

EFFECTS OF EXCHANGEABLE CATION COMPOSITION ON THE THERMAL EXPANSION/CONTRACTION OF CLINOPTILOLITE

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Abstract—To understand and predict the effects of a thermal pulse induced by a radioactive waste repository on clinoptilolite-bearing rocks, the lattice parameters of 6 natural and 3 cation-exchanged (Ca, K, Na) clinoptilolites were studied as a function of temperature. The samples were examined at room temperature, under vacuum, and at 50°C increments to 300°C using a high-temperature X-ray powder diffractometer. The unit cell of all samples decreased in volume between 20° and 300°C; Na-saturated clinoptilolite underwent the greatest volume decrease (8.4%) and K-saturated clinoptilolite the smallest (1.6%), of the clinoptilolites studied. The volume decrease for the Ca-saturated clinoptilolite was 3.6%. The highest percentage decrease for each sample was along the *b* axis, generally 80–90% of the total volume decrease. The change in the *a* axis was the smallest and was usually <5%, although 26.5% of the contraction of the Na-exchanged clinoptilolite was along *a*. The bulk of the volume contraction of many samples occurred on evacuation at room temperature, demonstrating that the observed changes were due to water loss and not to temperature-induced structural changes. Low-angle scattering was significantly reduced upon evacuation for every sample, and the 110 reflection of clinoptilolite at $7.45^{\circ}2\theta$ became obvious, whereas it was not in the untreated samples.

These data show that the effects of heating on the unit-cell volume of clinoptilolite depend strongly on the exchangeable cation content. Significant reductions in the unit-cell volumes of natural, mixed Na-K-Ca clinoptilolites could take place in rocks in a repository environment, particularly if the clinoptilolites occurred in unsaturated, dehydrated rock. The unit-cell volumes of clinoptilolites in partially saturated rocks at temperatures below 100°C, however, should not decrease significantly.

Key Words—Clinoptilolite, Dehydration, Exchangeable cation, Thermal expansion, X-ray powder diffraction, Zeolite.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) project of the U.S. Department of Energy is currently investigating a clinoptilolite-bearing tuff on the southwest boundary of the Nevada Test Site (NTS) at Yucca Mountain as a potential repository for high-level radioactive wastes (Vieth, 1983). Yucca Mountain consists of > 1800 m of volcanic tuffs ranging from nonwelded to densely welded and from vitric, nonzeolitized to completely zeolitized (Bish *et al.*, 1982). The rock unit tentatively identified as the repository horizon is moderately to densely welded and devitrified; it is underlain by a densely welded, glassy vitrophyre that overlies vitric to zeolitized nonwelded tuffs containing significant amounts of clinoptilolite and minor quantities of heulandite. The Na, K, and Ca content of the clinoptilolite varies significantly throughout the tuff, and the zeolite ranges from a Ca-rich clinoptilolite to (Na, K, Ca)-clinoptilolites to a Na-rich clinoptilolite with depth (Caporuscio *et al.*, 1982). Heulandite occurs locally and has not been thoroughly studied.

The NNWSI project has studied the effects of repository-induced temperature increases on the physical properties of the rocks and minerals in Yucca Mountain (Lappin, 1982; Bish *et al.*, 1982). Lappin attempt-

ed to relate the macroscopic thermal expansion behavior of tuff to published thermal expansion data for the constituent minerals. He found a significant variation in behavior from sample to sample, particularly for clinoptilolite-bearing samples (contraction of $\sim 0.008 \pm 0.02$ cm/cm). In addition, no thermal expansion data existed for clinoptilolite, and its thermal expansion had to be approximated. Zeolites of the clinoptilolite-heulandite series have been widely studied by the NNWSI project because of their abundance in Yucca Mountain, their excellent sorptive properties for many radionuclide cations, and their ability to reversibly contract and expand at temperatures below 200°C (Bish *et al.*, 1984). Their thermal stability contrasts with that of the common devitrification minerals quartz, cristobalite, and alkali feldspar.

Several natural and cation-exchanged clinoptilolites have been examined in this study using a high-temperature X-ray powder diffractometer to define the effects of exchangeable cation on thermal expansion/contraction. The lattice parameters under room conditions and under a 0.1-torr vacuum up to 300°C have been refined. The results of these experiments provide information on the effect of temperature on the crystal structure of cation-exchanged clinoptilolites and may

be used to predict the behavior of such clinoptilolites in a repository environment.

