

## FT - IR SPECTROSCOPIC STUDY OF FIBROUS NATURAL ZEOLITES

A. Godelitsas\*, D. Charistos\*, T. Zorba\*\*,  
A. Filippidis\*\*\* and D. Siapkas\*\*

### ABSTRACT

FT - IR absorption spectra (4000 - 400 cm<sup>-1</sup>) of fibrous natural zeolites (natrolite, mesolite, scolecite, thomsonite and edingtonite) were recorded and evaluated. On the basis of the assigned absorption bands, conclusions were drawn concerning the structural units of the zeolite crystals and especially the water molecules which are located inside the channels and usually associated with the exchangeable cations. Differences observed in the spectra are mainly attributed to cation effects and to the Si/Al ratio. The FT - IR spectra can be used for identification and characterisation of the zeolites in study.

### ΕΥΝΩΗ

Φάσματα απορρόφησης FT - IR (4000 - 400 cm<sup>-1</sup>) ινωδών φυσικών ζεολίθων (νατρόλιθου, μεσόλιθου, σκολεσίτη, τομσονίτη, εντιγκτονίτη) ελήφθησαν και αποτιμήθηκαν. Με βάση τις παρατηρούμενες ταινίες απορρόφησης γίνεται συζήτηση αναφορικά με τις δομικές μονάδες των κρυστάλλων των ζεολίθων και ειδικότερα με τα μόρια ύδατος τα οποία βρίσκονται μέσα στα κανάλια και συνήθως συνδέονται με τα ανταλλάξιμα κατιόντα. Διαφορές που παρατηρήθηκαν στα φάσματα αποδίδονται κυρίως στην επίδραση των κατιόντων και στο λόγο Si/Al. Τα φάσματα FT - IR μπορούν να χρησιμοποιηθούν για την ταυτοποίηση και το χαρακτηρισμό των ζεολίθων που μελετήθηκαν.

### INTRODUCTION

Infrared (IR) spectroscopy is a well known physical method widely used for identification and study of any kind of chemical substances and materials (e.g., NAKAMOTO 1986). The modern IR spectrometers almost always use Fourier Transform techniques of spectral detection and analysis based on the principle of the Michelson interferometer which is a device for analysing the frequencies present in a composite signal (e.g., FERRARO & KRISHNAN 1990).

Infrared and recently FT-IR spectroscopy have been extensively used for the study of geological materials and consequently for minerals (e.g., MOENKE 1962, 1966, FARMER 1974, GADSDEN 1975, ESTEP-BARNES 1977, Mc MILLAN & HOFMEISTER 1988). FT-IR spectroscopy is now one of the common techniques applied in mineral sciences and generally complements the other methods in a routine

\* Aristotle University of Thessaloniki, Dept. of General & Inorganic Chemistry, 540 06 THESSALONIKI, Greece.

\*\* Aristotle University of Thessaloniki, Dept. of Solid State Physics, 540 06 THESSALONIKI, Greece.

\*\*\* Aristotle University of Thessaloniki, Dept. of Mineralogy - Petrology - Economic Geology, 540 06 THESSALONIKI, Greece.

study. However, in some cases there are significant advantages over other methods since the spectra can be obtained for crystalline or amorphous solids, liquids or gases, and can be easily applied to materials involving elements of low atomic weight. Subsequently, the technique is very useful in the case of minerals which exhibit a microporous character (such as zeolites) and which usually hold a high content of hydrous components (water molecules and/or hydroxyl anions) in their structure (Mc MILLAN & HOFMEISTER 1988, PUTNIS 1992, HAWTHORNE 1993).

