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# ZEOLITES IN OLIGOCENE VOLCANIC ROCKS, DADIA-LEFKIMI AREA, THRACE, NORTHERN GREECE: MINERALOGY AND CATION EXCHANGE PROPERTIES

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## ABSTRACT

The diagenetic alteration of the Oligocene felsic volcanic rocks in the Dadia-Lefkimi area, Thrace, has led to a replacement of the parent glassy material from zeolite-bearing assemblages. The alteration is more intense in vitric tuffs forming pseudomorphic textures over the precursor glass shards. Mineralogical and petrographic investigation including thermal treatments, revealed that three authigenic mineral assemblages are present in these rocks:

(a) Clinoptilolite + celadonite + cristobalite
(b) Clinoptilolite ± mordenite + smectite + cristobalite
(c) Heulandite 2 + smectite + cristobalite

The distribution of the authigenic assemblages is not systematic in both the horizontal and the vertical sense. This is probably due either to fault tectonism (destruction of the original lithostratigraphic sequence) or to the lack of recognizable marker horizons or both. The assemblage (b) is the predominant one, with the clinoptilolite occurring both in the form of pseudomorphic replacements of glass shards and as a pore filling mineral. The cation distribution of the heulandite-group minerals is characteristic of heulandites with thermal behaviour 2 and 3. Although a clear relationship between the clinoptilolite/heulandite and mordenite was not found, textural features indicate that at least some mordenite might have been formed after clinoptilolite/heulandite.

The cation exchange capacity of the zeolite bearing rocks varies between 67 meq/100 gr and 136 meq/100 gr, with the highest values observed in the ash tuffs. The latter materials might find potential use as exchangers in both municipal and radioactive waste-water treatment.

## INTRODUCTION

Zeolitic alteration is a common feature of most volcanic rocks of intermediate and acid composition in the Tertiary basins of Rhodope area in northeastern Greece and southeastern Bulgaria (Aleksiev &

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Djourova, 1975; Arikas & Karafoti, 1989; Marantos et al., 1989; Skarpelis et al., 1987; Tsirambidis et al., 1989; Tsolis-Katagas & Katagas, 1990). The alteration of the glassy component of the volcanic rocks to zeolitic-bearing mineral assemblages is attributed to diagenetic processes (Skarpelis & Marantos, 1987; Tsolis-Katagas & Katagas (op. cit.) or to processes related to the "geo-autoclave" (Aleksiev & Djourova, op. cit.).

Zeolitic alteration halos may delineate base metal ore deposits and are useful tools in exploration (Utada et al., 1974). Zeolites have significant applications in the fields of pollution control, energy conservation, agriculture and aquaculture, mining and metallurgy, paper industry and medicine. Their use was expanded in the last years.

The purpose of this paper is to provide data on the mineralogy and cation exchange properties of the volcanic rocks of the Dadia-Lefkimi area, Evros county, Thrace, N. Greece.

## GEOLOGY

The Dadia-Lefkimi area, located 35 km north-northeast of Alexandroupolis, Western Thrace (Fig. 1, 2 ), is underlain by volcanic and sedimentary rocks that are part of the Tertiary basins in the broad area of Thrace. Volcanic rocks and mainly marine clastic sediments are observed in the Tertiary basins of Thrace. Their general stratigraphy in the Evros area includes from bottom to top:

a. a sequence of marine clastic rocks deposited over a metamorphic basement during Middle to Upper Eocene (200-1500 m in thickness); volcanic rocks, mainly of andesitic composition, appear in the upper part of the sequence.

b. dacitic, rhyodacitic and rhyolitic pyroclastics and lavas appear in the Lower-Middle Oligocene, interfingering with clastic sediments.

