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# Chemical and thermal modification of natural HEU-type zeolitic materials from Armenia, Georgia and Greece

G.E. Christidis<sup>a,\*</sup>, D. Moraetis<sup>a</sup>, E. Keheyan<sup>b</sup>, L. Akhalbedashvili<sup>c</sup>,  
N. Kekelidze<sup>c</sup>, R. Gevorkyan<sup>d</sup>, H. Yeritsyan<sup>e</sup>, H. Sargsyan<sup>e</sup>

<sup>a</sup>Department of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Greece

<sup>b</sup>Institute of Nuclear Chemistry, CNR, Monterotondo Scalo, Rome 00016, Italy

<sup>c</sup>Department of Physics, Tbilisi State University, P.O. Box 380028, Chavchavadze ave. 1, Tbilisi, Georgia

<sup>d</sup>Department of Mineralogy and Petrography, Yerevan State University, Alek Manukyan Str. 1, 375025 Yerevan, Armenia

<sup>e</sup>Solid State Radiation Physics Department, Yerevan Physics Institute, Alikhanyan Bros. St. 2, 375036 Yerevan, Armenia

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## Abstract

Three HEU-type zeolites from Armenia, Georgia and Greece formed from alteration of volcanic glass were treated with dilute KOH and subsequently either reacted with 6N HCl or heated at 700 °C. The raw materials and the reaction products were examined with X-ray diffraction (XRD), infrared spectroscopy (FTIR) and N<sub>2</sub> gas adsorption. The cation exchange capacity (CEC) of the zeolites was also determined. The Greek zeolite has thermal characteristics typical for heulandite I, while the Armenian and Georgian zeolites have characteristics typical for heulandite III (clinoptilolite). KOH treatment increased slightly specific surface area (SSA) and microporosity due to dissolution of amorphous material. Acid treatment increased significantly both specific surface area and microporosity, as determined by *t*-plots, and decreased CEC. This is attributed to partial dissolution of both Si-tetrahedra and free linkages, which yielded secondary micropores and destroyed specific exchange sites of the HEU-type zeolites. Heating decreased both specific surface area and microporosity.

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**Keywords:** Heulandite; Clinoptilolite; Treatment; Surface modification

## 1. Introduction

Zeolites are crystalline hydrated aluminosilicates of the alkalis and alkaline earths. Natural zeolites form in several geological environments such as hydrother-

mal, burial metamorphic, closed system (including alkaline lakes), open system and weathering profiles (Hay and Sheppard, 2001). They have a framework structure characterized by the existence of interconnected cavities or cages, occupied by the relatively large cations and water molecules (Gottardi and Galli, 1985). These cavities form pores of molecular dimensions. Zeolites have been utilized successfully by the chemical industry and in environmental protection over the last 40 years, because of their

\* Corresponding author. Tel.: +30-28210-37622; fax: +30-28210-37888.

E-mail address: [christid@mred.tuc.gr](mailto:christid@mred.tuc.gr) (G.E. Christidis).

remarkable physical and chemical properties which include molecular sieving, absorbing and cation exchange capacity (Mumpton, 1977; Breck, 1974; Hanson, 1995). More than 50 distinct species of natural zeolites and 100 types of synthetic zeolites are known at present.

Clinoptilolite (Gottardi and Galli, 1985) is a widespread natural zeolite belonging to the HEU-type zeolite group (Baerlocher et al., 2001). It is a thermally stable heulandite (heulandite-type III after Boles, 1972), characterized by high Si/Al ratio and predominance of Na and K in exchangeable sites (Alietti, 1972; Boles, 1972). Clinoptilolite has been utilized extensively in environmental applications such as treatment of wastewater from nuclear facilities (Mercer and Ames, 1978), remediation of radioactive soils (Nishita and Haug, 1972; Valcke et al., 1997), the treatment of sewage and agriculture effluents (Mercer et al., 1970; Marton and Marculescu, 1988), etc. In such environmental applications, clinoptilolite is valued for its high cation exchange selectivity for Cs, Sr and  $\text{NH}_4^+$  during ion exchange. More recently formation of surfactant-modified zeolites has yielded products with high adsorbing capacity for inorganic and organic molecules (Cadena and Cazares, 1996; Sullivan et al., 1998; Li et al., 2000).

The structure and subsequently physical and chemical properties of clinoptilolite may be modified by treatments such as heating and/or inorganic acid attack. Acid treatment usually modifies the silicate structure by formation of a non-crystalline-Si-layer and releasing of Al (Ragnarsdottir et al., 1996; Misaelides et al., 1996). The dissolution does not seem to occur via a step retreat but rather by a layer-by-layer dissolution, whereby the  $\text{H}^+$  cations attack the surface species  $>\text{SiOH}$  and either  $\text{Si-O-Al}$  or  $\text{Si-O-Si}$  bonds of the uppermost aluminosilicate layer (Yamamoto et al., 1996). The process is known as dealumination (Kühl, 1999) and can be compared to acid activation of smectites (cf. Tkac et al., 1994; Christidis et al., 1997). Acid-treated HEU-type zeolites have been tested as catalysts (Kallo, 1988; Benashvili et al., 1988). The purpose of this contribution is the treatment of HEU-type zeolitic materials from Armenia, Georgia and Greece with different reagents and high temperature and the examination of the influence of each treatment on important physical properties of the materials.

