

THE RELATIONSHIP BETWEEN THE THERMAL BEHAVIOR OF CLINOPTILOLITE AND ITS CHEMICAL COMPOSITION

KONSTANTINOS P. KITSOPOULOS[†]

Geology Department, Leicester University, Leicester LE1 7RH, UK

Abstract—The matrix of the Pliocene volcanoclastics from the Akrotiri area of the Santorini island (Greece) is dominated by clinoptilolite. Smectite, occasionally illite-smectite, opal-CT, cristobalite and mordenite are also present. The clinoptilolite-rich samples were heated at 460 and 560°C for 12 h and the reductions in the intensity of the 020 diffraction peak were measured. Electron microprobe analysis (EMPA) was then used to study the chemical composition of the clinoptilolite. Statistical analysis proved a strong and quantifiable relationship between the reduction of the 020 diffraction peak of the clinoptilolite and the Na/K ratio. A representative set of microprobe analyses of clinoptilolite was performed before any correlation with thermal behavior was attempted. The presence of K in the structure of clinoptilolite as well as its relationship with Na are most important in the thermal behavior of clinoptilolite.

Key Words—Chemical Composition, Clinoptilolite, 020 Diffraction Peak, Electron Microprobe Analysis, Greece, Santorini, Zeolites.

INTRODUCTION

The thermal behavior of the heulandite group of minerals has most often been investigated by monitoring the changes in the intensity of the 020 diffraction peak after heating (Mumpton, 1960; Mason and Sand, 1960; Shepard and Starkey, 1966; Alietti, 1972; Boles, 1972; Alietti *et al.*, 1974, 1977; Boles and Surdam, 1979). These studies resulted in a classification scheme for the heulandite group of minerals which distinguishes three sub-types: heulandite 1, 2 and heulandite type 3, *i.e.* clinoptilolite. Furthermore, the thermal behavior of the heulandite group of minerals was related to chemical composition, namely the amount of K, Na, Ca and Mg cations and the Si/Al ratio. It was generally believed, during early research, that minerals with large amounts of K in the structure and/or high Si/Al ratios (>4) were thermally resistant. In contrast, minerals with large amounts of Ca in the structure and/or low Si/Al ratios (<4) were thought to be thermally less resistant.

The subcommittee on zeolites of the International Mineralogical Association (Coombs *et al.*, 1998) suggested that minerals in the clinoptilolite series have $\text{Si/Al} > 4$ (clinoptilolite-K, -Na, -Ca) and those in the heulandite series have $\text{Si/Al} < 4$ (heulandite-Ca, -Sr, -Na, -K). Other studies proved that the thermal behavior is not influenced by the amount of the exchangeable cations and/or the Si/Al ratio alone. The type of the exchangeable cations (*i.e.* their ionic size and potential), their specific position within the structure, their coordination to H_2O molecules and their interactions with framework oxygens, and the connectivity of the zeolite structure also influence the thermal be-

havior of the clinoptilolite (Koyama and Takeuchi, 1977; Bish, 1984, 1988, 1993; Armbruster and Gunter, 1991; Armbruster, 1993).

The aim of this study was to investigate the relationship between the thermal behavior of clinoptilolite and its chemical composition, as illustrated by the reduction in the intensity of the 020 diffraction peak of the mineral. For this purpose we used clinoptilolite-rich samples taken from the Akrotiri area (Santorini island, Greece). The samples underwent thermal treatment and the reduction in the intensity of the 020 diffraction peak of the clinoptilolite was recorded. We also obtained a large number of electron microprobe analyses. A quantifiable relationship between the thermal and chemical composition data was established.

MATERIALS

The materials used in this study are from the well-described clinoptilolite-rich volcanoclastics of the Akrotiri area of Santorini island (Greece). According to Tsolis-Katagas and Katagas (1989) the formation of the zeolites resulted from the activity of interstitial water in the pile of volcanoclastic material. The different mineralogical assemblages and compositions were attributed by the same authors to variations in heat flow, the ionic activity in the interstitial waters, and the permeability. Kitsopoulos (1995, 1997) suggested that the formation of zeolites did not exactly follow a 'glass dissolution' path, but involved continuous reactions between solid and fluid components. These reactions were often controlled in numerous small closed subsystems, even within the area of individual glass particles.

[†] Present address: 16 Aiolou Str., Paleo Faliro, Athens, 175-61, Greece.

