

## X-RAY DIFFRACTION INTENSITY RATIOS $I(111)/I(\bar{3}11)$ OF NATURAL HEULANDITES AND CLINOPTILOLITES

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**Abstract**—Heulandite-group zeolites are abundant in the Miocene pyroclastics from Western Anatolia, Turkey. We investigated the relation between the  $I(111)/I(\bar{3}11)$  intensity ratios measured by X-ray diffraction (XRD) and the content of exchangeable cations for 15 samples of natural heulandite-group minerals gathered from the Gördes and Bigadiç regions of Western Anatolia. The intensity ratios range from 0.77 to 0.94 in natural heulandites and from 1.38 to 1.80 in natural clinoptilolites. The data obtained from Na-, K- and Ca-exchanged forms of a heulandite and clinoptilolite show that the intensity ratio increases with Na-, K- and Ca-exchange in heulandite and also with Na- and K-exchange in clinoptilolite, whereas it decreases with Ca-exchange in clinoptilolite. The intensity ratios were calculated using the known structural data of clinoptilolites to understand the effect of positions, amounts and kinds of exchangeable cations and water molecules. An increase in Na and Ca may increase or decrease the intensity ratio, depending on their sites and occupancies. Potassium causes a significant increase in the intensity ratio and an increase in Mg decreases the intensity ratio. There is a strong correlation between the intensity ratio  $I(111)/I(\bar{3}11)$  and  $(Na + K)/(Ca + Mg)$  ratio and thermal stability, both of which have been used to characterize heulandite-group minerals.

**Key Words**—Clinoptilolite, Heulandite, Natural Zeolites, Turkey, X-Ray Diffraction.

### INTRODUCTION

Heulandite-group minerals consist of heulandite and clinoptilolite, which are isostructural with an approximate chemical formula of  $(Ca, Na, K)_6 Al_6 Si_{30} O_{72} \cdot 24 H_2O$ . Distinguishing between these 2 minerals is important for 2 reasons: 1) It provides insights into the mineralogic zonation of diagenetic or hydrothermal environments. Heulandite and clinoptilolite may occur as alteration products in different zones (Utada 1971; Hay 1981). 2) It will help with the commercial applications of the heulandite-group minerals. The different physical and chemical characteristics of heulandite and clinoptilolite are important in their utilization (Mumpton 1981). Clinoptilolite is more stable towards dehydration than heulandite and more favorable as an adsorbent and catalyzer (Flanigen 1981). Heulandites and clinoptilolites have been distinguished on the basis of their cation contents and Si/Al ratios, with clinoptilolites having  $(Na + K) > Ca$  and  $Si/Al > 4$  and heulandites having  $Ca > (Na + K)$  and  $Si/Al < 4$  (Mason and Sand 1960; Boles 1972). Differences in thermal behavior as a function of the composition of the heulandite-group zeolites have been reported in the literature (Mason and Sand 1960; Mumpton 1960; Shepard and Starkey 1966; Alietti et al. 1977). Heulandites can be classified into 2 types on the basis of their thermal behavior. Type-1 heulandite exhibits no powder diffraction pattern after heating at 550 °C for 12 h, whereas type-2 heulandites still exhibit sharp powder patterns (Alietti 1972). On the other hand, the structure of clinoptilolite persists after heating at 550 °C, through 750 °C. According to Alietti (1972) and

Boles (1972), polymorphic transformations in the heulandites reveal the presence of 3 phases: A, B and I.

Although there are minor differences in X-ray powder diffraction (XRD) patterns of heulandites and clinoptilolites (Ames et al. 1958; Coombs 1958; Mason and Sand 1960; Mumpton 1960; Minato and Takano 1964; Merkle and Slaughter 1968; Brown et al. 1969; Wise et al. 1969; Boles 1972; Bish 1984), it has not been possible to differentiate between them unambiguously using XRD. Both heulandites and clinoptilolites have 2 diffraction lines in the range of 16.90–17.30 °2 $\theta$  (CuK $\alpha$  radiation) with  $d = 5.24$  Å ( $\bar{3}11$ ) and  $d = 5.11$  Å (111), respectively. The aim of this paper is to define a parameter for discriminating between heulandite and clinoptilolite based on their  $I(111)/I(\bar{3}11)$  intensity ratios. Fifteen heulandite- and clinoptilolite-rich samples and 1 Na-, K- and Ca-exchanged heulandite and 1 such clinoptilolite were used to study the  $I(111)/I(\bar{3}11)$  ratios of their X-ray patterns. These data allowed us to distinguish the intensity ratios of heulandites from that of clinoptilolites. The relationships between the intensity ratio, compositions and thermal stabilities of heulandite-group minerals were investigated in the natural samples. In addition, the intensities of 111 and  $\bar{3}11$  were calculated using published atomic coordinates and site occupancies of heulandite-group minerals with known structures, and an attempt was made to evaluate the theoretical relationship between composition and intensity ratio.