## 2. Materials and methods

The HEU-type zeolitic materials were collected from Armenia (Nor Kokhb deposit in Noyemberian region), Georgia (Khekordzula deposit) and Greece (Pentalofos Evros Area, Thrace in NE Greece). Detailed mineralogical and petrographic study of the Armenian zeolite has been carried out by Petrosov and Sadoyan (1998, 1999). The geological and mineralogical characteristics of the Georgian zeolite have been described by Gvaharia et al. (1974), while the Greek HEU-type zeolitic material deposits at Evros Area, NE Greece have been described by Tsolis-Katagas and Katagas (1990) and Marantos and Perdikatsis (1994). The Armenian and Georgian HEU-type zeolitic materials have been characterized as typical heulandite type III zeolites, i.e. (clinoptilolites) while the Greek materials are mixtures of heulandite type II and III (Marantos and Perdikatsis, 1994). All materials are rich in zeolites (heulandite content 80–90%) and contain minor amounts of quartz, plagioclase opal-CT smectite and mica. The mineralogical composition of the materials studied is given in Table 1.

The materials were dried at 105 °C, ground in ball mill and subsequently with pestle and mortar so as to pass from the 125- $\mu\text{m}$  sieves and stored at room temperature. The zeolites were subsequently treated with 0.25% KOH solutions at 50 °C for 90 min using a 1:10 solid to liquid ratio. The suspensions were filtered and the solids were washed until pH 7. This process, which is characterized alkali-activation caused partial K-exchange (see below). K-activated materials were stored in dessicator for a series of subsequent chemical and thermal treatments. Acid treatment was carried out with 6N HCl at 80 °C. The materials were treated twice for 40 min. The zeolites were washed thoroughly until

Table 1  
Mineralogical composition of the materials studied

Armenian HEU-type zeolitic material	Georgian HEU-type	Greek HEU-type zeolitic material
Clinoptilolite (M)	Clinoptilolite (M)	Heulandite (M)
Quartz (Min)	Plagioclase (Min)	Quartz (Min)
Plagioclase (Min)	Quartz (T)	Feldspar (Min)
Smectite (T)	Smectite (T)	Smectite (T)
		Biotite (T)
		Muscovite (T)

M = major phase, Min = minor phase, T = trace phase.

pH 7 between these two treatments. After the second treatment, the zeolites were filtered under vacuum, washed until pH 7 dried at 60 °C and ground gently with pestle and mortar so as to pass through a 125- $\mu$ m sieve. Finally, thermal treatment involved heating of the K-treated zeolites at 700 °C for 10 h. It is expected that heulandites of type I and possibly of type II would

be thermally unstable under these heating conditions (Gottardi and Galli, 1985). The heated materials were ground with pestle and mortar so as to pass through a 125- $\mu$ m sieve.

The mineralogical transformations of the acid and thermally treated materials were monitored by X-ray diffraction (XRD), using a Siemens D500 XRD

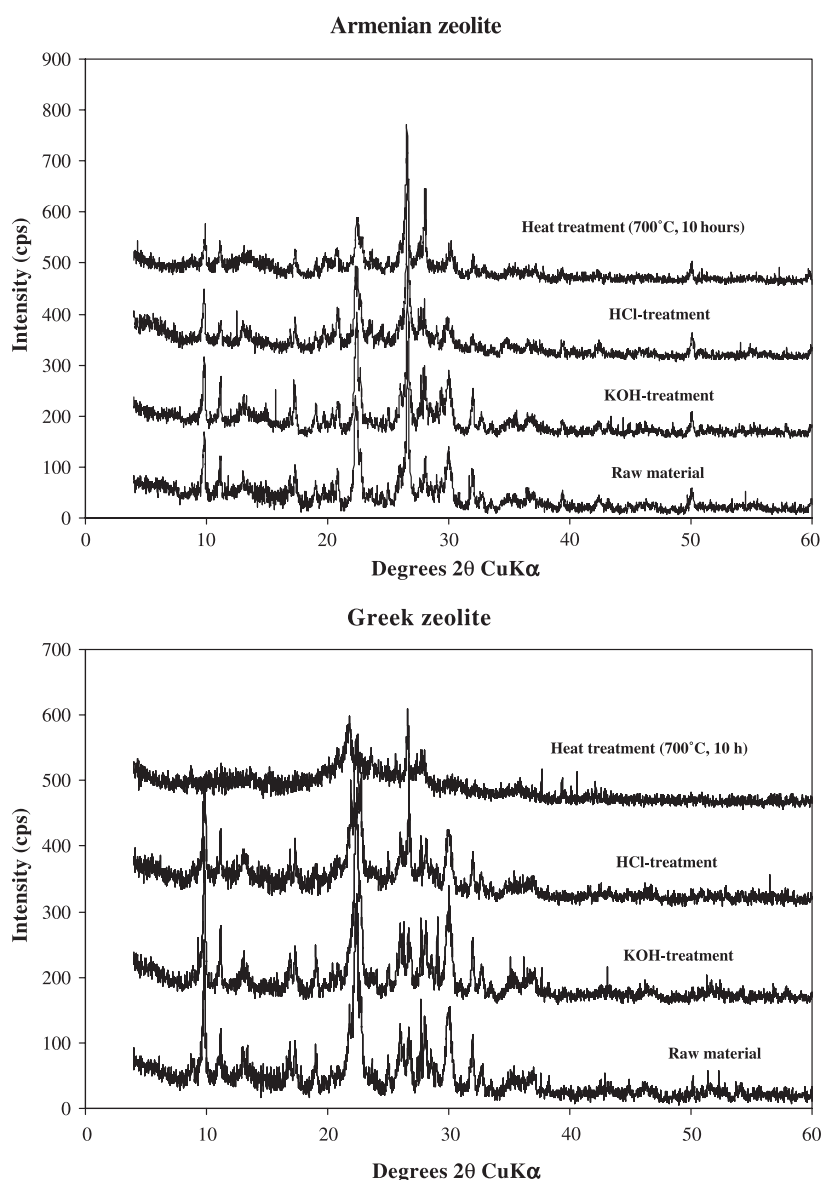


Fig. 1. X-ray diffraction traces of the raw and treated Greek and Armenian HEU-type zeolites.