ANALYTICAL METHODS

X-ray diffraction (XRD) and scanning electron microscopy (SEM)

The mineralogy of the samples was examined by means of XRD and SEM. For the XRD analysis, micronized powders were packed into Al holders. During mounting, extra care was taken not to apply excess force, to avoid preferred orientation effects. The samples were scanned from 2° to 65° at a speed of 1° min⁻¹ using CuK α radiation. The clay mineralogy was identified from the <2 μ m clay fraction using air-dried, glycolated and heated oriented mounts. Gold-coated freshly broken fragments were examined with an Hitachi S520 SEM operated at 20 kV and linked to a LINK AN1000 energy dispersive spectrometer.

Thermal tests

Following the initial XRD run the powders were heated at 460°C and at 560°C for 12 h at each temperature and run again. The counts per second (CPS) of the 020 diffraction peak of the clinoptilolites were recorded before and after firing. The differences in CPS which occurred were expressed as percentages.

Electron microprobe analysis (EMPA)

The chemical composition of the clinoptilolite was studied by preparing carbon-coated polished thin-sections which were analyzed using a JEOL JXA-8600 Superprobe linked to a LINK 860 EDS detector. The analytical conditions described in Kitsopoulos and Dunham (1998) were used for the analysis of the clinoptilolites. The accuracy, precision and detection limits of the EDS methods were discussed by Dunham and Wilkinson (1978).

RESULTS AND DISCUSSION

Mineralogy

The XRD and the SEM analyses confirmed that the Akrotiri volcanoclastics are dominated by clinoptilolite. They show a typical tabular, platy, and in places coffin-shaped habit with a characteristic monoclinic symmetry. The size of the majority of the clinoptilolite crystals varies from 8–10 μ m to ~20 μ m. In a few places, larger crystals, up to 30 μ m, are also found. Smectite, occasionally illite-smectite, and opal-CT, cristobalite, mordenite and halite were also identified. Pyrogenic phenocrysts of feldspars, amphiboles, Fe-Ti oxides and traces of quartz complete the mineralogy.

Thermal tests

During the thermal tests it was observed that polymorphic phases did not develop, nor was the structure completely destroyed during the firing tests. The reduction in the intensity of the 020 diffraction peak varied for all samples from 6 up to 45%. According to Alietti (1972), Boles (1972) and Boles and Surdam

(1979), this amount of reduction and the absence of any contracted phases suggest the presence of clinoptilolite.

Chemical composition of the clinoptilolites

The presence of absorbed moisture, the charging by the beam current and the volatilization of light elements are often considered as common analytical problems during the analysis of zeolite minerals. This means that large sets of microprobe analyses of clinoptilolite cannot be taken easily from each sample. By taking this into account, plus the need for a representative number of analyses from each sample, and having studied the thermal data it was decided to proceed with the analysis of clinoptilolite from four samples. These four samples represent the widest possible thermal change during the first and the second firing tests.

As a result, 75 electron microprobe analyses were obtained from all four representative samples. The mean values for each sample are given in Table 1. The value of the Si/Al ratio ranges from 4.37 to 5.18 (mean 4.72, sd 0.19), much greater than 4, which, according to Boles (1972) and Coombs *et al.* (1998) clearly characterizes the analysed minerals as clinoptilolites.

The relationship between the thermal behavior and the chemical composition

The study of the relationship between the thermal behavior of clinoptilolite and its chemical composition, by correlating XRD and EMPA data, is a complex task for several reasons.

First, appropriate thermal behavior and chemical composition factors to be used for the correlation have to be chosen carefully. The thermal behavior of clinoptilolite is well expressed by the behavior of the 020 peak of the mineral. On the other hand, it is known that the presence of the exchangeable cations, mainly K and Na, influence the thermal behavior of clinoptilolite. In this study, the statistical analysis of the chemical composition data showed a distinct correlation between the sum of monovalent (Na + K) cations and the sum of the divalent (Ca + Mg) cations (Figure 1). The sum of Na and K in the structure of clinoptilolites increases as the sum of Ca and Mg decreases. It seemed that a clear competition existed in the structure of the Akrotiri clinoptilolites between the two pairs of the exchangeable cations (Na-K and Ca-Mg). Therefore, the correlation between the thermal behavior and the chemical composition should somehow involve the use of a factor representing the simultaneous presence of Na and K. For this reason the use of the Na/K ratio was considered to be necessary.