### Fibrous natural zeolites and their IR spectra

According to GOTTARDI & GALLI (1985) the group of the fibrous natural zeolites includes the minerals natrolite ( $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}]\cdot 16\text{H}_2\text{O}$ ), tetranatrolite (tetragonal natrolite), paranatrolite (pseudoorthorhombic natrolite), mesolite ( $\text{Na}_{16}\text{Ca}_{16}[\text{Al}_{48}\text{Si}_{72}\text{O}_{240}]\cdot 64\text{H}_2\text{O}$ ), scolecite ( $\text{Ca}_8[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}]\cdot 24\text{H}_2\text{O}$ ), thomsonite ( $\text{Na}_4\text{Ca}_8[\text{Al}_{20}\text{Si}_{20}\text{O}_{80}]\cdot 24\text{H}_2\text{O}$ ), edingtonite ( $\text{Ba}_2[\text{Al}_4\text{Si}_6\text{O}_{20}]\cdot 8\text{H}_2\text{O}$ ) and gonnardite ( $\text{Na}_2\text{Ca}_2[\text{Al}_9\text{Si}_{11}\text{O}_{40}]\cdot 12\text{H}_2\text{O}$ ). The most common are natrolite, mesolite, scolecite, thomsonite and edingtonite which usually occur in altered volcanic rocks in many areas of the world (GOTTARDI & GALLI 1985, TSCHERNICH 1992). Fibrous natural zeolites have also been reported in ophiolitic rocks of Southern Greece (PHOTIADES & ECONOMOU 1991). On the basis of their structural characteristics the above mentioned zeolites are generally grouped in three structural groups (MEIER & OLSON 1992) : the NAT-type group (natrolite-tetranatrolite/paranatrolite-, mesolite, scolecite and gonnardite), the THO-type group (thomsonite) and the EDI-type group (edingtonite).

The structure of the fibrous zeolites is characterised by an aluminosilicate framework consisting of secondary building units (SBU) of the 4=1 type. These SBU are connected with each other to form characteristic chains (structural subunits - SSU) of the *fi* type. Those chains are further interconnected parallelly to [001] forming a three dimensional spatial network. Because of this arrangement of the SSU, 4-membered and 8-membered tetrahedral rings are created inside the framework. Successive 8-membered rings constitute open channels (2.6 X 3.9 Å for NAT-type, 2.3 X 3.9 Å & 2.2 X 4.0 Å for THO-type and 2.8 X 3.8 Å for EDI-type) proper to hold exchange-able cations and water molecules. It is notable that the structure of the fibrous zeolites is relatively "closed" with framework densities ( $T_{\text{sites}} / 1000 \text{ \AA}^3$ ) varying from 16.6 (edingtonite) to 17.8 (natrolite). The total pore volume is also varying from 22% for natrolite to 36% for edingtonite (SMITH 1988, Van KONINGSVELD 1991, TSITSISH-VILI et al. 1992, MEIER & OLSON 1992).

Infrared spectroscopic investigations concerning the fibrous natural zeolites have been carried out by several authors (e.g., MILKEY 1960, YUKHENEVICH et al. 1961, MOENKE 1962, 1966, PÉSCI-DONÁTH 1966, HAMAD 1977, PECHAR & RYKL 1980, 1983, PECHAR 1985, 1988, GOTTARDI & GALLI 1985, MIRZAI & DUBININ 1988). The above mentioned literature indicates, from one site of view, that a lot of work has been elaborated on this subject. In fact, complete spectroscopic investigations accompanied by detailed assignments have been performed almost only for natrolite. Deficiencies are observed in the case of the other fibrous zeolites while in some papers selected regions of the zeolite spectra are presented or even in some other the wavenumbers of the peaks are not listed. Furthermore, it should be noted that some of the IR spectra reported have been recorded by conventional grating IR spectrophotometers which do not always guarantee precision and high resolution.

The aim of the present study was the achievement of Fourier Transform Infrared (FT-IR) absorption spectra of certain well-characterised fibrous

natural zeolites (natrolite, mesolite, scolecite, thomsonite, edingtonite) in order to obtain information for their structural units and to detect aspects which can be used for identification and characterisation purposes.

#### MATERIALS AND METHODS

The fibrous natural zeolites investigated in the present study are well characterised samples from different localities of the world. The natrolite sample (supplied by Dr. F. Krantz / Bonn a. Rh.) is from Bennau, Westerwald, Germany and occurs as colorless distinguished fine acicular crystals on basaltic rock. The mesolite and scolecite (supplied by Dr N. Albantakis / Co, Athens, Greece) are from Poona, India and occur as radiating aggregates of fine colorless acicular crystals in basalt cavities. The thomsonite sample (supplied by Dr R.S.W. Braithwaite, UMIST, UK) is from Skye, Scotland and occurs as radiating bladed colorless crystals developed on chabazite in small basalt cavities. The edingtonite sample (also supplied by Dr R.S.W. Braithwaite, UMIST, UK) is from Shropshire, England and occurs in dolerite joint planes as white prismatic crystals developed on pale-green prehnite.