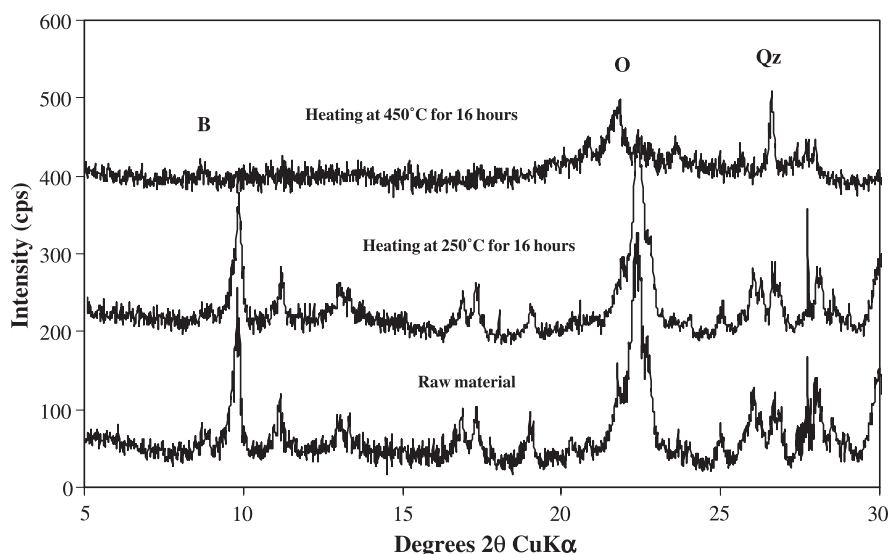


Fig. 2. X-ray diffraction traces of the Greek **HEU**-type zeolitic material heated at 250 and 450 °C for 16 h. O=opal-CT, Qz=quartz.

operating at 35 kV and 35 mA, with a graphite monochromator, using CuK $\alpha$  radiation. A 0.02° scanning step and 1-s scanning time per step was used. Infrared spectroscopy (FTIR) spectra of the raw materials and the products from chemical and thermal treatments were obtained with a Perkin-Elmer 1000 FTIR spectrometer. Approximately 2 mg of material was diluted by 200 mg KBr. FTIR spectra were obtained in the 400–4000-cm<sup>-1</sup> range with transmission mode, using 25 scans. Adsorption–desorption isotherms of the raw materials and the products from chemical and thermal treatments were obtained by N<sub>2</sub> gas adsorption using a NOVA 2200 surface area analyzer (Quantachrome). Samples were outgassed overnight at 140 °C under vacuum

Table 2

CEC (meq/100 g) of the various **HEU**-type zeolites, before and after various treatments

CEC of the <b>HEU</b> -type zeolites (meq/100 g)			
Treatment	Greek	Armenian	Georgian
Raw material	147	136	181
Acid treatment	108 (0.73)	81 (0.6)	54 (0.3)
Heating	9.5 (0.06)	66 (0.45)	118 (0.65)

Values in brackets indicate the fraction of the original CEC attained after each treatment.

(10<sup>-2</sup> Torr). Specific surface area was determined by BET equation (Brunauer et al., 1938) using the  $P/P_0$  range 0–0.35 of the adsorption branch of the isotherms, while pore size distribution was determined from the desorption branch of the isotherms. Cation exchange capacity was measured by saturation with K<sup>+</sup> (KCl 1 M) and then by replacement of K by Cs<sup>+</sup> (CsCl 1 M) and measurement of the concentration of

Table 3

FTIR results for the materials studied

Absorption bands of the zeolites studied (cm <sup>-1</sup> )		
Armenian	Georgian	Greek
466 <sup>a</sup>	462 <sup>a</sup>	464 <sup>a</sup>
521	524	514
604	610	600
670,682 <sup>b</sup>	670 <sup>b</sup>	662 <sup>b</sup>
694	705	
724 <sup>b</sup>	726 <sup>b</sup>	710 <sup>b</sup>
778		
1028 <sup>c</sup>	1032 <sup>c</sup>	1034 <sup>c</sup>
1202	1202	1192

Remaining bands are attributed to free linkages (ring structure pore opening, etc.).

<sup>a</sup> T–O bending.

<sup>b</sup> Symmetric tetrahedral stretching.

<sup>c</sup> Asymmetric tetrahedral stretching.