BACKGROUND

The dehydration behavior and polymorphism of heulandite have been thoroughly investigated (Boles, 1972; Alberti, 1973; Alberti and Vezzalini, 1983; Galli *et al.*, 1983); however, the details of the changes occurring upon heating structurally similar clinoptilolite and the effect of different exchange-cation compositions are not as thoroughly studied. Furthermore, much of the work on clinoptilolite has concentrated on its high-temperature thermal stability. Mumpton (1960) and Boles (1972) suggested that the higher thermal stability of clinoptilolite compared to heulandite can be used to differentiate the two minerals, and Boles noted that the thermal stability of clinoptilolites and heulandites was related to the number of divalent cations per unit cell and to the Si/Al ratio. Shepard and Starkey (1966) stated that Ca-exchanged clinoptilolite behaved similarly to heulandite, but that the temperature of inversion to a phase resembling heulandite B was about 75°C higher than for heulandite. Other investigations of Ca-exchanged clinoptilolite (e.g., Mumpton, 1960), as well as those in this laboratory have not substantiated these findings. Shepard and Starkey (1966) reported that end-member K- and Na-clinoptilolites were more stable than natural clinoptilolite, and that Na-clinoptilolite began to contract below 350°C and re-expanded above 350°C. Alietti *et al.* (1974) examined the thermal behavior of natural and Na-, Ca-, and K-exchanged clinoptilolite from Hungry Valley, Nevada, and monitored changes of the 020 reflection on a heating X-ray diffractometer and with a conventional diffractometer after heating. Although changes in lattice parameters were not measured, they found significant decreases in the 020 spacing above 200°C for the Na-exchanged clinoptilolite and above ~350°C for the Ca-exchanged sample. Their K-exchanged material showed little decrease in the 020 lattice spacing up to 800°C.

In a thermal analysis study, Knowlton *et al.* (1981) described three types of water associated with clinoptilolite—external water, loosely bound zeolitic water, and tightly bound zeolitic water, that came off at 75°, 171°, and 271°C, respectively. They concluded that the so-called external water that came off below 75°C was adsorbed on the surface of grains in the powdered sample; they suggested that structural changes associated with the loss of the external water may be a thermal effect rather than a result of dehydration. Knowlton *et al.* also found that the temperatures of water desorption were about 50°C higher under a nitrogen atmosphere than under vacuum. Both of these results have some bearing on the results of the present study. The effect of water vapor pressure on the unit cell of clinoptilolite has not been examined to date, although Simonot-

Grange and Cointot (1969) found that increased water vapor pressure increased the temperature of the thermal transformations of heulandite.

EXPERIMENTAL METHODS

Sample preparation and analysis

The samples examined in this study were all >95% clinoptilolite as determined by X-ray powder diffraction. Natural clinoptilolites were obtained from Minerals Research, Clarkson, New York, and are as follows: #25524, Buckhorn, New Mexico; #25525, Castle Creek, Idaho; #25526, Sheaville, Oregon; and #27054, Fish Creek Mountains, Nevada. In addition, a macrocrystalline sample of clinoptilolite from Agoura, California, and a clinoptilolite (UE4P-1660) from the Grouse Canyon Member of the Belted Range Tuff from Yucca Flat at the Nevada Test Site were examined. X-ray fluorescence analyses (Table 1) of the Minerals Research samples are from Sheppard and Gude (1982); the analysis of the Agoura clinoptilolite is from Wise *et al.* (1969).

Cation-exchanged varieties of the Castle Creek sample were prepared by mixing 2.5-g portions in 1.0 M solutions of Ca, K, and Na chloride. The treatment was repeated three additional times for 16 hr each at about 50°C. The solids were centrifuged and rinsed after each exchange. X-ray fluorescence analyses using fused pellets of the exchanged clinoptilolites (Table 1) show that the Ca and Na exchanges were only partial (55% and 85%, respectively). The Ca-exchanged clinoptilolite contained most of the original K and a minor amount of Na; the Na-exchanged material contained little Ca and roughly half of the original K. Harsher treatments, such as autoclaving, were not used in the cation exchanges to avoid recrystallization or alteration of the clinoptilolites. No analysis of sample UE4P-1660 was performed because of the small amount of material available.

