sample from Mantoudi

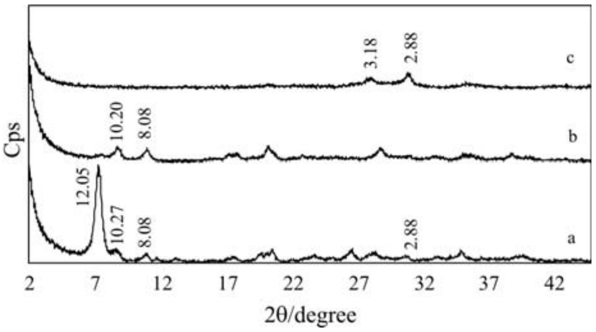

Fig. 3 XRD patterns of thermally treated sepiolite samples; a – 350, b – 720 and c – 820°C

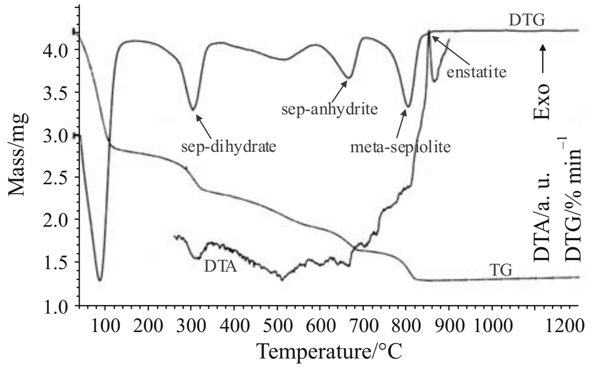

Fig. 4 TG/DTG and DTA curves of raw sepiolite

Study of sepiolites by thermogravimetric method

The DTG curve (Fig. 4) shows four intense peaks at about 100, 300, 650 and 800°C with a mass loss of 9.85, 2.6, 1.96 and 2.16%, respectively. The sharper and more intense peak at ~100°C is attributed to the loss of hygroscopic and zeolitic water (free water adsorbed on the surface and water trapped in the channels, respectively). The peak at ~300°C, is attributed to the loss of half the Mg-coordinated water followed by structural modifications (transformation to sepiolite dihydrate). The other half of Mg-coordinated water remains in the collapsed channels up to ~650°C when the dehydration of Sep2H_2O takes place producing sepiolite anhydrite [11]. The peak at ~800°C represents the dehydroxylation of the octahedrically coordinated hydroxyl groups. As a result of the dehydroxylation the so-called ‘sepiolite anhydrite’ is transformed into an amorphous phase named ‘meta-sepiolite’. The exothermic peak at ~850°C in the DTA curve corresponds to recrystallization of the dehydroxylated phase and the formation of enstatite ($MgSiO_3$).

The above transformations are represented by the following chemical reactions:

$$Mg_8Si_{12}O_{30}(OH)_4.(H_2O)_4.8H_2O\sim\sim> \\ Mg_8Si_{12}O_{30}(OH)_4.(H_2O)_4+8H_2O \quad \sim 100°C,$$

$$Mg_8Si_{12}O_{30}(OH)_4\cdot(H_2O)_4\cdot 8H_2O\sim\sim> \\ Mg_8Si_{12}O_{30}(OH)_4\cdot(H_2O)_2+2H_2O \quad \sim 300°C,$$

$$Mg_8Si_{12}O_{30}(OH)_4\cdot(H_2O)_4\cdot 8H_2O\sim\sim> \\ Mg_8Si_{12}O_{30}(OH)_4+2H_2O \quad \sim 650°C,$$

$$Mg_8Si_{12}O_{30}(OH)_4\cdot(H_2O)_4\cdot 8H_2O\sim\sim> \\ MgSiO_3+4SiO_2+2H_2O \quad \sim 800°C.$$

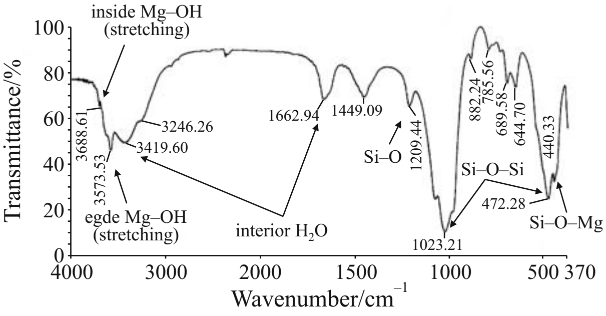

Fig. 5 FTIR spectrum of raw sepiolite

Study of sepiolites by FTIR

In the sepiolite FTIR spectrum (Fig. 5), bands at ~3689, ~3574 and 3419 cm^{-1} are attributed to the presence of different types of water molecules in the structure of the mineral (adsorbed and zeolitic water), octahedrically coordinated OH to Mg (inside Mg–OH) and edge Mg–OH bonds.