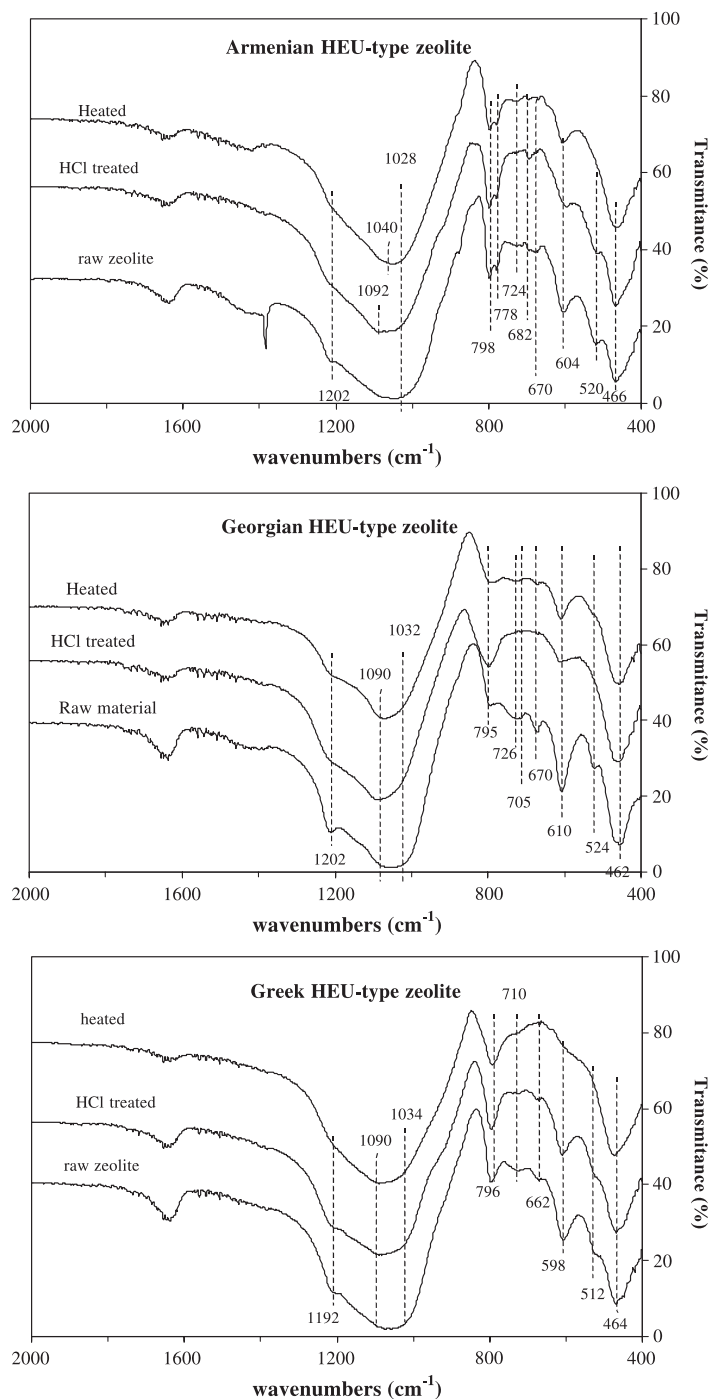


Fig. 3. FTIR spectra of the raw and treated Greek, Armenian and Georgian HEU-type zeolites.

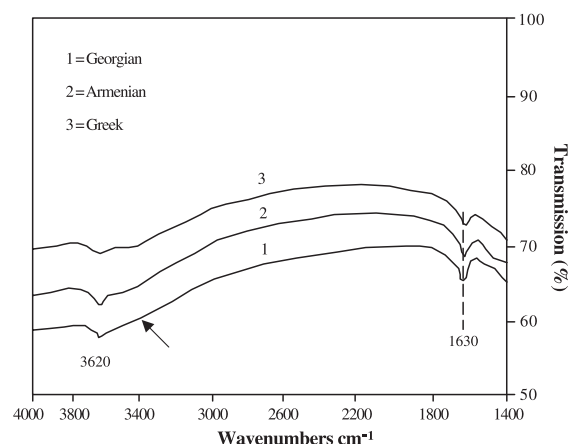


Fig. 4. FTIR spectra of the heated Greek, Armenian and Georgian HEU-type zeolitic materials.

K in the supernatant solution by atomic absorption spectrometry (Perkin-Elmer Analyst 100).

### 3. Results

#### 3.1. X-ray diffraction and cation exchange capacity

XRD results of the raw materials and reaction products are shown in Fig. 1. Prolonged heating at 700 °C did not affect significantly the Armenian and Georgian HEU-type zeolitic materials. The intensity of the [102] diffraction maximum of these materials decreases slightly and a slight increase of the background between 20° and 30° 2θ is observed. On the contrary, the Greek HEU-type zeolitic material collapsed and was replaced by a poorly crystallized phase resembling opal-CT (Fig. 1). Heating of all zeolites at 450 °C for 16 h (Boles, 1972) did not cause contraction of the Armenian and Georgian HEU-type zeolitic materials. Therefore, both materials have thermal behaviour typical of type III heulandites, i.e. clinoptilolites (Gottardi and Galli, 1985). The Greek material collapsed after prolonged heating at 450 °C and displayed insignificant contraction after heating at 250 °C (Fig. 2). Such a thermal behaviour is typical for type I heulandites. Also, Akhalbedashvili et al. (2002) observed that the Greek material collapses after heating at 400 °C under vacuum. It is interesting that Marantos and Perdikatsis (1994) reported type II heulandite at the Pentalofos deposit based on thermal behaviour. The

discovery of type I heulandite in the Pentalofos deposit suggests the existence of significant compositional variation of the HEU-type zeolite in this deposit.

Although alkali-treatment has been reported to cause layer-by layer dissolution of HEU-type zeolites similar to acid treatment (Yamamoto et al., 1996) in this study, KOH treatment does not seem to have affected significantly the zeolite structure. However, the resolution of the traces (peak/background ratio) increased slightly. Acid treatment with 6N HCl affected the structure of all zeolites. More specifically, the intensity of the [102] diffraction maximum decreases substantially. Also, the Georgian zeolite is more severely affected by acid treatment compared to its counterparts. Moreover, an increase of the background between 20° and 30° 2θ is evident, suggesting deposition of amorphous material due to acid dissolution of zeolites. Similar features have been observed by Misaelides et al. (1996) and are common during acid activation of smectite-rich clays (e.g. Christidis et al., 1997).

The results from cation exchange capacity (CEC) measurements are listed in Table 2. Both heating and acid treatment decrease the CEC of all HEU-type zeolites. Natural Georgian HEU-type zeolitic material displays greatest CEC compared to other two zeolites, while the Armenian and Greek zeolites have comparable CEC. The Greek zeolite displays best stability in acid treatment compared to the Armenian and the Georgian samples, but it does not display structural charge after heating due to structural collapse (Fig. 1). The observed CEC is attributed to small amounts of dehydroxylated smectite present and possibly to traces of residual clinoptilolite. It is interesting that the Georgian material retains most of its CEC after heating at 700 °C.