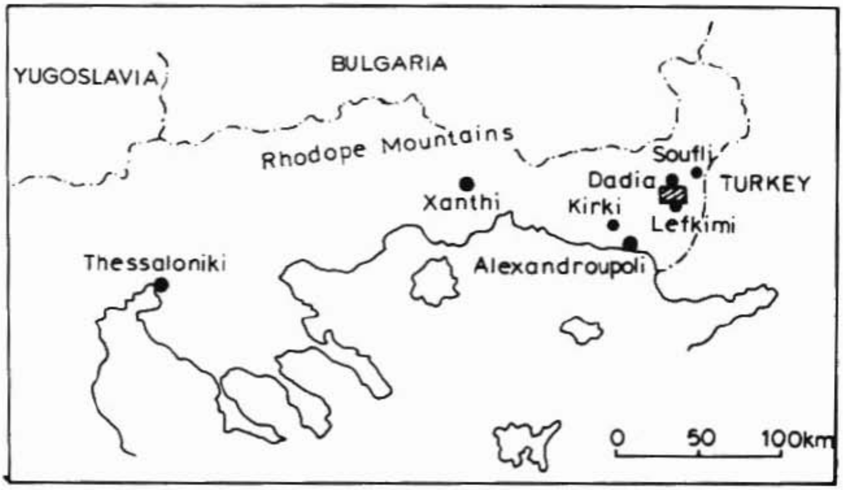

Fig. 1. Map of NE Greece showing area studied (shaded).