Second, the XRD pattern of clinoptilolite, obtained from a powdered sample, is obviously an 'imprint' of a very large number of crystals of the mineral in the powdered sample. This large number of clinoptilolite crystals

Table 1. Electron microprobe analyses of clinoptilolite from Santorini, Greece.

Sample (n)	S118 16			S108 17		
	Max	Min	Mean	Max	Min	Mean
SiO ₂	66.87	65.50	66.50	67.58	66.24	66.82
TiO ₂	0.00	0.00	0.05	0.00	0.00	0.02
Al ₂ O ₃	12.75	12.28	12.43	11.06	11.30	11.46
FeO	0.05	0.14	0.06	0.00	0.00	0.03
MnO	0.10	0.02	0.02	0.02	0.05	0.02
MgO	1.02	0.74	0.79	0.44	0.38	0.45
CaO	2.27	2.30	2.23	0.64	0.72	0.84
Na ₂ O	2.47	1.72	2.12	2.55	1.86	2.25
K ₂ O	2.34	2.84	2.46	4.33	5.28	4.54
Total	87.87	85.54	86.66	86.62	85.83	86.43
	cations per 72 oxygens					
Si	29.314	29.495	29.502	30.165	29.994	29.954
Ti	0.000	0.000	0.015	0.000	0.000	0.007
Al	6.587	6.517	6.498	5.818	6.030	6.052
Fe	0.018	0.053	0.021	0.000	0.000	0.013
Mn	0.037	0.008	0.008	0.008	0.019	0.008
Mg	0.666	0.497	0.522	0.293	0.256	0.300
Ca	1.066	1.110	1.058	0.306	0.349	0.403
Na	2.099	1.502	1.825	2.207	1.633	1.953
K	1.309	1.631	1.392	2.465	3.050	2.599
Na/K	1.60	0.92	1.31	0.90	0.54	0.75
	median Na/K: 1.26			median Na/K: 0.72		
E%	-3.89	3.53	2.34	-0.88	2.31	1.89
Sample (n)	S103 21			S129 21		
	Max	Min	Mean	Max	Min	Mean
SiO ₂	68.97	67.18	67.87	66.66	63.19	65.59
TiO ₂	0.04	0.00	0.04	0.00	0.00	0.02
Al ₂ O ₃	12.27	12.42	12.01	12.49	11.47	12.09
FeO	0.00	0.00	0.04	0.00	0.09	0.06
MnO	0.00	0.00	0.02	0.00	0.04	0.02
MgO	0.45	0.71	0.47	0.74	0.41	0.61
CaO	1.37	1.71	1.32	1.31	1.48	1.32
Na ₂ O	2.77	1.64	2.39	2.84	2.17	2.74
K ₂ O	3.56	3.76	4.02	3.36	3.33	3.33
Total	89.43	87.42	88.18	87.40	82.18	85.78
	cations per 72 oxygens					
Si	29.774	26.639	29.780	29.670	29.699	29.560
Ti	0.013	0.000	0.015	0.000	0.000	0.007
Al	6.243	6.458	6.212	6.300	6.354	6.422
Fe	0.000	0.000	0.015	0.000	0.035	0.022
Mn	0.000	0.000	0.008	0.000	0.016	0.009
Mg	0.290	0.467	0.308	0.190	0.287	0.407
Ca	0.634	0.808	0.620	0.640	0.745	0.640
Na	2.318	1.403	2.032	3.050	1.977	2.392
K	1.960	2.116	2.250	1.680	1.996	1.917
Na/K	1.18	0.66	0.90	1.81	0.99	1.25
	median Na/K: 0.92			median Na/K: 1.40		
E%	1.92	6.40	1.51	-1.46	5.80	0.71

n: number of analyses available from each sample.

m: mean values.

max: the analysis with the maximum Na/K value.

min: the analysis with the minimum Na/K value.

median: average of minimum and maximum Na/K values of each sample.