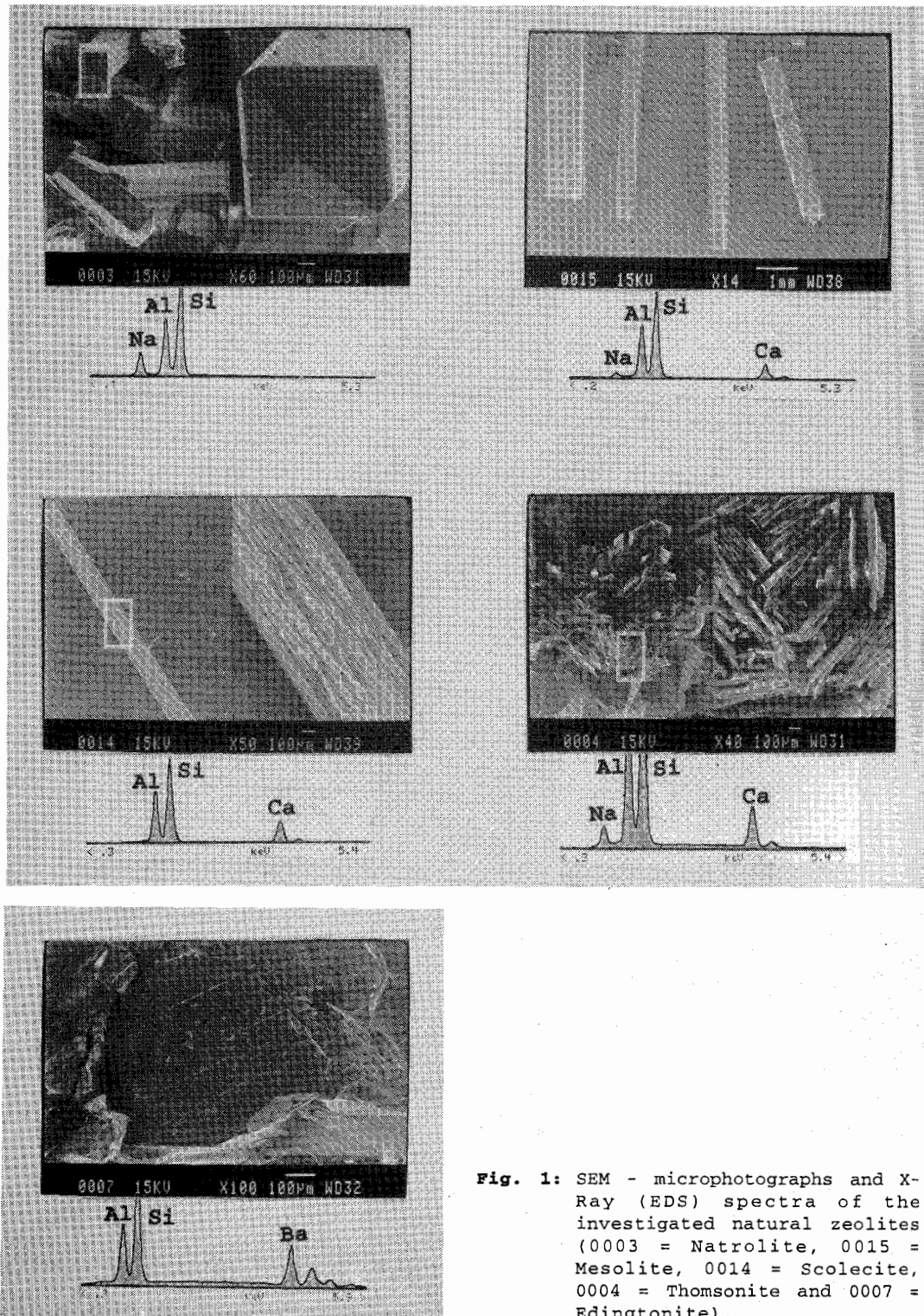
Pure crystals from all the samples were carefully detached from the rock, under a stereomicroscope, and cleaned using double-distilled water in ultrasonic bath. After cleaning the small stocks of the crystals were air-dried and placed for two weeks in a dessicator over saturated  $\text{Ca}(\text{NO}_3)_2$  solution (51% relative humidity) for equilibration of the hydrous components before any investigation. The materials were characterised by means of Powder XRD (Philips PW1820 diffractometer, Ni-filtered  $\text{CuK}\alpha$  radiation) and SEM (JSM 840-A JEOL SEM equipped with a LINK 10000 AN EDS). Thin sections of the zeolites were also investigated using a transmitted-light microscope.