#### 3.2. FTIR results

The results from the FTIR study are listed in Table 3 and Fig. 3. Assignment of the various absorption bands

Table 4  
Specific surface area of the HEU-type zeolites tested (m<sup>2</sup> g<sup>-1</sup>)

Specific surface area (m <sup>2</sup> g <sup>-1</sup> )			
Treatment	Greek	Armenian	Georgian
Raw material	17.1 (22.8)	19.6 (20.6)	16.8 (13.4)
Acid treatment	140	126	35.4
Heating	16.2	16.7	15.9

The values in brackets indicate after KOH treatment.

follows suggestions of Breck (1974). The FTIR bands obtained for the three materials are typical for minerals of the HEU-group (Russel and Fraser, 1994). The band at  $600\text{--}605\text{ cm}^{-1}$  is very intense in the Georgian HEU-type zeolitic material. The Greek HEU-type zeolitic material develops the same absorption bands systematically at a slightly lower frequency ( $\sim 10\text{ cm}^{-1}$ ) compared to its Armenian and Georgian counterparts (Table 3). This is a common feature of heulandite when compared with clinoptilolite (Russel and Fraser, 1994).

Heating and acid treatment with HCl decreased significantly the intensity of the bands, especially those attributed to free linkages (Fig. 3). In the acid-treated materials, the intensity of the band at  $1034\text{ cm}^{-1}$  (T–O asymmetric stretching) decreases and a new band appears at  $1090\text{ cm}^{-1}$ . This band is attributed to amorphous silica (Moenke, 1974) and is also present in acid-activated smectites (e.g. Madejova et al., 1998; Christidis et al., *in press*). The acid-treated Greek zeolite shows an additional band at  $930\text{ cm}^{-1}$ , which is also assigned to amorphous silica (Moenke, 1974;

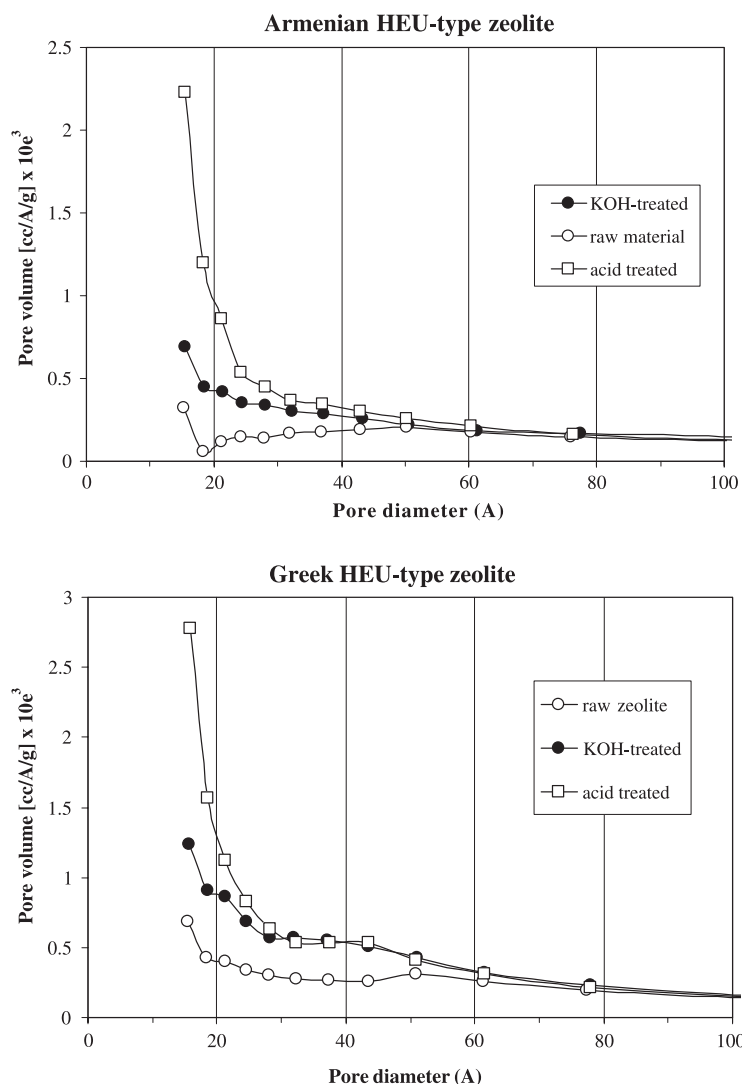


Fig. 5.  $\text{N}_2$  adsorption isotherms of the original and treated Greek and Armenian HEU-type zeolites.