More specifically:

- The band at ~3689 cm^{-1} corresponds to stretching (ν_{OH}) vibrations of hydroxyl groups attached to octahedral Mg ions located in the interior blocks of natural sepiolite [4, 12].
- The band at ~3574 cm^{-1} is assigned to the Mg-coordinated water (edge Mg–OH stretching vibration) [13].
- The bands at ~3419 and ~1663 cm^{-1} are due to the OH stretching and bending vibrations of water molecules, respectively, located in the interior of the channels (zeolitic or interior or channel water) [13].
- The band at ~1449 cm^{-1} is attributed to carbonate (dolomite) impurities.

Between 1400 and 400 cm^{-1}, bands characteristic of silicate minerals are observed, corresponding mainly to Si–O bonds in the tetrahedral sheet and to Mg–O stretching vibrations, in the octahedral sheet. The band at ~1209 cm^{-1}, is characteristic for minerals with tetrahedral sheet inversion and it is attributed to Si–O–Si bond [2].

- The bands at ~1023 and ~472 cm^{-1} are assigned to the Si–O–Si in plane vibrations [14].
- The band at ~785 and ~645 cm^{-1} may be attributed to Mg–OH_{inner} bending vibrations.
- The band at ~440 cm^{-1} is attributed to Si–O–Mg bonds (between the tetrahedral and the octahedral sheets) [14].

Table 1 Changes in the FTIR spectra of thermally treated sepiolite

raw sepiolite		350°C	720°C
Mg–coordinated water stretching vibrations	3574 cm^{-1}	slightly decreased	disappeared
Zeolitic water stretching vibrations	3419 cm^{-1}	significantly decreased	significantly decreased
Zeolitic water bending vibrations	1663 cm^{-1}	slightly decreased	significantly decreased
Si–O–Si vibration	1209 cm^{-1}	unchanged	disappeared
Si–O–Si in plane vibration	1023 cm^{-1}	unchanged	decreased
Octahedrically coordinated Mg–OH bending vibrations	786 cm^{-1}	unchanged	disappeared
Octahedrically coordinated Mg–OH bending vibrations	645 cm^{-1}	unchanged	decreased
Si–O–Si in plane vibration	473 cm^{-1}	unchanged	significantly decreased
Si–O–Mg vibration	440 cm^{-1}	unchanged	slightly decreased

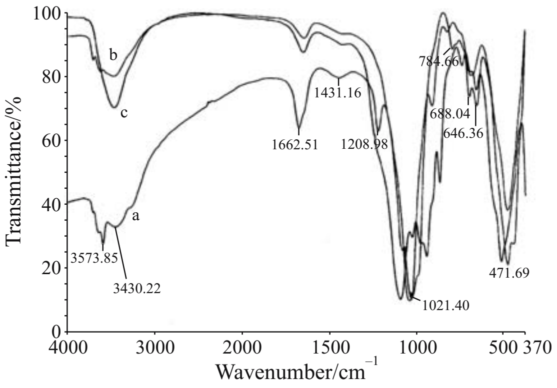

Fig. 6 The FTIR spectra of the calcined sepiolites; a – 350, b – 720 and c – 820°C

The FTIR spectra of the calcined sepiolites (Fig. 6) show the following changes:

- After heating up to 350°C (Fig. 6a), the vibrations due to zeolitic water at ~3419 and ~1663 cm^{-1}, were decreased, as well as the vibrations of Mg-coordinated water at ~3574 cm^{-1}. The vibrations of Si–O–Si (~1023 and ~474 cm^{-1}), Si–O–Mg (~440 cm^{-1}), as well as those of octahedrically co-ordinated OH-groups (at ~786 and ~645 cm^{-1}) remained unchanged.
- After heating up to 720°C (Fig. 6b) the vibrations of zeolitic water, Mg-coordinated water and octahedrically coordinated OH-groups, disappeared. Si–O–Si and Si–O–Mg vibrations were decreased.
- After heating up to 820°C (Fig. 6c), new vibrations at ~1084, ~933 and ~857 cm^{-1}, as well as at ~507, ~647 and ~729 cm^{-1}, appeared, due to Si–O stretching and Si–O–Si ('V' shaped) bending vibrations, respectively, of enstatite [9].

Conclusions

Studying raw and thermally treated sepiolites from the Mantoudi area, Euboea, Greece, by means of XRD in combination with TG/DTG and DTA and FTIR spectroscopy, we come to the following conclusions:

- The raw material is a nearly pure well crystallized sepiolite, with quartz and dolomite in minor amounts.
- Calcination of the samples up to 350, 720 and 820°C, results to the formation of 'sepiolite dihydrite', 'sepiolite anhydrite' and 'enstatite', respectively, as magnesium co-ordinated water and octahedrically co-ordinated hydroxyl groups are removed and the dehydroxylated phase recrystallize to enstatite ($MgSiO_3$).
- In the FTIR spectra of sepiolites thermally treated up to 350 and 720°C, the structure changes become obvious by decrease/disappearance of bands attributed to Mg-coordinated water (3574 cm^{-1}) and octahedrically coordinated OH-groups (786 and 645 cm^{-1}). Heating up to 820°C results to the formation of enstatite as shown by the new vibrations at 1084, 933, 857 and at 507, 647, 729 cm^{-1} corresponding to Si–O and Si–O–Si stretching and bending vibrations, respectively.

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