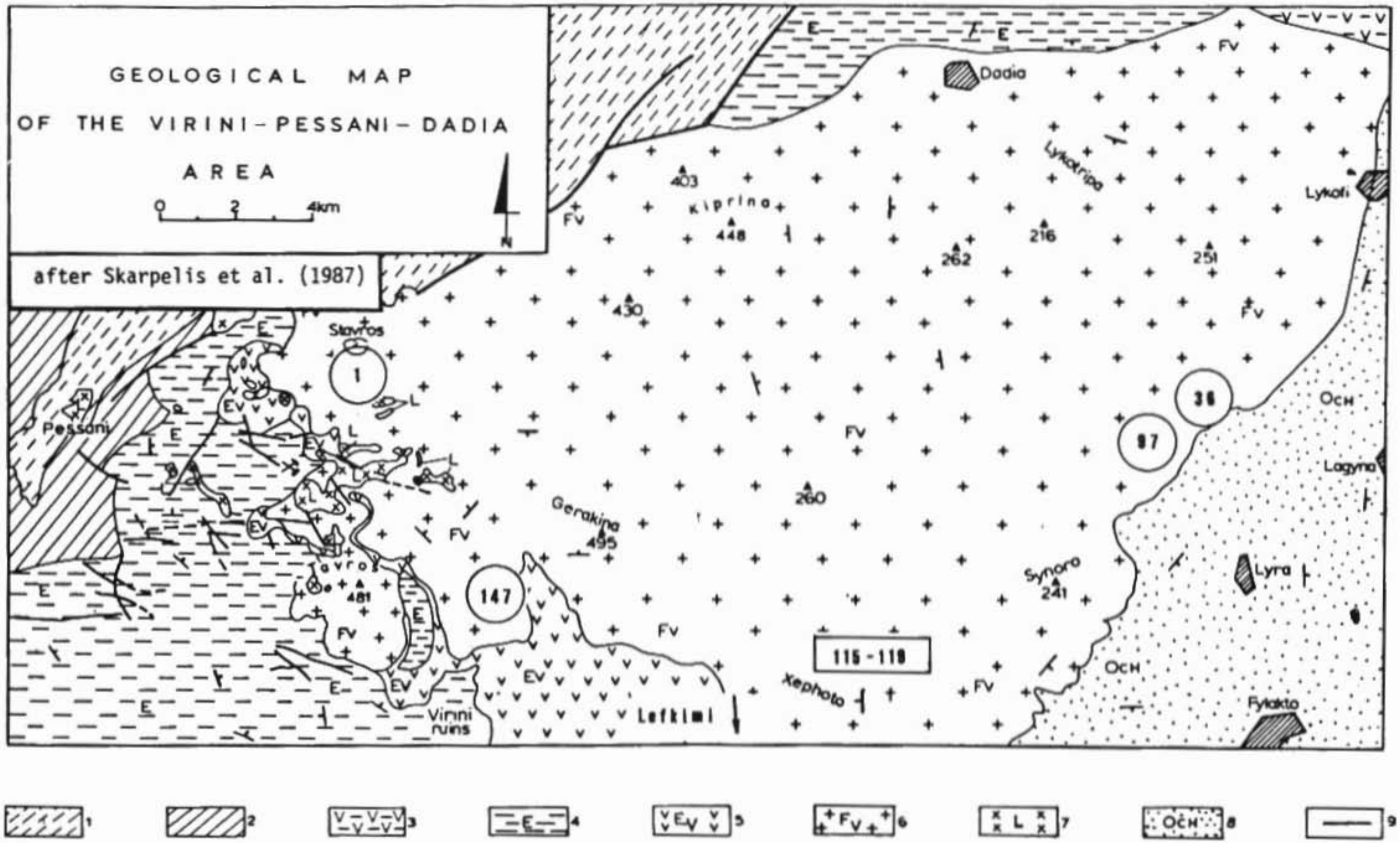

Fig. 2. Geological map of Virini-Pessani-Dadia area: *1* — serpentinized ultramafics, talc schists; 2 — epidote amphibolites, gneisses, augen gneisses, mica schists with marble intercalations; 3 — metabasic rocks of the Drymou-Melia Series (Mesozoic); 4 — Eocene clastic sediments; 5 — Eocene andesitic lavas and pyroclastics; 6 — felsic pyroclastics and lavas (Upper Oligocene); 7 — quartz-feldspar porphyries (Upper Oligocene); 8 — clastic sediments transgressively overlying the felsic volcanics (Chattian); 9 — fault

c. Upper Oligocene marine to shallow marine sediments (900-2000m), containing lenses of lignites, transgressively overlie the volcanic felsic rocks and are discordantly overlain by Middle-Upper Miocene and Pliocene sediments (200-1400m). In the northern part of the basins (e.g. Orestias basin) Miocene sediments are lacking.

Fault tectonics in Neogene and Quaternary times resulted in the formation of the Evros river basin. By this process blocks of the Tertiary lithologies, including Oligocene volcanics, were differentially uplifted, subsided and eroded until they were exposed.

Oligocene felsic lavas and pyroclastic rocks of submarine origin are the dominant volcanic types in the Dadia-Lefkimi area (Skarpelis et al., 1987). Andesitic rocks crop out locally in the southwestern part of the area (Fig. 2). The felsic volcanics include pyroclastic flow and fall deposits and lava flows and domes. The lavas range in composition from rhyolites to rhyodacites and dacites. Pyroclastic flows consisting of lapilli tuffs and pyroclastic breccia are poorly sorted and show little or no stratification. Pyroclastic falls are abundant and consist of ash crystal tuffs, ash vitric tuffs and lapilli tuffs. They are well sorted, thin bedded, rarely laminated. Recent petrological and geochemical studies (Skarpelis et al. 1987) have shown that these volcanics are part of a complete volcanic suite comprising basaltic andesites, dacites and rhyolites. They are part of the broad Tertiary province of volcanic rocks, formed by calc-alkaline magmas erupted in Eocene to Oligocene time in a continental margin setting (Innocenti et al., 1984; Papavasiliou & Sideris, 1984; Sideris, 1973).

## METHODS OF INVESTIGATION

X-ray powder diffraction (XRD) of bulk samples was used for the initial identification of the alteration minerals, using Ni-filtered CuKα radiation. The mode of occurrence and the paragenetic relationship between the original volcanic material and the alteration minerals were studied by optical microscopy, followed by scanning electron microscopy (SEM). The clay minerals were identified by XRD on the basis of the characteristic of the basal spacing after glycolation and heating of the < 2 μm clay fraction. The zeolites of the heulandite group were distinguished by applying thermal stability treatments according to Alietti (1972), Boles (1972) and Mumpton (1960) and by electron microprobe analysis. Electron microprobe analysis was carried out on an JEOL 8600 instrument operated at 20 kV and 8 nA beam current with a defocused beam (spot size 5 μm). Counting time was 20 sec. A ZAF correction program was used. The quality of zeolite microanalyses was checked by determining the molecular ratios of $Al_2O_3$ to (Ca+Mg+2Na+2K)O, which should be unity (Sheppard & Gude, 1969) and by estimating the balance error (E) which should be less than 10% (Alietti et al., 1977).