Samples of zeolite-rich rhyolite and rhyodacite tuff were collected from the Gördes and Bigadiç regions in West Anatolia, Turkey (Figure 1). Geology, petrography, geochemistry and diagenetic alteration of the

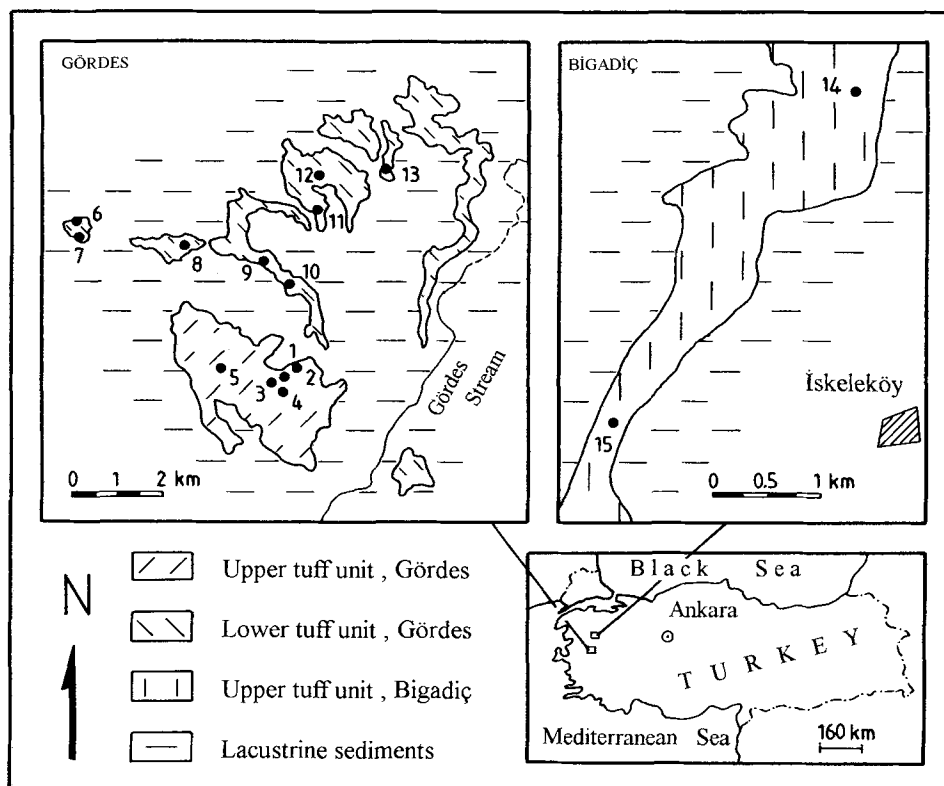


Figure 1. Simplified geological map of the Gördes and Bigadiç regions showing the sample locations.

Miocene pyroclastic rocks from the Gördes area have been described by Esenli and Özpeker (1993) and Esenli and Kumbasar (1994), who also give data on the unit-cell contents and thermal behavior of heulandites and clinoptilolites based on XRD, scanning electron microscopy (SEM), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (samples 1 to 7, 9 to 13, Table 1). Similar studies of the zeolite-rich pyroclastic rocks from the Bigadiç area were done by Baysal et al. (1986), Göktekin (1989), Sirkecioglu et al. (1990) and Esenli and Kumbasar (1994) (samples 14 and 15, Table 1). Three new samples (3, 5 and 8) from the Gördes area were examined in this study. Heulandite, clinoptilolite and other authigenic minerals (opal-CT, quartz, smectite, illite, celadonite, K-feldspar, analcime, calcite and dolomite) have formed by the diagenetic alteration of lacustrine glassy and crystal tuffs of Miocene age in the Gördes and Bigadiç regions. Pyroclastic rocks in Gördes region can be divided into 2 sequences: 1) the lower tuffs, with a thickness of 85 m, and 2) the upper tuffs, with a thickness of 70 m. Clinoptilolite (samples 6 to 13) is found in the lower tuff unit and heulandite-2 (samples 1 to 5) in the upper tuff unit. The pyroclastic rocks in the Bigadiç region, forming a sequence 250 m thick, occur as ash-size tuffs at the bottom and fine ash-size tuffs on top. Sample 14 was collected from

ash tuffs and sample 15 from fine ash tuffs, and both contain clinoptilolite. The identification of heulandite and clinoptilolite in these samples was based on their compositions and thermal stabilities (Table 1). Polymorphism was observed in 4 heulandite-2 samples based on the positions of the 020 reflections after heating for 12 h at 400 °C. Phases A and B in sample 2, phases A and I in sample 3 and phases A, B and I in samples 4 and 5 were found. The other samples did not show any polymorphism and contained only phase A.