X-ray powder diffraction

X-ray powder diffraction (XRD) analyses were performed on an automated Siemens D-500 system employing CuK α radiation and a graphite diffracted-beam monochromator. Peak positions and intensities were measured using the Siemens first-derivative peak-search routine, and quartz and silicon external standards were used to calibrate the instrument. Data for unit-cell refinements were collected from 2° to 40°2 θ , counting for 1.0 sec every 0.02°2 θ . Peak overlap and low intensities for most samples precluded the use of higher angle peaks in the refinements. Unit-cell parameters were refined using the least squares program of Appleman *et al.* (1963). Diffraction maxima were indexed with the aid of computer-calculated powder patterns; the automatic indexing feature of the Appleman program was not used. Peaks used in the cell refinements were the same as those used by Boles (1972) with the ad-

Table 1. Chemical analyses and structural formulae¹ of natural and exchanged clinoptilolites.

	25524 ²	25525 ²	25525-Ca	25525-K	25525-Na	25526 ²	27054 ²	Agoura ³
SiO ₂	63.4	61.6	65.24	65.27	67.18	65.9	65.4	69.15
TiO ₂	0.13	0.23	0.23	0.21	0.17	0.28	0.11	n.a. ⁵
Al ₂ O ₃	12.2	11.9	13.08	13.03	13.36	11.3	12.5	11.76
Fe ₂ O ₃	1.33	2.11	3.21	2.88	1.80	2.15	1.33	0.30
MgO	1.7	1.6	1.21	0.58	0.71	0.3	0.90	0.39
CaO	3.37	0.91	4.60	0.12	0.13	1.30	3.07	1.09
MnO	<0.02	0.11	0.03	0.03	0.02	<0.02	<0.02	n.a.
Na ₂ O	1.4	4.0	0.32	0.03	6.20	1.5	1.0	2.63
K ₂ O	1.12	1.53	1.27	10.70	0.70	4.55	3.32	3.13
LOI ⁴	15.06	14.8	n.a.	n.a.	n.a.	11.68	12.70	n.a.
Total	99.73	98.79	89.19	92.85	90.27	98.98	100.35	88.18
Si	14.42	14.28	14.20	14.24	14.40	14.75	14.51	15.05
Ti	0.02	0.04	0.04	0.03	0.03	0.05	0.02	—
Al	3.27	3.25	3.35	3.35	3.38	2.98	3.27	3.02
Fe ³⁺	0.23	0.37	0.53	0.47	0.29	0.36	0.22	0.01
Mg	0.58	0.55	0.39	0.19	0.23	0.10	0.30	0.13
Ca	0.82	0.23	1.07	0.03	0.03	0.31	0.73	0.25
Mn	0.00	0.02	0.01	0.01	0.00	0.00	0.00	—
Na	0.62	1.80	0.14	0.01	2.58	0.65	0.43	1.11
K	0.32	0.45	0.35	2.98	0.19	1.30	0.94	0.87

¹ Number of cations normalized to 36 oxygens.

² Analyses from Sheppard and Gude (1982).

³ Average of three analyses from Wise *et al.* (1969).

⁴ LOI = loss on ignition.

⁵ n.a. = not analyzed.

dition of the 110, 130, $\bar{5}12$, 530, $\bar{2}61$, and $\bar{3}51$ reflections.

XRD data were collected *in vacuo* and at elevated temperatures using an Anton-Paar medium-temperature heater on the Siemens diffractometer. The sequence for a given sample consisted of examining a sample under room conditions ($\sim 20^\circ\text{C}$, $\sim 35\%$ relative humidity), slowly evacuating the sample chamber to ~ 0.1 torr and equilibrating for at least 30 min prior to analysis, and then heating the sample at 50° increments from 50° to 300°C with at least a 30-min equilibration before examination. After the 300°C run, the heater was turned off, and the sample was cooled and re-examined *in vacuo* after being held at room temperature for at least 30 min. Each sample was examined one final time under room conditions, after equilibration for at least 30 min. Thirty minutes appeared to be an adequate equilibration time because the samples that were equilibrated overnight at temperature showed no significant additional changes. The temperature was measured with a Pt-resistance thermometer at a point immediately beneath the sample cavity, within the sample holder.