The FT-IR spectra of the investigated natural zeolites were performed by means of a BRUKER IFS 113V FT-IR spectrometer at the FT-IR laboratory of the Aristotle University. The samples were examined using the KBr-pellet technique. For this purpose some crystals of each sample were carefully ground in an agate mortar and 2 mg of the produced crystalline powder were mixed with 200 mg KBr (Merck, spec troscopic grade) before pressing for pellet preparation. A blank pellet of pure KBr was also prepared and used as a background. The FT-IR absorption spectra were recorded in the  $4000\text{-}400\text{ cm}^{-1}$  region (mid - FT-IR absorption spectra) using a glowbar as radiation source and a DTGS/KBr detector. The scanner velocity was 10.51 KHz and the resolution achieved was  $2\text{ cm}^{-1}$ . The spectra were evaluated on the basis of the analogue BRUKER FT-IR computer software (OPUS IR - 2).

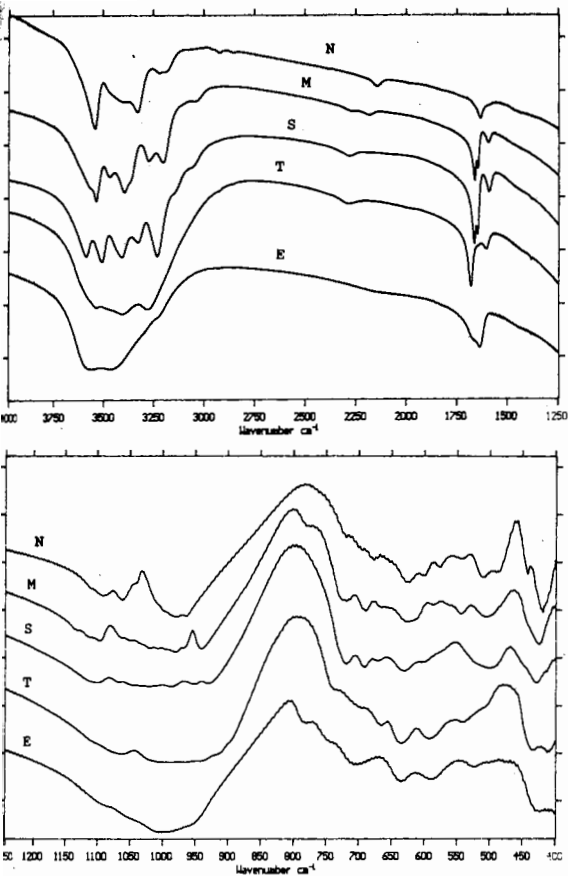
#### RESULTS AND DISCUSSION

The XRD and SEM analyses (Fig. 1) showed that the separated material contained only the appropriate zeolite phases. The FT-IR absorption spectra of the investigated natural zeolites are shown at Figure 2 and the main absorption bands are presented in Table 1. The spectra are characterised by absorption bands in the ranges  $3800\text{-}2800\text{ cm}^{-1}$ ,  $2400\text{-}2000\text{ cm}^{-1}$ ,  $1700\text{-}1600\text{ cm}^{-1}$ ,  $1250\text{-}850\text{ cm}^{-1}$  and  $850\text{-}400\text{ cm}^{-1}$ .

The absorption bands in the range  $3800\text{-}1600\text{ cm}^{-1}$  are generally due to the vibrations of the hydrous components present in the crystals of the zeolites (RYSKIN 1974, AINES & ROSSMAN 1984, ROSSMAN 1988). Particularly the  $3800\text{-}2800\text{ cm}^{-1}$  bands are attributed to the assymmetric and symmetric stretching vibrations  $\nu(\text{O-H})$ , while those in the range  $1700\text{-}1600\text{ cm}^{-1}$  to the bending  $\nu_{\text{bend}}(\text{H}_2\text{O})$  vibrations. The weak peaks in the range  $2400\text{-}2000\text{ cm}^{-1}$  could possibly be attributed to a combination of stretching and bending vibrations. There-



**Fig. 1:** SEM - microphotographs and X-Ray (EDS) spectra of the investigated natural zeolites (0003 = Natrolite, 0015 = Mesolite, 0014 = Scolecite, 0004 = Thomsonite and 0007 = Edingtonite).