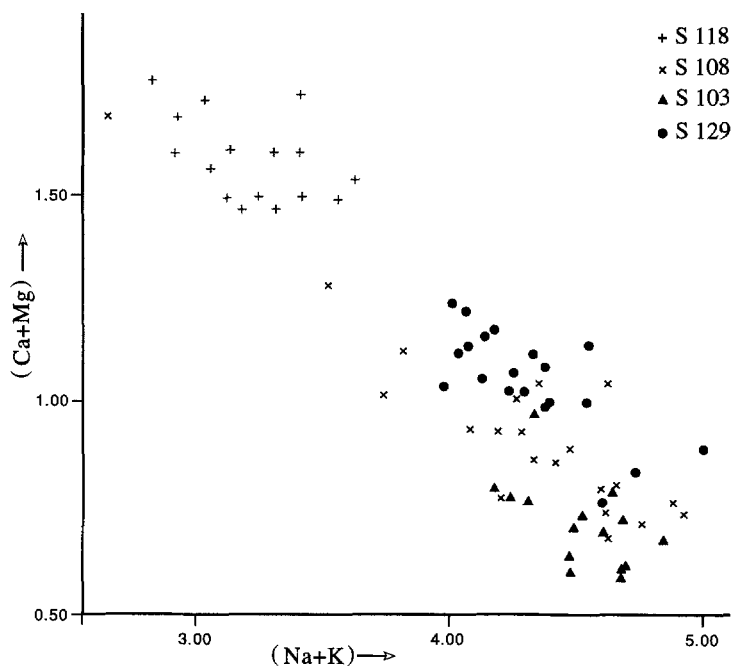


Figure 1. (Na + K) vs. (Ca + Mg) plot for clinoptilolite minerals from Akrotiri (Santorini island), Greece.

from which the XRD image is obtained could have quite variable chemical composition. In contrast, each electron microprobe analysis usually represents the composition of a single crystal of clinoptilolite. A single analysis will hardly be representative of the chemical composition of all the different crystals present, unless the variations in the chemical composition of the clinoptilolite minerals under investigation are negligible (quite unusual). Therefore, the correlation of a single microprobe analysis to the thermal behavior, as seen by XRD and the 020 peak, is highly unlikely to be successful. A large number of analyses should be available to correspond to the expected wide range of chemical composition of the clinoptilolites in a sample.

Finally, even if a chemical composition factor has been chosen and a large number of analyses are available from a clinoptilolite-rich sample, the most appro-

priate way to compile a representative value for the specific chemical composition factor has to be decided. In this study we considered two approaches: the calculation of a median and a mean value. The median Na/K ratio was calculated by averaging the minimum and maximum values of Na/K available from each sample. The analyses from which the minimum and the maximum values of Na/K were calculated for each sample are also given in Table 1. The mean Na/K ratio was calculated by using the total number of analyses from each sample. All data, along with the reductions of the 020 peak, are given in Table 2.

The 020 diffraction peak vs. the Na/K ratio

Median Na/K ratio. When the median Na/K value was plotted against the reduction in the 020 peak during the first thermal test R1 (460°C, 12 h), (Figure 2A) the correlation coefficient was found to be 0.99. The correlation coefficient of the Na/K to the reduction during the second thermal test R2 (560°C, 12 h) was -0.97 (Figure 2B). Finally the correlation coefficient of the Na/K to the total reduction (R1 + R2) was 0.97 (Figure 2C). All plots clearly demonstrated that the thermal behavior of the clinoptilolite is directly dependent on the Na/K ratio.

Mean Na/K ratio. Considering the mean Na/K ratio, the correlation coefficient values were lower than when the median values were used. The plot of the mean Na/K value vs. R1 had a correlation coefficient value of 0.92 (Figure 3A), the Na/K vs. R2 a value of

Table 2. Na/K values and reductions of the 020 diffraction peak of clinoptilolite from Santorini, Greece.

Sample	Na/K median	Na/K mean	R1 %	R2 %	R1 + R2 %
S108	0.72	0.75	8.72	15.29	24.01
S103	0.92	0.90	12.70	11.60	24.30
S118	1.26	1.31	23.50	5.41	28.91
S129	1.40	1.25	31.37	-1.97	29.40

Median: median Na/K value; mean: mean Na/K value; R1: reduction of the intensity of 020 diffraction peak after heating at 460°C for 12 h; R2: reduction in the intensity of the 020 diffraction peak after heating at 560°C for 12 h; R1 + R2: total reduction.