## METHODS

### XRD, Thermal Tests

A Philips diffractometer and  $\text{CuK}\alpha$  radiation were used for all X-ray analysis. Samples were ground and sieved to less than 44  $\mu\text{m}$  and 2 mounts for each sample were prepared. The peak heights of all reflections were measured on 2 diffractograms for each of the 15 samples at 1 °2 $\theta$  per min through the angular range of 2–60 °2 $\theta$ . Finally the intensities of the 111 and  $\bar{3}11$  reflections were measured relative to the 131 peak which has the highest intensity in the patterns. The 131 peak is actually composed of the 131, 400 and 330 reflections. However, it is seen from the calculated XRD patterns that compositional variations in heu-

Table 1. Unit-cell chemistry and thermal stability data of heulandites and clinoptilolites from Gördes and Bigadiç regions (West Anatolia).

Sample	Analysis	Element								Chemical parameter		Thermal stability $I(020)$ at 550 °C/ $I(020)$
		Si	Al	Fe	Mg	Ca	K	Na	Error (%)	Si/Al	Na + K/ Ca + Mg	
1 (G-3)	1	29.25	6.93	0.08	0.44	2.03	0.88	0.16	17.4	4.22	0.42	0.00
2 (G-8)	1	29.52	6.46	0.04	0.53	2.22	0.70	0.20	1.6	4.57	0.33	—
2 (G-8)	2	29.14	6.64	0.11	0.60	2.51	0.78	0.10	4.9	4.39	0.28	—
2 (G-8)	Average	29.33	6.55	0.08	0.57	2.37	0.74	0.15	2.1	4.48	0.30	0.14
3 (G-11)	1	29.12	7.00	0.21	0.48	2.13	0.74	0.14	18.2	4.16	0.34	0.00
4 (G-12)	1	29.00	6.47	0.45	0.44	2.56	1.07	0.05	2.8	4.48	0.37	0.00
5 (OR-11)	1	29.08	6.86	0.14	0.38	2.21	0.80	0.24	12.5	4.24	0.40	0.00
6 (SOF-2)	1	29.69	5.81	0.33	0.30	1.69	2.73	0.09	9.7	5.11	1.42	—
6 (SOF-2)	2	29.72	6.18	0.07	0.20	1.89	2.20	0.08	3.3	4.81	1.11	—
6 (SOF-2)	Average	29.71	6.00	0.20	0.25	1.79	2.47	0.09	6.6	4.95	1.25	0.56
7 (SOF-8)	1	30.04	5.53	0.26	0.36	1.46	2.47	0.32	9.9	5.43	1.53	—
7 (SOF-8)	2	29.95	5.92	0.37	0.42	1.15	1.94	0.23	18.5	5.06	1.38	—
7 (SOF-8)	Average	30.00	5.73	0.32	0.39	1.32	2.21	0.28	2.4	5.24	1.46	0.68
8 (KIR-4)	1	29.81	5.85	0.28	0.44	1.53	2.18	0.33	5.0	5.10	1.27	0.56
9 (KIR-7)	1	29.82	5.94	0.26	0.28	1.18	2.85	0.26	2.8	5.02	2.13	0.72
10 (KIR-8)	1	29.59	5.96	0.10	0.30	1.89	2.77	0.18	17.3	4.96	1.35	0.69
11 (AY-2)	1	30.09	5.61	0.31	0.34	1.21	2.47	0.29	1.0	5.36	1.78	0.59
12 (KUZ-8)	1	29.94	5.89	0.27	0.22	0.92	2.90	0.51	8.3	5.08	2.99	—
12 (KUZ-8)	2	29.86	6.02	0.10	0.14	1.30	2.65	0.54	0.8	4.96	2.22	—
12 (KUZ-8)	Average	29.90	5.96	0.19	0.18	1.11	2.78	0.53	4.2	5.02	2.57	0.88
13 (KO-6)	1	29.84	5.87	0.39	0.72	1.24	1.64	0.28	7.2	5.08	0.98	—
13 (KO-6)	2	29.37	6.37	0.25	0.77	1.44	1.95	0.18	1.1	4.61	0.96	—
13 (KO-6)	3	30.03	5.65	0.20	0.62	1.33	2.03	0.28	5.8	5.32	1.18	—
13 (KO-6)	Average	29.75	5.96	0.28	0.70	1.34	1.87	0.25	0.6	4.99	1.04	0.57
14 (BC-1)	1	28.95	7.00	0.00	1.25	0.97	1.90	0.88	2.9	4.14	1.25	—
14 (BC-1)	2	29.29	6.66	0.00	0.79	1.08	2.30	0.98	5.1	4.40	1.72	—
14 (BC-1)	Average	29.12	6.83	0.00	1.02	1.03	2.10	0.93	4.2	4.26	1.48	0.72
15 (BF-2)	1	29.65	6.49	0.02	1.05	1.48	0.64	0.41	6.5	4.57	0.42	—
15 (BF-2)	2	29.65	6.44	0.18	1.02	1.53	0.32	0.50	11.8	4.60	0.32	—
15 (BF-2)	3	29.47	6.71	0.00	1.07	1.57	0.41	0.36	10.9	4.39	0.29	—
15 (BF-2)	Average	29.59	6.55	0.07	1.05	1.53	0.46	0.42	9.6	4.52	0.34	0.34

Table 2. The relative intensities of 111 and  $\bar{3}11$  and intensity ratios  $I(111)/I(\bar{3}11)$  of the samples given in Table 1.