RESULTS AND DISCUSSION

The cell dimensions of all samples under room conditions are shown in Table 2, and cell dimensions as a function of temperature are shown in Figures 1–9. Calculated standard errors are not shown in the illus-

trations, but the errors listed in Table 2 are representative of the errors recorded from room temperature to 300°C . The points labeled “RT” in Figures 1–9 represent data collected under room conditions, and “VAC1” and “VAC2” represent the data obtained under vacuum before and after heating, respectively.

The data in Figures 1–9 show that the unit cell of the Na-exchanged clinoptilolite underwent the greatest volume decrease (8.4%) and that of the K-exchanged clinoptilolite underwent the smallest volume decrease (1.6%). The Si/Al ratios for all samples ranged from 4.24/1 to 4.98/1, but the variations in volume decrease appear to reflect mainly changes in the nature of the exchangeable cations. Few consistent trends were noted in the room-temperature unit-cell data, but the room temperature volume of the exchanged samples decreased in the order $\text{K} > \text{Na} > \text{Ca}$, the same order found by Shepard and Starkey (1966).

The unit-cell dimensions of sample 25525-Na decreased abruptly between 50° and 100°C in both the *a* and the *b* directions and then increased slightly from 150° to 300°C . The XRD pattern changed significantly between 50° and 100°C ; the 020 reflection decreased from 8.85 to 8.48 Å. To follow this volume decrease more closely, the sample was examined at 75°C , between the 50° and 100°C examinations, with a 30-min equilibration time. At 75°C , the 020 reflection split into two reflections of almost equal intensity at 8.78 and 8.49 Å. The presence of two separate 020 reflections

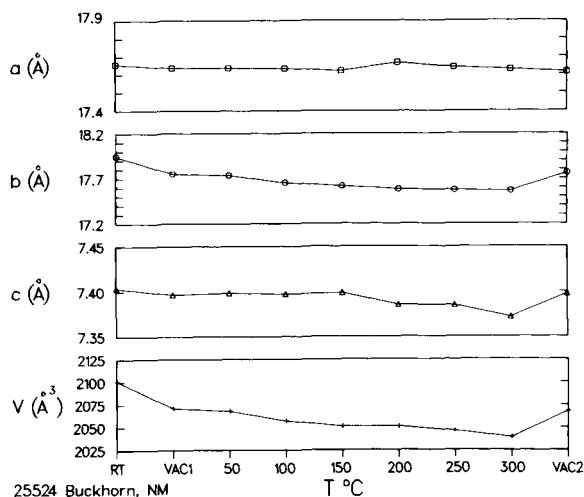


Figure 1. Unit-cell parameters of clinoptilolite 25524, Buckhorn, New Mexico, as a function of temperature.

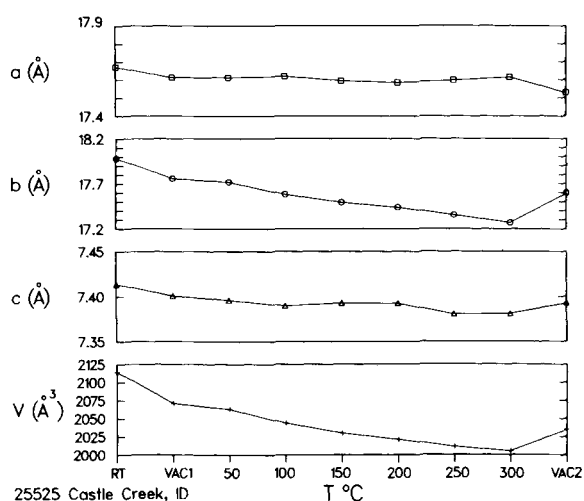


Figure 2. Unit-cell parameters of clinoptilolite 25525, Castle Creek, Idaho, as a function of temperature.

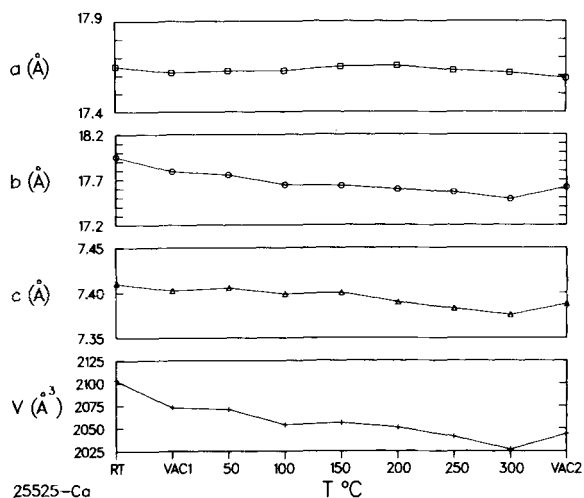


Figure 3. Unit-cell parameters of Ca-exchanged clinoptilolite 25525 as a function of temperature.