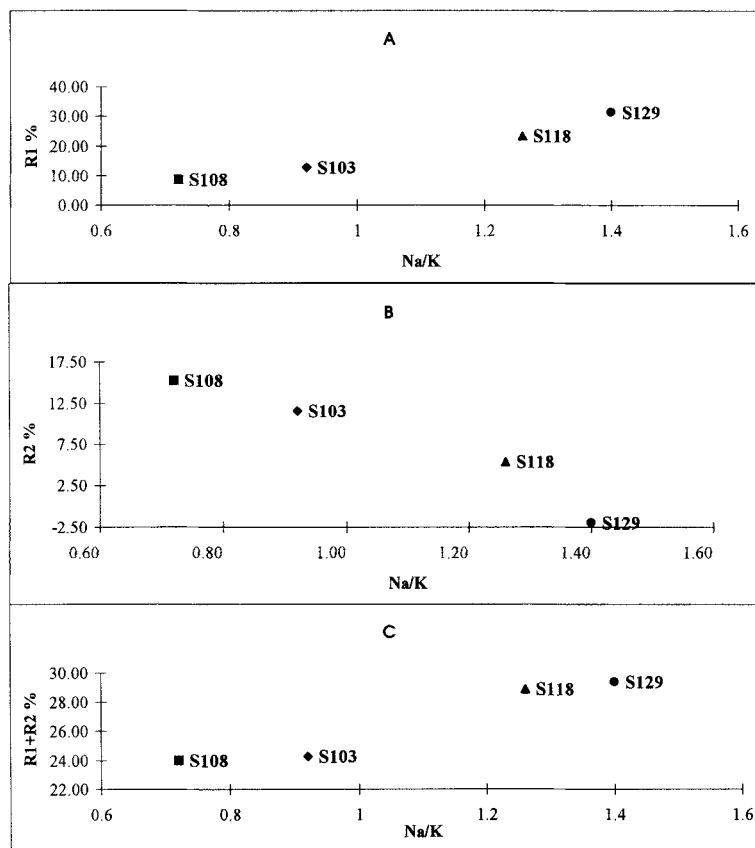


Figure 2. Na/K vs. the reduction in the intensity of the 020 diffraction peak during thermal testing. R1: 460°C for 12 h, R2: 560°C for 12 h, R1 + R2: total reduction. The value of the Na/K ratio is the median value of the lowest and the highest Na/K values obtained from the same sample.

–0.88 (Figure 3B), and the Na/K vs. the total reduction (R1 + R2) a value of 0.97 (Figure 3C). The correlation coefficient values changed because the Na/K value of sample S129 (Table 2) was lowered from 1.40 (the median value) to a mean value of 1.25. This lowering of the mean Na/K value was simply the result of having available a set of unevenly distributed analyses. In S129 most of the analyses available, 17 of 21, show Na/K values from 0.99 up to 1.38 and only four analyses have Na/K values of 1.78–1.82.

The rest of the samples (S103, S108 and S118) have mean Na/K values similar to their median Na/K values: 0.75 for S108, 0.90 for S103, and 1.31 for S118. This is because the analyses available from each of the three samples (S103, S108 and S118) are evenly distributed between the minimum and maximum Na/K values. So, the use of a median or a mean calculation approach leads to similar values.

The role of K and Na

From Table 2 it is obvious that during the first R1 thermal test the reduction in the 020 peak of clinoptilolite decreases as the samples become K rich. The reduction for S108, which is the most K rich among

the four samples, is 8.72%. The reduction progresses and reaches 31.37% for the most Na-rich sample (S129, Na/K 1.40). In contrast, during the second R2 thermal test the level of reduction in the 020 peak of clinoptilolite decreases as the samples become Na rich. The reduction is minimal for the most Na-rich sample (S129) and gradually reaches 15.29% for the most K-rich sample (S108). (Although all peak intensities were recorded by a computerized system and the samples were carefully X-rayed immediately after heating, the very small gains of ~2% (S129) of the peak intensity observed may not actually be real, but represent some variability in measurement, *e.g.* drifting, or a slight rehydration). As can be seen in Table 2 the samples having a Na/K ratio value close to 1 (*i.e.* similar amounts of Na to K) the reduction is equally distributed between the two firing stages. The reductions for S103 during the R1 and R2 test are 12.70% and 11.60%, respectively.