**Fig. 2:** FT - IR absorption spectra of the investigated zeolites. N = Natrolite, M= Mesolite, S= Scolecite, T= Thomsonite, E = Edingtonite.

actions related to the water molecules are weaker. For the NAT-type zeolites the spectra seem to be more complicated because their structure is denser and the interactions related to the water molecules are stronger. However, the differences between the NAT-type zeolites which have the same framework and opening, especially at the bending vibrations could be attributed to their different exchangeable cations.

The bands in the range 1250-400  $\text{cm}^{-1}$  are generally due to the vibrations of the aluminosilicate framework of the zeolites (MOENKE 1974, FLANIGEN 1976). The 1250-850  $\text{cm}^{-1}$  very broad absorption band can be attributed to the asymmetric internal T-O stretching vibrations of the  $\text{PO}_4$  (T = Si, Al) primary tetrahedral building units (PBU) and the bands in the range 850-400  $\text{cm}^{-1}$  possibly both to the symmetric vibrations of the  $\text{PO}_4$  units and to vibrations related with the link-ages between the  $\text{TO}_4$  tetrahedra.

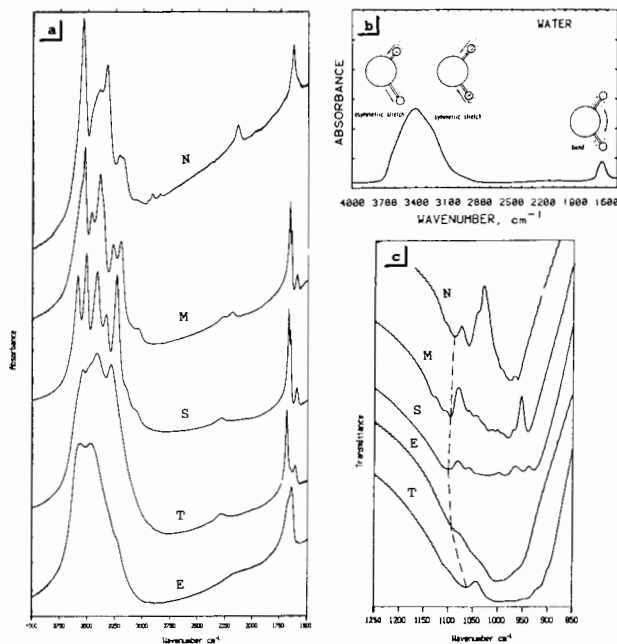
The similar framework of the investigated zeolites should result to identical spectra in the region 1250-850  $\text{cm}^{-1}$  (Fig. 3c). In fact, inspite

fore, the bands in the range 3800-1600  $\text{cm}^{-1}$  are related to the water molecules located inside the channels of the zeolites and/or associated with exchangeable cations.

For comparison reasons, the IR spectrum of pure liquid water is presented along with the spectra of the investigated zeolites at the same region (Fig 3 a&b). It is evident that the IR spectra of the zeolitic water differ from the relevant spectrum of pure liquid water. This could be attributed to the fact that the water molecules of the zeolites being in a restricted space inside the channels of the crystal structure, are strongly associated with the exchangeable cations and besides interact with the framework oxygens forming hydrogen bonds. Furthermore, the differences observed between the individual zeolite spectra in this region are due to the different kind and charge of the cations in each zeolite and the different channel sizes. Subsequently, the FT-IR spectrum of edingtonite seems to be simpler compared with the others because its structure is the most open and the inter-

**Table 1.:** The main FT - IR absorption bands of the investigated zeolites (vs=very strong, s=strong, m=medium, w=weak, sh=shoulder).

<u>Natrolite</u> : 3540s, 3470sh, 3400m, 3329s, 3220m, 3183sh, 2143w, 1634m, 1110sh, 1093s, 1063s, 1042sh, 982vs, 965vs, 677m, 623s, 602s, 577m, 542m, 509s, 488s, 442m, 419s.
<u>Mesolite</u> : 3569sh, 3536s, 3468m, 3395m, 3358sh, 3275m, 3202m, 3043sh, 2270sh, 2181w, 1663m, 1647w, 1593w, 1097s, 1020s, 982vs, 942s, 719m, 689m, 629s, 587m, 544m, 506m, 425s.
<u>Scolecite</u> : 3585s, 3507s, 3409s, 3328s, 3233s, 3140sh, 3053sh, 2280w, 1665m, 1648m, 1592w, 1101s, 1067s, 1021vs, 988vs, 952s, 930s, 720m, 691m, 671m, 630s, 501s 429s.
<u>Thomsonite</u> : 3539s, 3470sh, 3404s, 3282s, 2282w, 1682m, 1605w, 1063s, 995vs, 968vs, 940s, 915sh, 665m, 635s, 593s, 542m, 436s, 412s.
<u>Edingtonite</u> : 3558s, 3468s, 3220sh, 1677sh, 1639m, 1093sh, 1007vs, 953sh, 701m, 635s, 592s, 524m.