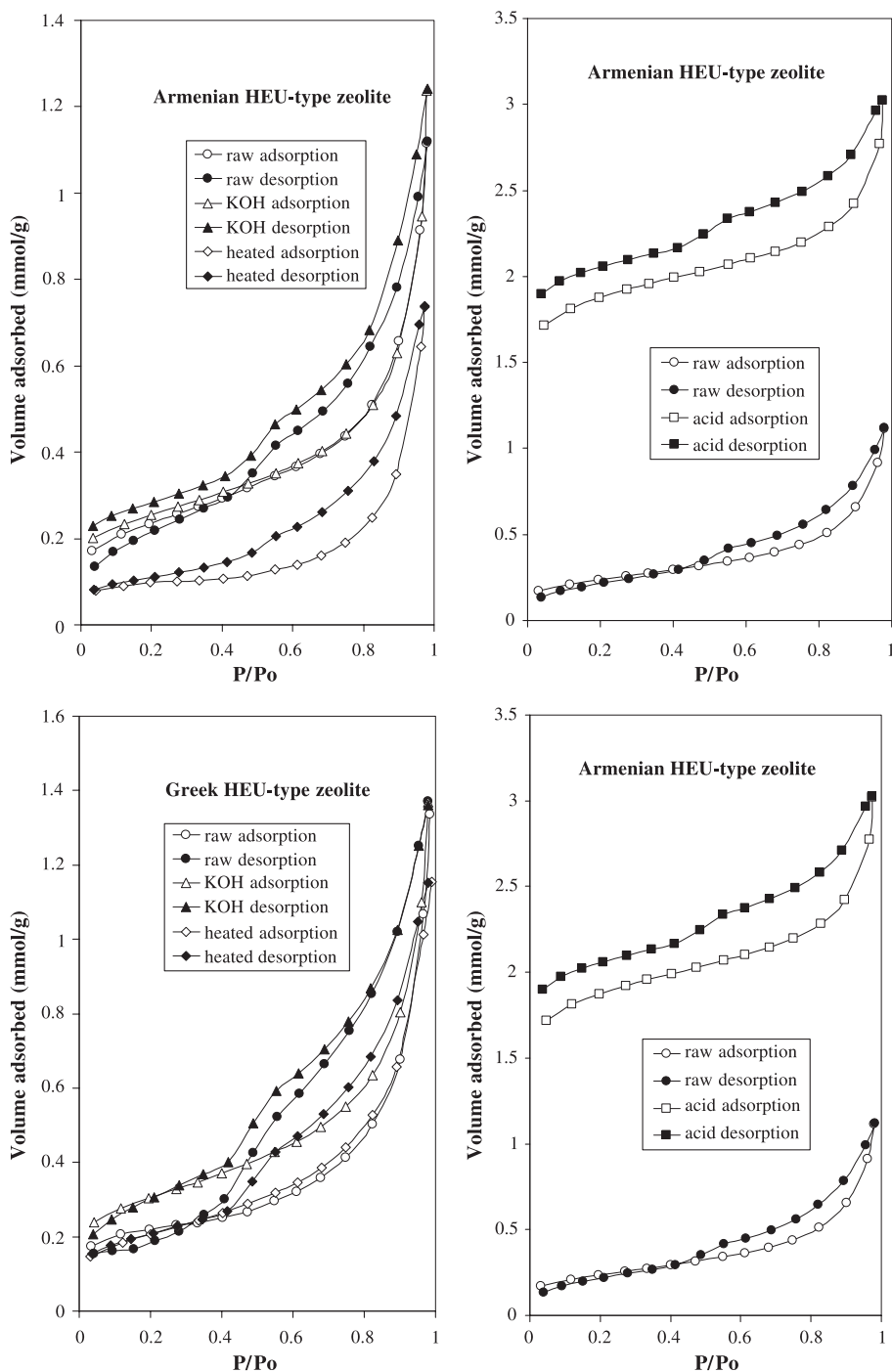


Fig. 6. Pore size distribution of the raw and treated Greek and Armenian HEU-type zeolites.

Misaelides et al., 1996). In the heated materials, the intensity of the bands at  $3600\text{--}3620\text{ cm}^{-1}$  (OH stretching) and  $1630\text{ cm}^{-1}$  (H–O–H bending) decrease significantly but are not eliminated, even in the Greek zeolite (Fig. 4). By contrast, Joshi et al. (1997) observed a nearly total elimination of the OH-stretching bands for HEU-type zeolites heated above  $500\text{ }^{\circ}\text{C}$ . The difference is attributed to the presence of dioctahedral Al-smectite in all three samples examined, which may not dehydroxylate completely at  $700\text{ }^{\circ}\text{C}$ . Also, the band at  $1630\text{ cm}^{-1}$  is attributed to  $\text{H}_2\text{O}$  molecules associated with interlayer cations of smectite. The intensity of the band at  $3420\text{ cm}^{-1}$ , which is assigned to loosely bonded water molecules (arrow in Fig. 4), is affected by heating to a lesser degree.

The heated Greek material is essentially collapsed. Also, the structure of acid-treated Georgian HEU-type zeolitic material was more intensively affected compared to the heated material. On the contrary, the structure of this zeolite is sufficiently retained after heat treatment. In general, acid treatment with HCl destroys both free linkages and Si-tetrahedra (Fig. 3). Also, with the exception of the Greek zeolite, which collapsed, the structure of the remaining materials remains intact after heating. The decrease in intensity and the broadening of bands related with free linkages may indicate structural distortion (Joshi et al., 1997). Finally, all materials display a significant increase of the band at  $795\text{--}800\text{ cm}^{-1}$  after each treatment. This band is also attributed to amorphous silica or the opal-CT-like phase (heated Greek zeolite) formed during

treatments by dissolution of the zeolite structure (Moenke, 1974; Madejova et al., 1998; Christidis et al., in press).

### 3.3. Surface area and pore size distribution

The specific surface areas of the zeolites are listed in Table 4, while adsorption–desorption isotherms are shown in Fig. 5. All materials display type-II isotherms (Sing et al., 1985). Acid treatment caused a five-fold increase of specific surface area (SSA) of the Greek and Armenian zeolites. On the contrary, the SSA of the Georgian HEU-type zeolitic material was not affected significantly by acid treatment. KOH treatment did not affect adsorption–desorption isotherms significantly, while heating decreased adsorption of  $\text{N}_2$  gas, for all three zeolites compared to their raw counterparts (Fig. 5). Both heated and KOH-treated samples display isotherms with type III hysteresis attributed to  $\text{N}_2$ -condensation in mesopores (Sing et al., 1985). Acid treatment modified adsorption isotherms. In both Armenian and Greek acid-treated zeolites, hysteresis due to  $\text{N}_2$  retention in micropores is observed. This feature is more pronounced in the Armenian zeolite (Fig. 5). Nevertheless, similar to their untreated counterparts, the acid-treated zeolites display type III hysteresis.