From the above, it is clear that K is responsible for the thermal resistance of the clinoptilolite during the first heating at 460°C. Equally, though, Na is responsible for the thermal resistance of the clinoptilolite during the second heating at 560°C. So both K and

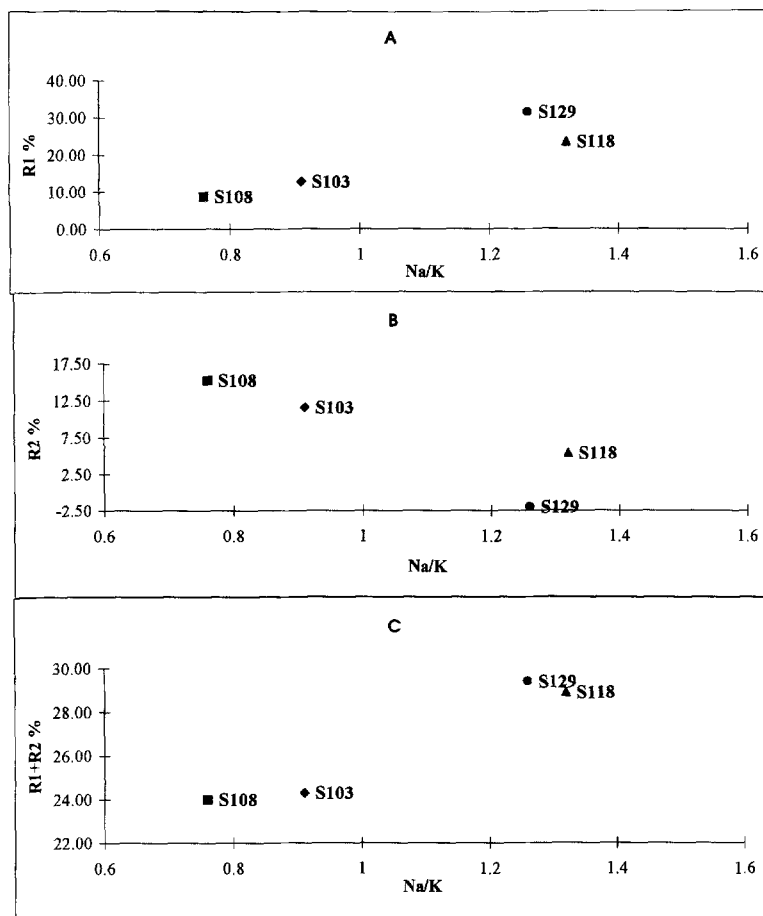


Figure 3. Na/K vs. the reduction in the intensity of the 020 diffraction peak during thermal testing. R1: 460°C for 12 h, R2: 560°C for 12 h, R1 + R2: total reduction. The value of the Na/K ratio is the mean value of all the Na/K values obtained from the same sample.

Na, as well as their interrelationship, are responsible for the thermal behavior of the clinoptilolite as is seen by the behavior of the 020 peak.

In the literature, both the Si/Al ratio and the presence of divalent cations (Ca and Mg) with the large amount of coordinated H₂O associated with them, have been invoked as additional factors influencing thermal behavior. In this study, the samples with the higher Si/Al ratio and the lowest Ca content showed the highest thermal stability. Therefore, the influence of the Si/Al ratio and the Ca content cannot be dismissed as being insignificant. However, in the literature, the Si/Al ratio and the divalent cations have also been related to some obscure phenomena of thermal behavior. For example, clinoptilolites with a Si/Al ratio >4 have been reported to show an intermediate thermal behavior, whereas clinoptilolites with large amounts of Ca showed high thermal stability (Alietti *et al.*, 1977).

In contrast, the presence of monovalent cations mainly of the low ionic potential K, and secondly of the intermediate ionic potential Na, has always been

related in the literature to the thermal stability of clinoptilolite.

Other evidence for the relationship between Na/K and thermal behavior

Some evidence for the existence of the relationship between the Na/K ratio and the thermal behavior can be found as reported by Alietti *et al.* (1977). The relationship was not discussed by these authors who examined Ca-rich clinoptilolites and although an intermediate to low thermal stability was expected (because they were Ca-rich), the minerals showed a thermal behavior (resistance) similar to clinoptilolite. Alietti *et al.* (1977) stated: "The calcic-magnesian heulandites of group 3 (clinoptilolites) have a modest potassium content, but this prevails over the sodium." If the amount of K present was modest, but still prevails over Na, then, the Na/K ratio should be <1.