The cation exchange capacity of seven bulk samples was determined using a Kjeldahl microsteam apparatus. The samples were saturated with 1N ammonium acetate and washed with methanole. The method applied was that of Jeffery et al. (1989).

## PETROGRAPHY AND MODE OF OCCURRENCE

The authigenic minerals recognized in the volcanic rocks of the

Dadia-Lefkimi area were clinoptilolite, heulandite, mordenite, clay minerals and cristobalite. Dacitic lava fragments in pyroclastics were slightly altered to clay mineral assemblages. Lavas of rhyodacitic and rhyolitic composition, especially those showing perlitic texture, presented partial alteration to zeolites and clay minerals. Zeolites, however, are widespread in the pyroclastics, especially in vitric tuffs.

The vitric tuffs contain larger amounts of zeolites than the other pyroclastics. The tuffs are massive, thin bedded and well sorted. Typically they consisted predominantly of pumice fragments, bubble-wall glass, and perlitic lava fragments. Crystal fragments of K-feldspar, plagioclase, quartz and biotite were present in small amounts. Petrographic study showed that the primary texture was well preserved and that the glass was completely replaced by authigenic minerals.

The following authigenic mineral assemblages were identified:

(a) clinoptilolite + celadonite + cristobalite
(b) clinoptilolite and / or mordenite + smectite + cristobalite
(c) heulandite 2 + smectite + cristobalite

Clinoptilolite in these assemblages corresponds to heulandite with thermal behaviour 3 after Alietti (1972) and Alietti et al. (1977). The regional distribution of these mineral assemblages was not systematic either laterally or vertically in the volcanic pile, and hence distinct mappable alteration zones were not detected. This is probably due to the destruction of the original volcanic stratigraphy by faults and to the lack of recognizable marker horizons, useful for lithostratigraphic correlations among volcanic units. The alteration of tuff beds to assemblage (b) above was predominant.

The zeolites commonly occur in aggregates with individual crystals of 10-80 μm size making up the matrix in altered pyroclastics and as complete replacements of pumice fragments, bubble-wall glass shards, and non-vesicular glass fragments, especially those with perlitic structures. Clinoptilolite occurred as tabular crystals with long axes oriented perpendicular to shard margins and filling pore spaces (Figure 3). Clinoptilolite aggregates are pseudomorpic on the shards. Mordenite occurred as fine, hair-like crystals scattered over clinoptilolite, clay minerals and cristobalite in cavities formed by the dissolution of glass shards (Figure 4). It also occurred as radial aggregates of fibrous crystals lining walls of cavities that contained spherules of cristobalite. In this occurrence clay mineral aggregates (smectite or celadonite) were found to surround the zeolite and cristobalite mass. Celadonite results in a green-bluish colouring of the tuffs. Alternation of thin films of clay minerals by zeolites was common in perlitic glass fragments (Figure 5a) and in glass shard pseudomorphs (Figure 5b). The paragenetic relationship mordenite to clinoptilolite could not be determined with certainty due to the fine grain size of the mordenite. The occurrence of mordenite over clinoptilolite aggregates suggests that at least some of the mordenite formed later than the clinoptilolite.

Cristobalite is the only authigenic silica mineral appearing in the volcanic rocks studied. It occurs in spherules associated with zeolite aggregates.