Modifications in pore size distribution of the Armenian and Greek zeolites after various treatments are shown in Fig. 6. KOH treatment resulted to a moderate increase of mesoporosity (pore size ranging between 20 and  $500\text{ \AA}$ ) and microporosity (pores  $<20\text{ \AA}$ ) for

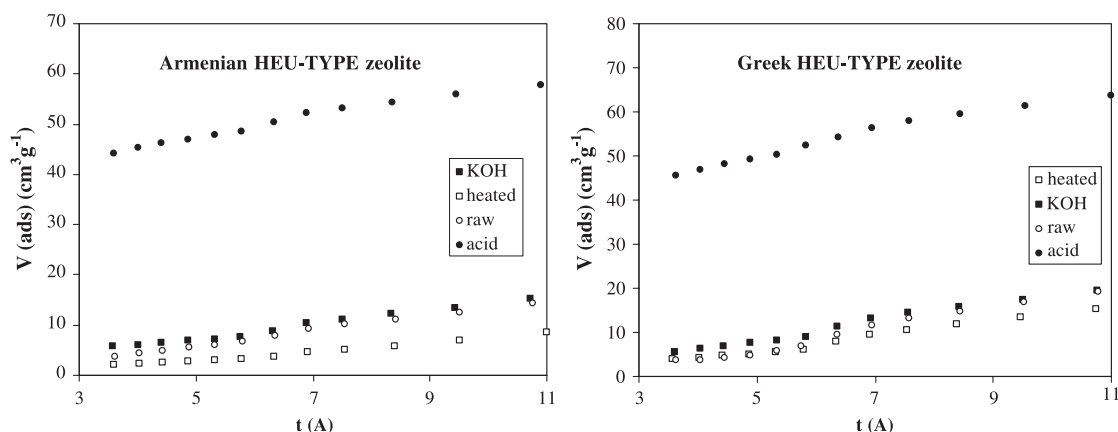


Fig. 7.  $t$ -plots of the raw and treated Greek and Armenian HEU-type zeolites.

Table 5

Specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) allocated to the external surfaces and the micropores of the natural and the treated HEU-type zeolites

	Armenian		Georgian		Greek	
	External	Micropore	External	Micropore	External	Micropore
Raw	15.57	4.03	12.55	4.25	14.30	1.30
Acid-treated	21.98	104.04	12.73	13.53	25.66	99.77
KOH-treated	13.11	5.79	11.24	2.34	17.31	5.49
Heated			11.57	2.20	16.65	0

both zeolites, while acid treatment resulted to a significant increase of microporosity and to a lesser degree of mesoporosity. The significant increase of microporosity in the acid-treated Greek and Armenian zeolites is clearly illustrated in the  $t$ -plots (Fig. 7, Table 5). A  $t$ -plot is a plot of the volume of gas adsorbed versus  $t$ , the statistical thickness of an adsorbed film, and is used for quantitative evaluation of microporosity (Sing et al., 1985). In this study,  $t$  (Å) was determined by means of the de Boer equation:

$$t(\text{Å}) = \left[ \frac{13.99}{0.034 + \log\left(\frac{P_0}{P}\right)} \right]^{1/2}$$

Most of the surface area of the acid-treated Armenian and Greek zeolites, accessible to  $\text{N}_2$  gas is attributed to micropores (Table 5). However, this is not the case for the acid-treated Georgian HEU-type zeolitic material. Also, KOH treatment increased slightly both micropore surface area and micropore volume (Table 5). On the contrary, heating decreased microporosity of all the zeolites studied. Therefore, it is evident that the various treatments influenced the HEU-type zeolites to a different degree.

#### 4. Discussion

Acid and thermal treatments are frequently applied on zeolites in order to modify their physical and chemical properties (Kallo, 1988; Kühl, 1999). Acid treatment causes dealumination of zeolites through removal of Al from the zeolite framework and replacement of exchangeable cations by  $\text{H}^+$ . Clinoptilolite can progressively lose Al yielding a framework without charge. Moreover, hydrogen zeolites are stabilized when their  $\text{NH}_4^+$  forms are heated up to high temperatures (see review by Kühl, 1999). HEU-type zeolites are known

to have variable thermal properties, which stem from their different structural characteristics (Alietti, 1972; Alietti et al., 1974; Boles, 1972; Bish, 1990). In this study, the different HEU-type zeolites responded to a different degree to the various treatments.

KOH treatment has modified the zeolites studied by means of (a) partial replacement of exchangeable cations by K via ion exchange, (b) dissolution of the amorphous material (usually Si-rich gels) always present in such raw materials, which form from alteration of volcanic glass, and (c) mild layer-by-layer dissolution of the zeolite structure (Yamamoto et al., 1996). The amount of K offered during treatment corresponds to 0.45 meq/g of zeolite, i.e. about 30% of the total CEC of the Armenian and Greek HEU-type zeolitic materials and 25% of the total CEC of their Georgian counterpart. This amount of K is adequate for at least partial K-exchange, especially if it is considered that all natural heulandites contain small amounts of exchangeable K (Table 1). Indeed, it was found that K occupied up to 20% more exchangeable sites after activation. K-rich clinoptilolites tend to be thermally stable (Koyama and Takeuchi, 1977) and thus the remarkable thermal stability of Armenian and Georgian HEU-type zeolitic materials could be explained. Nevertheless, K-exchange did not improve thermal stability of the Greek HEU-type zeolitic material. Therefore, the results obtained suggest that the thermal behaviour of type I heulandite is not improved by ion exchange but seems to depend, at least partially, on the composition of the framework. Structural features such as the Si/Al ratio are important, and Si-rich heulandites (clinoptilolites) are thermally more stable. This behaviour of heulandites has been described in the past (Alietti et al., 1974; Bish, 1990).