Sample	Relative intensity†		Intensity ratio $I(111)/I(\bar{3}11)$
	111	$\bar{3}11$	
1 (heulandite)	20	24	0.83
2 (heulandite)	17	21	0.81
3 (heulandite)	15	18	0.83
4 (heulandite)	17	22	0.77
5 (heulandite)	16	17	0.94
6 (clinoptilolite)	21	15	1.40
7 (clinoptilolite)	28	19	1.47
8 (clinoptilolite)	16	11	1.45
9 (clinoptilolite)	20	12	1.67
10 (clinoptilolite)	20	13	1.54
11 (clinoptilolite)	20	13	1.54
12 (clinoptilolite)	27	15	1.80
13 (clinoptilolite)	22	13	1.69
14 (clinoptilolite)	22	13	1.69
15 (clinoptilolite)	22	16	1.38

† Relative to 131.

landites and clinoptilolites proportionally affect the intensities of these reflections in the same manner. The intensity values of 111 and  $\bar{3}11$  reflections for each sample are given in Table 2.

Samples mounted on a glass slide were heated at 400 and 550 °C for 12 h (Alietti 1972) to determine the thermal stabilities of heulandite-group minerals using the 020 reflection. The intensity measurements of the 020 reflection before and after heating were made on the same, unperturbed sample mount. Reduction of the 020 intensity was investigated after heating, and the  $I(020)$  at 550 °C/ $I(020)$  ratio was used to estimate the thermal stability of the heulandites and clinoptilolites.

#### Chemical Composition

Compositions of heulandites and clinoptilolites were obtained semiquantitatively with a JEM-7330 type scanning electron microscope and a Tracor-Northern 5400 energy-dispersive X-ray spectrometer (EDX). Structural formulas were calculated on the basis of 72 oxygens. When the sample was analyzed 2 times or more, the average value was taken. The quality of the

analyses was calculated by evaluating the balance error,  $E$  (Table 1), given by Gottardi and Galli (1985). Although  $E$  values of 4 samples (1, 3, 5 and 10) were over 10%, their thermal characteristics unambiguously indicated their nature; therefore, these samples were also used in the present study.

#### Exchange Experiments

Two samples rich in heulandite and clinoptilolite (G-8 and SOF-2) were modified into Na-, K-, Ca-enriched forms, and the intensity ratios of resulting materials were measured. The 90–150  $\mu\text{m}$  size fractions from ground natural samples were washed several times with distilled water and dried. Ion exchange was performed using solutions of 1  $M$  NaCl, KCl and  $\text{Ca}(\text{NO}_3)_2$ , and 50 mL solution was used per 1 g solid material. Ion-exchange experiments were carried out at room temperature for 5 h and were repeated 7 times in order to approach the maximum capacity. The samples were then washed and dried.

#### Calculated Diffraction Patterns

The relationship between exchangeable cations and the  $I(111)/I(\bar{3}11)$  ratio for heulandite-group zeolites was investigated using calculated diffraction patterns. The atomic coordinates determined by Koyama and Takeuchi (1977) were used to calculate the intensities of the 111 and  $\bar{3}11$  reflections for Agoura and Kuruma, and Succor Creek (Armbruster and Gunter 1991) heulandite-group zeolites. Site occupancies of Na, Ca, K and Mg cations and that of water molecules of Agoura clinoptilolite were changed, and XRD patterns were calculated for each resultant composition. The site occupancy of only 1 type of cation was increased or decreased in steps of about 10% of the site occupancy of that cation as found in the Agoura clinoptilolite and XRD patterns were calculated for each change. Intensities were calculated using XPOW version 2.0 (Downs et al. 1993).

### RESULTS

#### Natural Samples

The 5 strongest reflections found in the XRD patterns of heulandites and clinoptilolites from the Grdes and Bigadi regions are 131, 020,  $\bar{4}21$ , 350 and  $\bar{2}22$ , in decreasing order. No difference in the  $d$ -spacings of reflections of heulandite and clinoptilolite samples were recognized. However, there are differences in the intensity of the 220,  $\bar{3}11$  and 111 reflections for these 2 minerals. Although the 220 reflection at  $d = 5.90 \text{ \AA}$  has very low intensity (average relative intensity 5/100) in clinoptilolite, it is not observed in heulandite patterns. We thought that the intensities of  $\bar{3}11$  ( $d = 5.24 \text{ \AA}$ ) and 111 ( $d = 5.11 \text{ \AA}$ ) reflections have a distinctive character to allow discrimination between heulandite and clinoptilolite. The relative intensities of the

111 and  $\bar{3}11$  reflections of the samples studied are given in Table 2. In general, the average intensity values for 111 and  $\bar{3}11$  are 17/100 and 20/100 in heulandites and 20/100 and 13/100 in clinoptilolites, respectively. The differences in the intensities of 111 and  $\bar{3}11$  for heulandites and clinoptilolites are better observed using the  $I(111)/I(\bar{3}11)$  ratios (Table 2). The intensity ratio  $I(111)/I(\bar{3}11)$  is in the range of 0.77–0.94 for 5 heulandites and in the range of 1.38–1.80 for 10 clinoptilolites. Average values are 0.84 for heulandites and 1.56 for clinoptilolites.