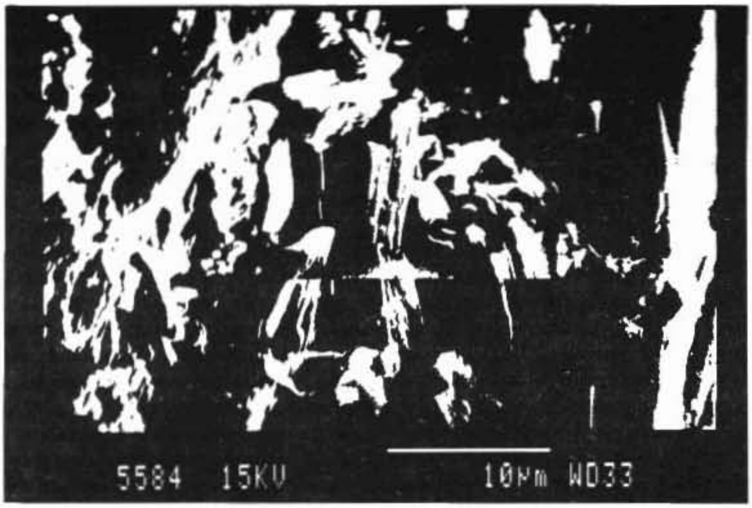

Fig. 3. Scanning Electron Microscope (SEM) photograph of clinoptilolite that replaced a glass shard.

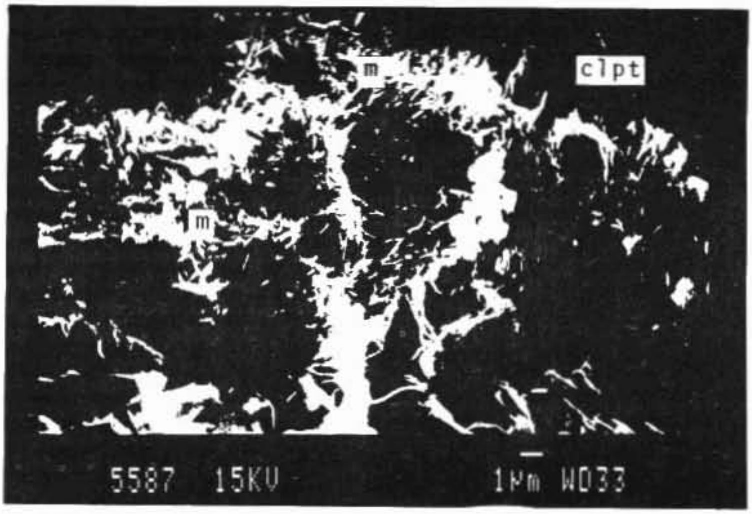

Fig. 4. Scanning Electron Microscope (SEM) photograph of mordenite fibres (m) associated with clinoptilolite (clpt).

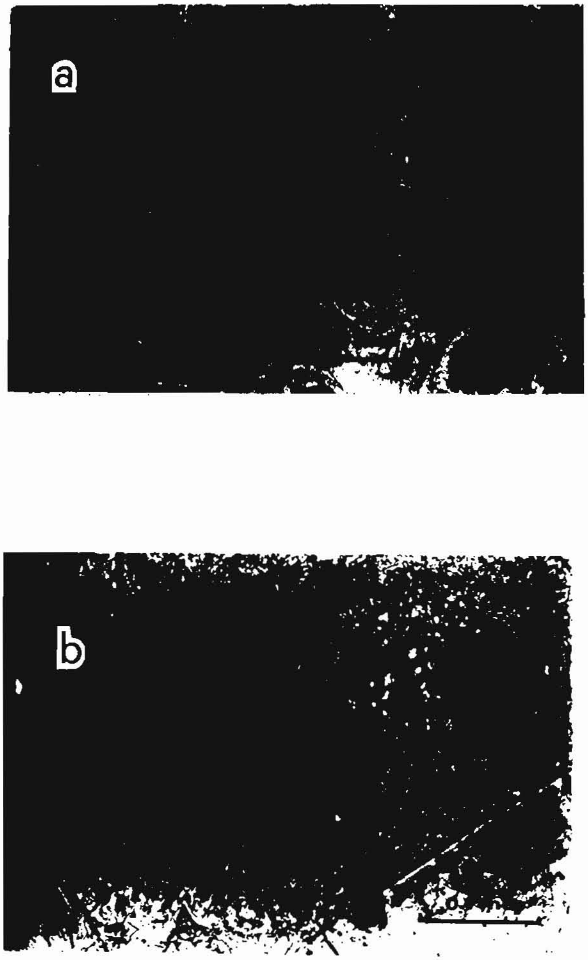

Fig. 5. Microphotographs showing pseudomorphs of clay minerals (cm) and clinoptilolite (clpt) after: (a) perlitic glass fragments and (b) glass shards (plane polarized light).