The slight increase of the peak/background ratio in the XRD traces after KOH treatment is attributed to dissolution of amorphous or poorly crystallized material, which resulted to a residual increase of the zeolite

content. This material is expected to block micropores and its dissolution would increase microporosity and render a greater amount of external surface area available to  $N_2$  molecules. Therefore, the observed increase of surface area and microporosity (Table 5) can be explained. Nevertheless, the observed increase of microporosity especially for the acid-treated heulandites includes only a fraction of actual zeolite channels. This is because the  $t$ -plots are meaningful only for  $t$ -values greater than 3.5 Å, close to the kinetic diameter of  $N_2$  (3.64 Å according to Breck, 1974). The framework of the HEU-type zeolites contains a network of channels with dimensions  $3.0 \times 7.6$  and  $3.6 \times 4.6$  Å parallel to the  $c$ -axis (A and B channels) and  $2.6 \times 4.7$  Å (C channels) parallel to the  $a$ -axis (Armbruster and Gunter, 2001). Thus, only channels with dimensions  $3.6 \times 4.6$  Å parallel to the  $c$ -axis could be accessible to  $N_2$  gas, due to molecular sieve effects. Recent kinetic studies (Aguilar-Armenta et al., 2001) have shown that at 150-s equilibrium time used in this study, Na- and K-saturated HEU-type zeolites adsorb 0.3 mmol of  $N_2$  per gram at  $P/P_0$  0.60 (450 Torr). Also, Ca-saturated HEU-type zeolite adsorbs 0.4 mmol of  $N_2$  per gram at the same pressure. In this study, although the original materials adsorbed comparable  $N_2$  volumes, the acid-treated materials adsorbed considerably higher volumes of  $N_2$  for similar reaction times and partial pressure (Fig. 6).

Untreated (i.e. natural) HEU-type zeolite crystals form aggregates several tens of microns in diameter (Mumpton and Ormsby, 1976; Moraetis, unpublished data). Among these crystals, there are micropores, which are not accessible by  $N_2$  gas molecules. Acid treatment breaks up these aggregates thereby increasing external surface area. Simultaneously partial dissolution of the zeolite framework and deposition of amorphous material takes place (Fig. 1). The decrease of the intensity in the IR bands of free linkages of all three zeolites (Fig. 3) suggests that removal of Al during layer-by-layer dissolution (Yamamoto et al., 1996) breaks up free linkages of heulandite, which create pore openings, thereby destroying the original heulandite channels forming secondary micropores. These secondary micropores have larger diameter than the original channels and thus are accessible to  $N_2$ . It is thus suggested that  $N_2$ -adsorption may not be important in actual HEU-type zeolite channels. Moreover, a fraction of exchange sites are no longer available due

to disruption of free linkages, yielding a decrease of the CEC of the three HEU-types zeolites. These exchange sites are possibly M1 and M3 sites which are close to the intersection of the A and C channels of clinoptilolite (Koyama and Takeuchi, 1977).

The heated HEU-type zeolites display a lower specific surface area and microporosity compared to the original materials. In the case of the Greek HEU-type zeolitic material, this is expected because the material is not thermally stable and decomposes to an opal-CT like phase (Figs. 1 and 2). In the remaining materials, the observed change of the surface properties during heating is attributed to increasing agglomeration of clinoptilolite crystals, due to modifications in the zeolite structure at high temperature. Agglomeration may occur via sintering of the clinoptilolite crystals during heating at high temperatures. Also, both the Armenian and the Georgian HEU-type zeolitic materials display decreasing intensity and broadening of diffraction maxima after heating without peak migration (Fig. 1), suggesting partial decomposition, but not contraction of the zeolite framework. Decomposition is expected to yield amorphous material. Both sintering and formation of amorphous material blocked micropores and decreased the amount of external surface area accessible to  $N_2$  gas molecules. As expected, decomposition of heulandite structure decreased the number of available exchange sites decreasing CEC. It is therefore suggested that heating has an opposite effect on heulandite surface compared to KOH treatment. Moreover, the results of this study suggest that before heating treatment is applied on HEU-type zeolites, the thermal behaviour of the materials (e.g. presence of heulandite I) must be established.

## 5. Conclusions

Examination of three different heulandites from Armenia, Georgia and Greece after acid and thermal treatment yielded the following conclusions.

1. According to their response to thermal treatments, the Greek zeolite is a type-I heulandite, while the Armenian and the Georgian zeolites are type III heulandites (typical clinoptilolites).
2. Both HCl treatment and heating modified the CEC and structure of the zeolites tested. The Georgian

**HEU**-type zeolitic material was not decomposed after heating at 700 °C, but was not stable enough during acid treatment. Greek **HEU**-type zeolitic material displayed opposite behaviour. The response of Armenian **HEU**-type zeolitic material was intermediate.

3. Structural modifications associated with HCl-treatment include increase of specific surface area and meso- and microporosity. Increase of microporosity is attributed to formation of secondary micropores by dissolution of free linkages. Similar, albeit to less intense, textural modifications were caused by KOH treatment, and are attributed to dissolution of amorphous material and possibly partial dissolution of the Si-tetrahedra. On the contrary, heating decreased both specific surface area and microporosity due to partial decomposition or/and sintering of the heulandite crystals.
4. The CEC of the three materials is not associated directly with surface properties. Instead their ability to adsorb metals (including radionuclides) is associated with their framework structure, which in turn is affected by the various treatments used in this study. The observed decrease in the CEC of all heulandites after various treatments is attributed to partial decomposition of the zeolites, both dissolution of Si-tetrahedra and disruption of the free linkages.

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