The intensity ratio is proportional to some chemical parameters, most importantly to Ca and K. The correlation coefficients,  $r$ , of the relation between intensity ratio and individual cations are 0.58 for Na, 0.81 for K, 0.92 for Ca and 0.02 for Mg (Figure 2). The intensity ratio is also strongly correlated with the  $(\text{Na} + \text{K})/(\text{Ca} + \text{Mg})$  ratio, ( $r = 0.85$ ), and moderately with the Si/Al ratio ( $r = 0.68$ ) (Figure 3). The relationship between the intensity ratio and thermal stability  $I(020)$  at  $550^\circ\text{C}/I(020)$  ratio is particularly strong ( $r = 0.96$ ) (Figure 4). However, because heulandites are not stable above  $550^\circ\text{C}$ , they should not be considered in this correlation. The correlation coefficient of the intensity ratio-thermal stability relationship for clinoptilolites only is 0.76. Heulandites and clinoptilolites form separate domains in the diagrams (Figures 2, 3 and 4), and the boundary values of intensity ratio between heulandite and clinoptilolite are about 1.10–1.20.

#### Exchanged Forms

The 111 and  $\bar{3}11$  intensities and the  $I(111)/I(\bar{3}11)$  ratios for untreated heulandite (Sample 2) and clinoptilolite (sample 6) and their K-, Na- and Ca-enriched forms are given in Table 3. The K content clearly affects the 111 and  $\bar{3}11$  intensities, particularly for heulandite. The relative intensity of  $\bar{3}11$  decreases by  $\sim 35\%$  on K-exchange of heulandite and by 15% on K-exchange of clinoptilolite. The 111 intensity increases by  $\sim 30\%$  and  $\sim 15\%$  in K-exchanged heulandite and clinoptilolite, respectively. Na exchange increases the 111 intensity by about 40% in heulandite and by about 25% in clinoptilolite, whereas the  $\bar{3}11$  intensity does not change significantly by Na substitution. An increase in Ca reduces the relative intensities of both reflections (Table 3). The K, Na and Ca exchanges increase the intensity ratio by about  $\sim 90$ ,  $\sim 30$  and  $\sim 20\%$ , respectively, in heulandite. The intensity ratio increases by  $\sim 30\%$  and 20% in K- and Na-exchanged clinoptilolite, whereas it decreases by  $\sim 30\%$  in Ca-exchanged clinoptilolite.

#### Site Occupancy

Koyama and Takeuchi (1977) recognized 4 extra-framework cation positions in heulandite-group minerals: M(1), M(2), M(3) and M(4), where M(1) and