Based on the findings of the present study the peculiar thermal behavior that Alietti *et al.* (1977) believed they found, *i.e.* Ca-rich clinoptilolite phases be-

having thermally like clinoptilolites, is actually not that peculiar. In the same work, Alietti *et al.* (1977) reported that only heulandites of type 1 appear richer in Na (therefore, $\text{Na/K} > 1$), while heulandites of type 2 (an intermediate thermal behavior) are richer in K ($\text{Na/K} < 1$). It is obvious that in all cases the value of the Na/K ratio influenced the thermal behavior of the clinoptilolites studied.

The structural evidence

The influence of K and Na in the thermal behavior of clinoptilolite is related to the type of cations and their position in the structure of the mineral. Clinoptilolite is characterized by a sheet-like organization perpendicular to the *b* axis (Alberti, 1975) and the presence of three channels. Two channels (A and B) defined by 10- and 8-membered tetrahedral rings are situated parallel to *c*, and a third channel (C) defined by 8-membered rings which is situated parallel to the *a* axis. The intersection of the channels creates two cages of unequal size in which the cations are located (Armbruster and Gunter, 1991).

Koyama and Takeuchi (1977) and Armbruster and Gunter (1991) showed that K fully occupies a certain cation site, M(3), which is coordinated by six framework oxygen atoms and three H_2O molecules. This cation site is located at the center of the 8-membered ring of the channel C (parallel to α). Koyama and Takeuchi (1977) believed that in order to collapse the channel and see evidence of the destruction, the rings should collapse. They also accepted that during dehydration even small amounts of K can prevent the rings from collapsing, even when a considerable amount of the H_2O molecules had been driven off. On the other hand, the dehydration of clinoptilolite starts with loss of H_2O molecules coordinated to Na (Na found in the 10-membered ring channel), and at the same time Na migrates to the cavity wall of channel A (Armbruster and Gunter, 1991).

The thermal destruction, which is due to the behavior of Na, may somehow be balanced by the maintenance of the structure due to K. Therefore, any form of thermal behavior (*e.g.* reduction of the intensity of the 020 peak) observed by XRD is the result of the simultaneous behavior of K and Na. The Na/K ratio can be considered as a simultaneous imprint of the behavior of K and Na. Also, Koyama and Takeuchi (1977) concluded that the larger the occupancy of K at M(3), the more significant the resistance that the framework shows, and Armbruster and Gunter (1991) accepted that as dehydration progresses, some Na cations can possibly migrate to M(3). In this case, the Na/K ratio can also show the degree of K occupancy in the relevant site.

CONCLUSIONS

The correlation between the thermal behavior of clinoptilolite and its chemical composition requires a rep-

resentative set of EMPA data to be obtained from a sample. The presence of K and Na in the structure of clinoptilolite as well as their relationship play an important role in the thermal behavior of the mineral. As a result, a strong, statistically significant, quantifiable relationship between the reduction of the 020 diffraction peak of clinoptilolite and the Na/K ratio is established.

ACKNOWLEDGMENTS

The author is grateful to Ansel Dunham of the Geology Department of Leicester University (UK) for supervising his PhD work during a very difficult period of his life. Sadly, Prof. Dunham passed away on January 18th, 1998.

The author would like to thank H. Louka for checking the manuscript and the Geology Department of Leicester University for providing the necessary analytical facilities. A number of microprobe analyses of clinoptilolite were performed at the Department of Earth Sciences, Bristol University, UK, during a visit by the author in March 2000 under the scheme "Access to large-scale geochemical facilities", funded by the EU. The critical reviews and helpful suggestions by J.R. Boles, R.A. Sheppard and an anonymous reviewer helped to improve the manuscript further. The State Scholarship Foundation (SSF) of Greece is acknowledged for providing financial support. The author is also grateful to R. Wilson, N. Marsh, C. Cunningham, R. Branson, S. Button and R. Kelly of the Geology Department of Leicester University and to S. Kearns of the Department of Earth Sciences, Bristol University for their valuable help on technical aspects.