**Fig. 3:** a) FT - IR spectra of the zeolites, expressed in absorbance units, in the region 4000 - 1500  $\text{cm}^{-1}$ . b) Infrared spectrum of pure liquid water (after AINES & ROSSMAN 1984). c) FT - IR spectra of the zeolites in the region 1250 - 850  $\text{cm}^{-1}$ . For abbreviations see Fig. 2.

of the appeared differences, the likeness of this very broad band among the zeolites is obvious, considering extensive overlapping of bands due to vibrating groups having bonds with small energy differences. Some dissimilarities in the shape of this band could possibly be attributed to the kind and charge of the cations which are associated with the framework inside the lattice and which influence the charge distribution

of the adjacent  $\text{TO}_4$  vibrating groups. Therefore, although the NAT-type zeolites have precisely the same frame-work, exhibit differences in their FT-IR spectra in the  $1250\text{-}850\text{ cm}^{-1}$  region due to the cation effect mentioned above. On the other hand the simplicity of thomsonite and edingtonite spectra in the same region could mainly be explained taking into account their smaller framework density.

However, it should be mentioned that in the case of thomsonite a considerable shift to lower frequencies (about  $30\text{ cm}^{-1}$ ) is observed (Table 1 and Fig. 3c). This is clearly shown in the region of  $1101\text{-}1063\text{ cm}^{-1}$ . This shift is attributed to the lower Si/Al ratio (equal to 1.0) of thomsonite, compared to the corresponding ratio of the other investigated zeolites (Si/Al ratio = 1.5).

### CONCLUSIONS

The FT-IR absorption bands of the fibrous natural zeolites, presented in this study, in the range  $3800\text{-}1600\text{ cm}^{-1}$  are due to the water molecules located inside the channels. The differences observed are attributed to the associated cations and the type of the channels. The bands in the range  $1250\text{-}400\text{ cm}^{-1}$  are generally due to the vibrations of the aluminosilicate framework of the zeolites. The differences observed in the  $1250\text{-}850\text{ cm}^{-1}$  region are attributed to cation effects and to the framework density, while the assigned shifts are related to the Si/Al ratio.

The FT-IR spectra of the zeolites in study, can be generally used for identification and characterisation purposes. The most significant regions for this aim are those of  $1700\text{-}1600\text{ cm}^{-1}$  and  $1250\text{-}850\text{ cm}^{-1}$ .

### ACKNOWLEDGEMENTS

We express our gratitude to Dr. R.S.W. Braithwaite (UMIST, UK) for providing the thomsonite and edingtonite samples and to Dr. E. Pavlidou and M.Sc. V. Kyriakopoulos for their assistance in the SEM studies.

### REFERENCES

- AINES, R. and ROSSMAN, G. (1984). Water in minerals? A peak in the infrared. - *J. Geophys. Res.*, 89(B6), 4059-4071.
- ESTEP-BARNES, P. (1977). Infrared spectroscopy. In J. ZUSSMAN (Ed.) *Physical methods in determinative mineralogy, 2nd edition, Academic Press, London*, 11, 259-603.
- FARMER, V. (1974). The infrared spectra of minerals. Mineralogical Society monograph 4, London.
- FERRARO, J. and KRISHNAN, K. (1990). Practical Fourier Transform Infrared spectroscopy. Academic Press, San Diego.
- FLANIGEN, E. (1976). Structural analysis by infrared spectroscopy. In J. RABO (ed.) *Zeolite chemistry and catalysis, ACS Monograph 171*, 80-117.
- GADSDEN, J. (1975). Infrared spectra of minerals and related inorganic compounds. Butterworths, London.
- GOTTARDI, G. and GALLI, E. (1985). Natural zeolites. Springer - Verlag, Berlin.
- HAMAD, S. el. (1977). An experimental study of the water molecules in