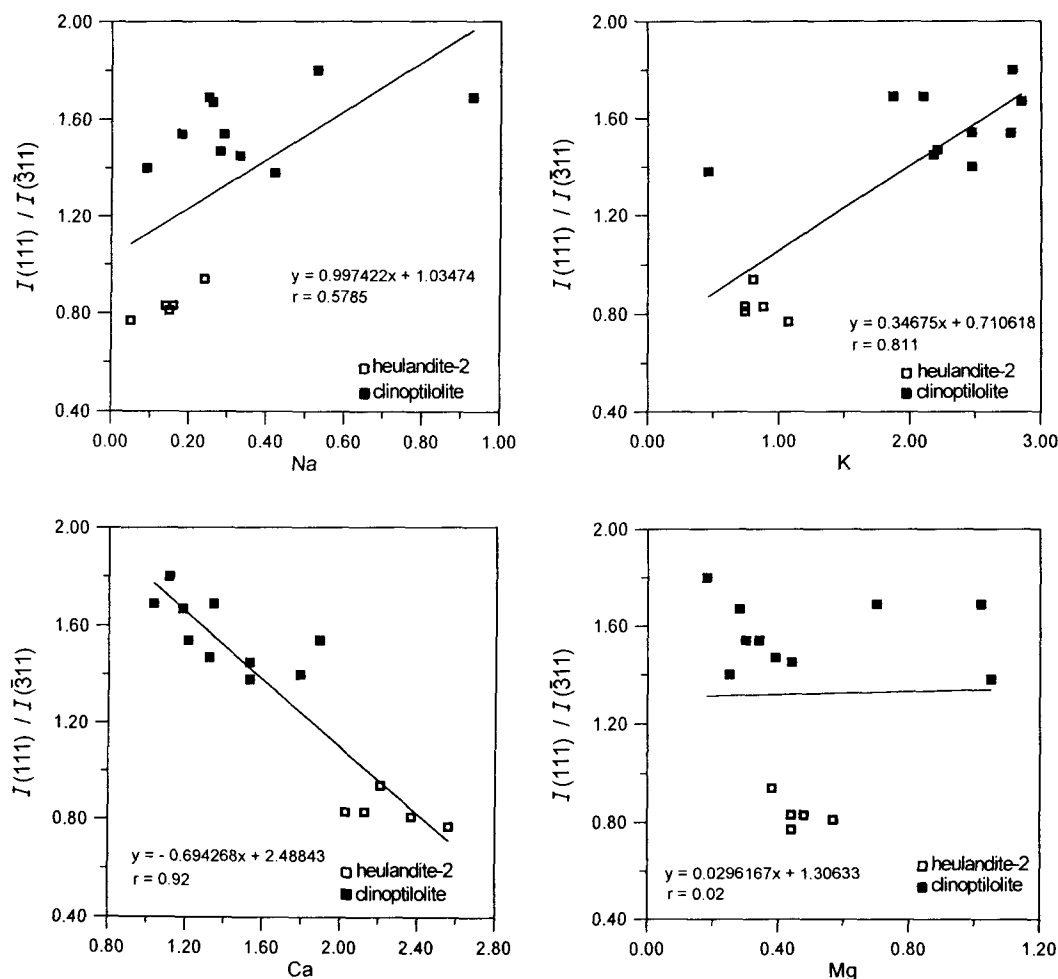


Figure 2. The intensity ratio  $I(111)/I(\bar{3}11)$  vs. Na, K, Ca and Mg contents of 15 heulandites and clinoptilolites from Gördes and Bigadiç regions (West Anatolia).

M(2) are occupied by Na and Ca, M(3) is occupied by K and M(4) is occupied by Mg. In clinoptilolite, M(1) and M(2) are rich in Na, whereas in heulandite they are rich in Ca. The occupancy of K in the M(3) site in clinoptilolite is higher than that in heulandite. Smyth et al. (1990), Armbruster and Gunter (1991) and Gunter et al. (1994) have also assigned the same sites for the exchangeable cations.

The effect on the intensity ratio of changing the site occupancy of exchangeable cations and water molecules in Agoura clinoptilolite was studied. The  $I(111)/I(\bar{3}11)$  intensity ratios were calculated using the atomic coordinates and site occupancies of heulandite-group minerals from Agoura and Kuruma (Koyama and Takeuchi 1977) and Succor Creek (Armbruster and Gunter 1991). The occupancies of M(1), M(2), M(3) and M(4) sites were changed one by one taking into account the total possible cation contents of heulandite group minerals, that concurrent occupation of M(3) and M(1) is forbidden and the maximum occupancy of Ca in M(2)

site is 0.50 (Armbruster and Gunter 1991). Calculated changes are given in Table 4. An increase in Na or in Ca in the M(1) site caused a slight increase in the  $I(111)/I(\bar{3}11)$  intensity ratio. An increase in Ca and Na in the M(2) site caused a decrease in the intensity ratio. An increase in K in the M(3) site increased the intensity of both the 111 and  $\bar{3}11$  reflections and the intensity ratio. An increase in Mg in M(4) site decreased the 111 intensity, increased the  $\bar{3}11$  intensity and decreased the intensity ratio. Consequently, increases in the occupancy of M(1) and M(3) increased the intensity of 111 significantly, and increases in M(2) and M(4) decreased the intensity. An increase in any cation sites caused an increase in the intensity of  $\bar{3}11$ .

Koyama and Takeuchi (1977) classified water molecules in heulandite-group zeolites into 2 categories. Those which fall into the first category have a maximum occupancy of 1.0, regardless of change in the chemical composition. Those in the second category have variable occupancies which may change from

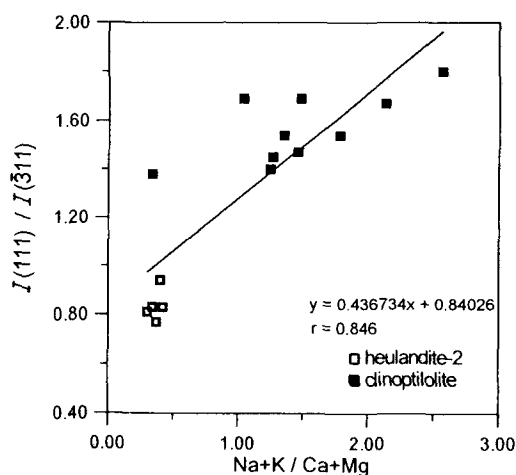
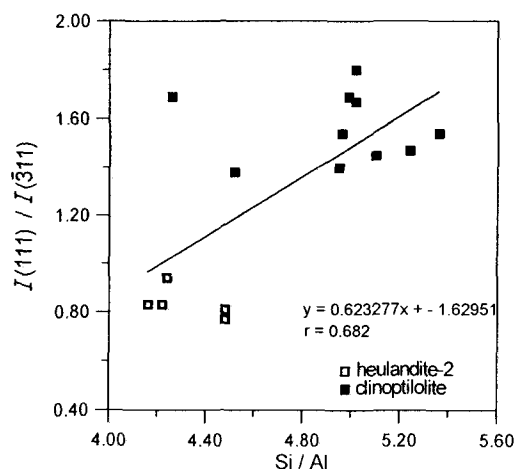


Figure 3. The intensity ratio  $I(111)/I(\bar{3}11)$  vs. chemical parameters of 15 heulandites and clinoptilolites from Gördes and Bigadiç (West Anatolia).