## HEULANDITE-GROUP ZEOLITE CHEMISTRY

Microprobe analyses of heulandite-group zeolites from several samples, ratios of Si/Al and divalent to monovalent cation ratios are given in Table 1. The divalent cations predominate over monovalent and potassium over sodium. The Si/Al ratios range between 4.29 to 4.90

Table 1. Representative microprobe analyses of heulandite-group zeolites

| | 119-1 | 119-2 | 147-1 | 147-2 | 147-3 | 115-5 | 115-9 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 68.6 | 64.8 | 66.2 | 67.3 | 66.5 | 64.43 | 66.4 |
| $Al_2O_3$ | 12.00 | 11.90 | 13.10 | 12.90 | 13.00 | 11.47 | 11.43 |
| FeO | - | - | - | - | - | 0.03 | - |
| MgO | 0.95 | 1.05 | 1.30 | 1.20 | 1.30 | 0.62 | 0.59 |
| CaO | 3.40 | 3.40 | 5.00 | 4.40 | 4.40 | 2.88 | 3.03 |
| $Na_2O$ | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.37 | 0.22 |
| $K_2O$ | 1.90 | 1.80 | 0.60 | 0.50 | 0.40 | 4.64 | 3.05 |
| TOTAL | 87.05 | 83.15 | 86.40 | 86.50 | 85.80 | 84.44 | 84.72 |
| Structural formulas on the basis of 72(O) | | | | | | | |
| Si | 29.96 | 29.68 | 29.16 | 29.47 | 29.36 | 29.64 | 30.01 |
| Al | 6.18 | 6.42 | 6.80 | 6.66 | 6.76 | 6.21 | 6.09 |
| Fe | - | - | - | - | - | 0.01 | - |
| Mg | 0.62 | 0.72 | 0.85 | 0.78 | 0.86 | 0.43 | 0.39 |
| Ca | 1.59 | 1.67 | 2.36 | 2.06 | 2.08 | 1.42 | 1.45 |
| Na | 0.17 | 0.18 | 0.17 | 0.17 | 0.17 | 0.33 | 0.19 |
| K | 1.06 | 1.05 | 0.34 | 0.28 | 0.22 | 2.72 | 1.76 |
| Balance error % | 9.41 | 7.09 | -1.90 | 8.38 | 7.91 | 8.21 | -7.00 |
| Si/Al | 4.85 | 4.62 | 4.29 | 4.43 | 4.34 | 4.77 | 4.90 |
| biv/mon | 1.60 | 1.94 | 6.32 | 6.34 | 7.40 | 0.61 | 0.96 |

hence, these zeolites would be Si-rich clinoptilolites according to the definition of Boles (1972), and heulandite group 3 (clinoptilolite) according to the definition of Alietti (1972) and Alietti et al. (1977). In the triangular diagram $Si_{36}O_{72}$-$(Ca,Mg)_{4.8}Al_{9.6}Si_{26.4}O_{72}$-$(Na,K)_{9.6}Al_{9.6}Si_{26.4}O_{72}$ (Fig. 6) by Alietti et al. (1977) and reported by Gottardi & Galli (1985), the compositions of heulandite group zeolites from Dadia-Lefkimi area plot in the fields of heulandites with thermal behaviour 2 and 3.

## CATION EXCHANGE CAPACITY

The cation exchange properties of zeolites were studied long ago (Ames, 1960; Barrer, 1978). Zeolites are excellent ion exchangers with capacities of up to 3 or 4 meq/gr, competing with other natural exchangers (e.g. montmorillonitic clays) and organic resins in certain applications, especially in cases of exchange of large cations from aqueous solutions. Heulandite-group zeolites are highly selective for ammonium ions and are useful in extraction of ammoniacal nitrogen from sewage, aquaculture, and agricultural effluents.