REFERENCES

- Alberti, A. (1975) The crystal structure of two clinoptilolites. *Tschermarks Mineralogische und Petrographische Mitteilungen*, **22**, 25–37.
- Alietti, A. (1972) Polymorphism and crystal-chemistry of heulandites and clinoptilolites. *American Mineralogist*, **57**, 1448–1462.
- Alietti, A., Gottardi, G. and Poppi, L. (1974) The heat behavior of the cation exchanged zeolites with heulandite structure. *Tschermarks Mineralogische und Petrographische Mitteilungen*, **21**, 291–298.
- Alietti, A., Brigatti, M.F. and Poppi, L. (1977) Natural Ca-rich clinoptilolites (heulandites of group 3): New data and review. *Neues Jahrbuch für Mineralogie Monatshefte*, **H11**, 493–501.
- Armbruster, T. (1993) Dehydration mechanism of clinoptilolite and heulandite: Single-crystal X-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K. *American Mineralogist*, **78**, 260–264.
- Armbruster, T. and Gunter, M.E. (1991) Stepwise dehydration of heulandite-clinoptilolite from Succor Creek, Oregon, USA: A single-crystal X-ray study at 100 K. *American Mineralogist*, **76**, 1872–1883.
- Bish, D.L. (1984) Effects of exchangeable cation composition on the thermal expansion/contraction of clinoptilolite. *Clays and Clay Minerals*, **32**, 444–452.
- Bish, D.L. (1988) Effects of composition on the dehydration behavior of clinoptilolite and heulandite. Pp. 565–576 in: *Occurrence, Properties and Utilization of Natural Zeolites* (D. Kollo and H.S. Sherry, editors). Akademiai Kiado, Budapest.
- Bish, D.L. (1993) Thermal behavior of natural zeolites. Pp. 259–269 in: *Natural Zeolites '93: Occurrence, Properties, Use* (D.W. Ming and F.A. Mumpton, editors). International Committee on Natural Zeolites, Brockport, New York.

- Boles, J.R. (1972) Composition, optical properties, cell dimensions, and thermal stability of some heulandite group zeolites. *American Mineralogist*, **57**, 1463–1493.
- Boles, J.R. and Surdam, R.C. (1979) Diagenesis of volcano-genic sediments in a Tertiary saline lake; Wagon Bed Formation, Wyoming. *American Journal of Science*, **279**, 832–853.
- Coombs, D.S. *et al.* (1998) Recommended nomenclature for zeolite minerals: Report of the Subcommittee on Zeolites of the International Mineralogical Association, commission on New Minerals and Minerals Names. *European Journal of Mineralogy*, **10**, 1037–1081.
- Dunham, A.C. and Wilkinson, F.C.F. (1978) Accuracy, precision and detection limits of energy-dispersive electron-microprobe analyses of silicates. *X-Ray Spectrometry*, **7**, 50–56.
- Kitsopoulos, K.P. (1995) The mineralogy, geochemistry, physical properties and possible industrial applications of volcanic zeolitic tuffs from Santorini and Polyegos Islands, Greece. Ph.D. thesis, Leicester University, Leicester, UK, 442 pp.
- Kitsopoulos, K.P. (1997) Genesis of heulandite group of minerals in pyroclastics (Santorini, Greece). Implications for models of zeolitization of volcanoclastic materials. *Zeolite '97, 5th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Ischia (Naples, Italy), September 1997. Program and Abstracts Volume*, 195–197.
- Kitsopoulos, K.P. and Dunham, A.C. (1998) Compositional variations of mordenite from Polyegos island, Greece: Na-Ca and K-rich mordenite. *European Journal of Mineralogy*, **10**, 569–577.
- Koyama, K. and Takeuchi, Y. (1977) Clinoptilolite: the distribution of potassium atoms and its role in thermal stability. *Zeitschrift für Kristallographie*, **145**, 216–239.
- Mason, B. and Sand, L.B. (1960) Clinoptilolite from Patagonia: The relationship between clinoptilolite and heulandite. *American Mineralogist*, **45**, 341–350.
- Mumpton, F.A. (1960) Clinoptilolite redefined. *American Mineralogist*, **45**, 351–369.
- Shepard, A.O. and Starkey, H.C. (1966) The effect of exchanged cations on the thermal behaviour of heulandite and clinoptilolite. *Mineralogical Society of India, IMA Volume*, 155–158.
- Tsolis-Katagas, P. and Katagas, C. (1989) Zeolites in pre-caldera pyroclastic rocks of the Santorini Volcano, Aegean Sea, Greece. *Clays and Clay Minerals*, **37**, 497–510.
- E-mail of corresponding author: LL1@otenet.gr
(Received 20 December 1996; revised 15 January 2001; Ms. 97-012; A.E. Ahmet R. Mermut)