- natrolite. - *Bull. Geol. Soc. Finland*, 49, 1-6.
- HAWTHORNE, F. (1993). Minerals, mineralogy and mineralogists: past, present and future. - *Canad. Mineral.*, 31, 253-296.
- KONINGSVELD, H. van. (1991). Structural subunits in silicate and phosphate structures. In H. van BEKKUM, E. FLANIGEN & J. JANSEN (Eds.) *Introduction to zeolite science and practice*, Elsevier, Amsterdam, 35-76.
- Mc MILLAN, P. and HOFMEISTER, A. (1988). Infrared and Raman spectroscopy. In F. HAWTHORNE Ed. *Spectroscopic methods in mineralogy and geology, Reviews in Mineralogy 18*, Am. Mineral. Society, 99-159.
- MEIER, W. and OLSON D. (1992). Atlas of zeolite structure types. Butterworth-Heinemann, London.
- MILKEY, R. (1960). Infrared spectra of some tectosilicates. - *Am. Mineralogist*, 45, 990-1007.
- MIRZAI, J. and DUBININ, M. (1988). IR-spectroscopic investigation of dehydration process of the natrolite group natural zeolites. In D. KALLO & H. SHERRY (Eds.) *Occurrence, properties and utilization of natural zeolites*, Akademiai Kiado, Budapest, 265-273.
- MOENKE, H. (1962). *Mineralspectren*, I. Akademie - Verlag, Berlin.
- MOENKE, H. (1966). *Mineralspectren* II. Akademie - Verlag, Berlin.
- MOENKE, H. (1974). Silica, the three-dimensional silicates, borosilicates and beryllium silicates. In V. Farmer (Ed.) *The Infrared spectra of minerals*, *Mineralogical Society monograph 4*, 365-382.
- NAKAMOTO, K. (1986). Infrared and Raman spectra of inorganic and coordination compounds. 4th edition, J. Wiley and Sons, New York.
- PECHAR, F. and RYKL, D. (1980). Infrared spectra of the natural zeolites of the natrolite group. - *Cas. mineral. geol.*, 25(3), 239-251 (in Czech).
- PECHAR, F. and RYKL, D. (1983). Study of the vibrational spectra of natural natrolite. - *Can. Mineralogist*, 21, 689-695.
- PECHAR, F. (1985). Study of the O-D character of the natrolite structure by i.r. spectroscopy. - *Zeolites*, 5, 139-144.
- PECHAR, F. (1988). Investigation of the disordered condition of natrolite, mesolite and thomsonite by means of IR reflection spectra. In D. KALLO & H. SHERRY (Eds.) *Occurrence properties and utilization of natural zeolites*, Akademiai Kiado, Budapest, 309-319.
- PECSI-DONATH, E. (1966). On the relationships between lattice structure and "zeolite water" in gmelinite, heulandite and scolecite. - *Acta Min. Petr. Univ. Szeged*, 17(2), 143-158.
- PHOTIADES, A. and ECONOMOU, G. (1991). Alteration hydrothermale sous marine des basaltes et des dolerites (facies zeolitique) de l'unité moyenne "volcanique" de l'Argolide septentrionale (Peloponnese, Grece). - *Bull. Geol. Soc. Greece*, XXV/2, 301-319.
- PUTNIS, A. (1992). *Introduction to Mineral Sciences*. Cambridge University Press.
- ROSSMAN, G. (1988). Vibrational spectroscopy of hydrous components. In F. HAWTHORNE (Ed.) *Spectroscopic methods in mineralogy and geology, Reviews in Mineralogy 18*, Am. Mineral. Society, 193- 204.
- RYSKIN, Y. (1974). The vibrations of protons in minerals : hydroxyl, water and ammonium. In V. FARMER (Ed.) *The Infrared spectra of miner-*



- als, *Mineralogical Society monograph 4*, 137-181.
- SMITH, J. (1988). Topochemistry of zeolites and related materials. - *Chem. Rev.*, 88, 149-182.
- TSCHERNICH, R. (1992). Zeolites of the world. Geoscience Press Inc., Phoenix.
- TSITSISHVILI, G., ANDRONIKASHVILI, T., KIROV, G. and FILIZOVA, L. (1992). Natural zeolites. Ellis Horwood, Sussex.
- YUKHENEVICH, A., KARYAKIN, A., KHITAROV, N. and SENDEROV, E. (1961). Infrared spectroscopic study of some zeolites and the nature of the water bond in natrolite. - *Geokhimiya*, 10, 937-944.