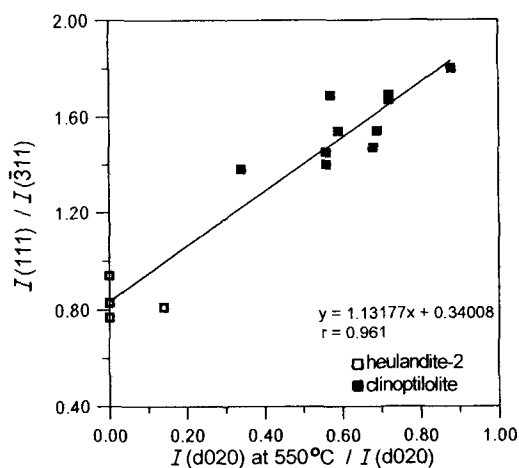


Figure 4. The intensity ratio  $I(111)/I(\bar{3}11)$  vs. thermal stability  $I(d020)$  at 550 °C/ $I(d020)$  of 15 heulandites and clinoptilolites from Gördes and Bigadiç (West Anatolia).

Table 3. The relative intensities of 111 and  $\bar{3}11$  and intensity ratios  $I(111)/I(\bar{3}11)$  for natural and cation-exchanged heulandite and clinoptilolite from Gördes region.

Sample	Relative intensity†		Intensity ratio $I(111)/I(\bar{3}11)$
	111	$\bar{3}11$	
2 (heulandite), untreated	17	21	0.81
2 (heulandite), K-exchanged	22	14	1.57
2 (heulandite), Na-exchanged	24	23	1.04
2 (heulandite), Ca-exchanged	13	13	1.00
6 (clinoptilolite), untreated	21	15	1.40
6 (clinoptilolite), K-exchanged	24	13	1.85
6 (clinoptilolite), Na-exchanged	26	15	1.73
6 (clinoptilolite), Ca-exchanged	14	14	1.00

† Relative to 131.

one specimen to another. Water molecules in the second category, namely W(1), W(2), W(3) and W(7), are associated with cations at M(1), M(3), M(2) and M(4), respectively, whereas W(5) and W(6) are associated with cations at both M(1) and M(4). The site occupancies of water molecules with variable occupancies in Agoura clinoptilolite were changed one by one and the intensity ratios were calculated for each composition. When the water molecules are not included in the intensity calculations, the intensity ratio  $I(111)/I(\bar{3}11)$  increases. When the occupancies of water molecules at W(1), W(2) and W(6) are increased, the intensity ratio increases, whereas an increase in the occupancy of W(3), W(5) and W(7) decreases the intensity ratio.

## DISCUSSION

The intensities of the 111 and  $\bar{3}11$  reflections of heulandites and clinoptilolites are primarily influenced by the positions, contents and kinds of the extra-framework cations and water molecules. The  $I(111)/I(\bar{3}11)$  ratios of natural heulandite and clinoptilolite samples increase with increasing K and Na and decrease with increasing Ca contents. The variation of intensity ratio with Mg content is not clear in the natural samples. Data obtained from Na-, K- and Ca-exchanged forms and also determined from calculated XRD patterns of clinoptilolite accord well with the data from natural heulandites and clinoptilolites and

Table 4. Calculated changes in 111 and  $\bar{3}11$  intensities and intensity ratios as a function of exchangeable-cation composition.

Increase in occupancy	Relative intensity†		Intensity ratio $I(111)/I(\bar{3}11)$
	111	$\bar{3}11$	
in M 1	increase	increase	increase
in M 2	decrease	increase	decrease
in M 3	increase	increase	increase
in M 4	decrease	increase	decrease

† Relative to 020.

explain the source of this variation. Although the actual contents of Na, K and Ca in exchanged samples were not known, the effect on the intensity ratio of increasing or decreasing Na, K and Ca in exchanged samples was observed. The average values of 111 and  $\bar{3}11$  intensities and the intensity ratio observed on the XRD patterns of exchanged forms of heulandite and clinoptilolite are 25, 19 and 1.40 for Na-exchanged samples; 23, 14 and 1.71 for K-exchanged samples; and 14, 14 and 1.40 for Ca-exchanged samples. These results confirm the results found by the calculated XRD patterns. An increase in M(1) increases and an increase in M(2) decreases the intensity ratio. The M(1) sites are occupied mainly by Na (Na + Ca) and the M(2) sites by Ca (Ca + Na) (Koyama and Takeuchi 1977). The variation of intensity ratio is controlled mainly by the variation of the 111 reflection. Occupation of Ca, which has a higher scattering factor than that of Na, in M(1) and M(2) increases the effect on the intensity of 111 and thus, the intensity ratio.