The results from the C.E.C. measurements are given in Table 2. The zeolite rich materials can be separated into two main groups according to their cation exchange properties. The first is characterized by low cation exchange capacity and corresponds to rhyolitic-rhyodacitic lavas, which have been slightly altered (Samples 97, 36, 116). The second is characterized by high cation exchange capacity (samples 1, 115, 118, 119) and corresponds to material derived from rhyolitic-rhyodacitic ash tuffs. The ammonium exchange capacities of these ash tuffs are slightly higher than of tuffs in the area of Metaxades, which have C.E.C. between 68.4 to 105.4 meq/gr (Marantos et al., 1989).

Table 2. Cation exchange capacity of zeolitic volcanics

| Sample No | 1 | 36 | 97 | 115 | 116 | 118 | 119 |
|---|---|---|---|---|---|---|---|
| C.E.C.(meq/gr) | 1.36 | 0.72 | 0.67 | 1.12 | 0.77 | 1.25 | 1.31 |
| Zeolite mineralogy: | mord | clpt<br>±mord | clpt | clpt | clpt | clpt | clpt |

Rock type: 36, 97, 116: rhyolitic-rhyodacitic lavas
1, 115, 118, 119: rhyolitic-rhyodacitic ash vitric tuffs

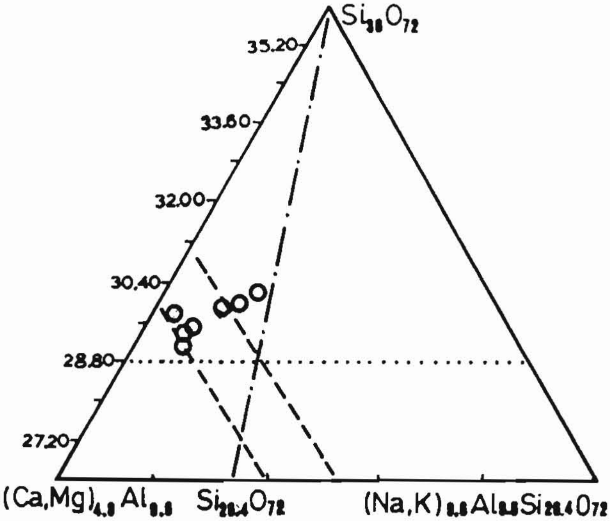

*Fig. 6. Mole plot of analyzed clinoptilolite samples in the diagram by Alietti et al. (1977). The analyzed clinoptilolite samples plot in the field of heulandites with thermal behaviour 2 and 3. The dashed-dotted line is the boundary heulandite-clinoptilolite, whereas the dotted line is the boundary between heulandite and clinoptilolite after Boles (1972).*

## CONCLUDING REMARKS

Heulandite, mordenite and clinoptilolite are the main authigenic minerals in the alteration assemblages of Oligocene intermediate and acid volcanic rocks of the Dadia-Lefkimi area. The zeolites commonly occur in aggregates making up the matrix in altered lavas and pyroclastics.

Ash vitric tuffs are the rock types containing the higher proportions of zeolites. As Hay (1966) suggested, zeolite formation and distribution is largely controlled by the initial composition, porosity and permeability of the host rock, the P/T conditions of burial (in case of diagenetic origin) and the chemistry of the pore fluids. The higher degree of alteration of pyroclastic rocks relative to lavas in the area studied indicates that porosity and permeability were among the major factors controlling the degree of replacement of volcanic glass by authigenic minerals.

The higher ammonium exchange capacities of the ash tuffs relative to lavas should be related to the higher contents in zeolites, since clay minerals occur in very low proportions. The cation exchange properties of the zeolitic ash tuffs might make them favorable material for potential application as exchangers in fields, in which ion exchange is of prime importance, like the municipal and radiactive wastewater treatment. The next step of the current research is to investigate the selectivity for various cations for each of the materials with high cation exchange properties. This will determine the potential use of these materials as exchangers.

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