The influence on the intensity ratio of cations at M(1) and M(2) is related to the occupancies and to the scattering powers of the cations. This is observed in the results obtained from Kuruma, Agoura and Succor Creek samples. Succor Creek clinoptilolite is rich in Na and poor in K (Armbruster and Gunter 1991), and the intensity ratio calculated from the structural data is 1.11, which is low because of its low K content. On the other hand, the intensity ratios of Kuruma and Agoura clinoptilolites are 1.65 and 1.36, respectively. The Kuruma sample is richer in Ca and poorer in K (Koyama and Takeuchi 1977), whereas the distribution of Na is similar in both samples. The occupancy of Ca at M(1) is higher in Kuruma clinoptilolite than in Agoura clinoptilolite, causing an increase in the intensity ratio. A low Mg content in M(4) also increases the intensity ratio of Kuruma sample.

The reverse influence of Mg at the M(4) site on the intensity ratio is not observed on natural samples. This is attributed to the relative levels of Ca and Mg in the natural samples, i.e., when the Mg content is high, the Ca content is low and vice versa. Ca has a greater effect on the intensity ratio because of its greater scattering power than Mg. The influence of K on M(3) is very significant on the  $I(111)/I(\bar{3}11)$  ratio. Data obtained from natural samples, exchanged forms and calculated patterns show that, as K increases, a significant increase occurs in the 111 intensity and the  $\bar{3}11$  intensity also increases slightly. Because of its high scattering factor, K has a large effect on intensities and on the intensity ratio. Since Na + Ca at M(1) and K at M(3) increase and Ca + Na at M(2) and Mg at M(4) decrease the intensity ratio, the relationship between the  $(\text{Na} + \text{K})/(\text{Ca} + \text{Mg})$  ratio and the intensity ratio is very significant. The Si/Al ratio affects the intensity ratio only slightly because of their very similar scattering factors. However, the most important aspect of

Al is its effect on the Ca population in M(2) (Armbruster 1993). Water molecules associated with cations at M(1) and M(3) increase the intensity ratio. This relation is correlative with the (Na + Ca) content at M(1) and the K content at M(3). Water molecules associated with Mg at M(4) and Ca and Na at M(2) sites decrease the intensity ratio, as do Mg, Ca and Na in these sites.

The relationship between chemistry and intensity ratio of heulandite-group minerals also reveals a relationship between their thermal behavior and intensity ratio. Polymorphic behavior of heulandite-group minerals and their lattice destruction temperatures are related to their extra-framework cations and therefore to their Si/Al ratios. Bish (1984) reported that a volume decrease of clinoptilolite reflects changes in the nature of the exchangeable cations. The K occupies a site in the clinoptilolite structure different than Na or Ca (Koyama and Takeuchi 1977; Galabova 1979), which affects the thermal contraction behavior. Koyama and Takeuchi (1977) concluded that large cations, particularly K in M(3), plug the C channel which prevents the structure from collapsing. This was confirmed by Galli et al. (1983), who studied K-exchanged heulandite. Alietti et al. (1974) found that the structure of Ca-exchanged clinoptilolite collapses at lower temperatures, but the structure of their K-exchanged materials persists up to 800 °C. The M(2) sites are populated mostly by divalent cations. Since Ca has the highest ionic potential, an increase in Ca content at M(2) causes breaking of oxygen bonds (Alberti and Vezzalini 1983). Our natural samples, which are rich in Ca and poor in K, show polymorphism and their  $I(020)$  at 550 °C/ $I(020)$  ratios are low (mostly 0.00) (Table 1). On the contrary, samples rich in K do not show any polymorphism and their thermal stability ratios are high. The variation of intensity ratio as a function of exchangeable cation composition of heulandite group minerals also provides an estimation of their thermal stabilities.

## CONCLUSION

XRD patterns of Gördes and Bigadiç (West Anatolia) heulandites and clinoptilolites are similar with respect to most of their intensities and  $d$ -values. However, 111 and  $\bar{3}11$  have different intensities, and this difference is especially distinctive for 111. Heulandite and clinoptilolite were distinguished using the ratio of intensities of 111 and  $\bar{3}11$ . The value of this intensity ratio is below 1.00 for heulandites and over 1.30 for clinoptilolites. This approach was further tested and confirmed using the data obtained from cation-exchanged samples and using calculated intensities as a function of exchangeable-cation composition. An increase in K and Na contents leads to an increase in the intensity ratio, whereas increase in Ca and Mg results in a decrease in the intensity ratio. The K and Ca

contents have the most significant effect on the intensity ratio. Beyond the kinds of cations, the site occupancy also affects the intensity ratio. Further control on the intensity ratio is provided by water molecules in the structure. The  $(\text{Na} + \text{K})/(\text{Ca} + \text{Mg})$  ratio and thermal characteristics of heulandite-group minerals are normally used to discriminate between heulandite and clinoptilolite. A high correlation is found between these parameters and the intensity ratio  $I(111)/I(\bar{3}11)$ .

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