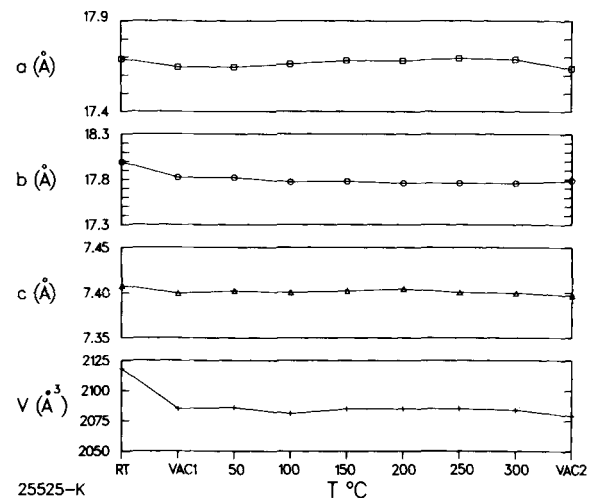


Figure 4. Unit-cell parameters of K-exchanged clinoptilolite 25525 as a function of temperature.

suggests that dehydration at this temperature is kinetically controlled. The Na-saturated sample did not re-expand upon cooling in a vacuum. The unit cell of clinoptilolite 25525-Ca gradually decreased along *b* up

to 300°C and re-expanded significantly along *b* in a vacuum at room temperature. The unit cell of the K-saturated sample contracted primarily along *b* on evacuation and remained relatively constant up to

Table 2. Unit-cell parameters of natural and exchanged clinoptilolites.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Volume (Å ³)
25524, Buckhorn, New Mexico	17.656 (4)	17.946 (3)	7.404 (1)	116.37 (1)	2101.4 (4)
25525, Castle Creek, Idaho	17.671 (5)	17.983 (5)	7.414 (2)	116.19 (2)	2114.1 (7)
25525-Ca, Castle Creek, Idaho	17.650 (4)	17.951 (5)	7.410 (1)	116.42 (1)	2102.5 (6)
25525-K, Castle Creek, Idaho	17.690 (8)	17.990 (8)	7.408 (2)	116.03 (3)	2118.3 (9)
25525-Na, Castle Creek, Idaho	17.682 (7)	17.956 (6)	7.424 (1)	116.26 (2)	2113.6 (8)
25526, Sheaville, Oregon	17.634 (5)	17.875 (7)	7.403 (1)	116.30 (2)	2091.8 (7)
27054, Fish Creek Mountains, Nevada	17.633 (4)	17.907 (4)	7.399 (1)	116.29 (1)	2094.4 (5)
UE4P-1660, Nevada Test Site	17.664 (5)	17.971 (7)	7.408 (2)	116.26 (2)	2108.7 (8)
Agoura, California	17.662 (7)	17.929 (4)	7.407 (2)	116.42 (3)	2100.6 (8)

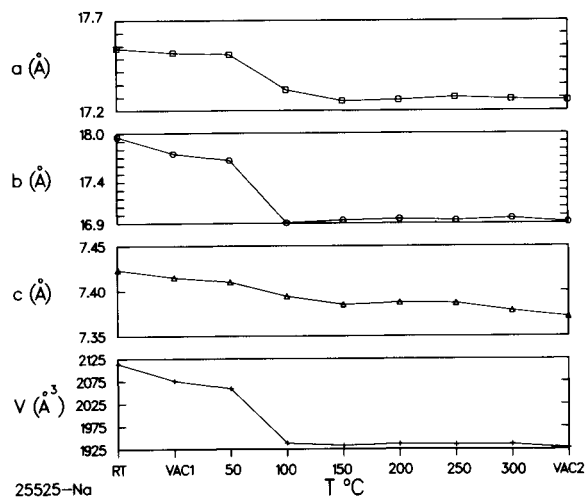


Figure 5. Unit-cell parameters of Na-exchanged clinoptilolite 25525 as a function of temperature.

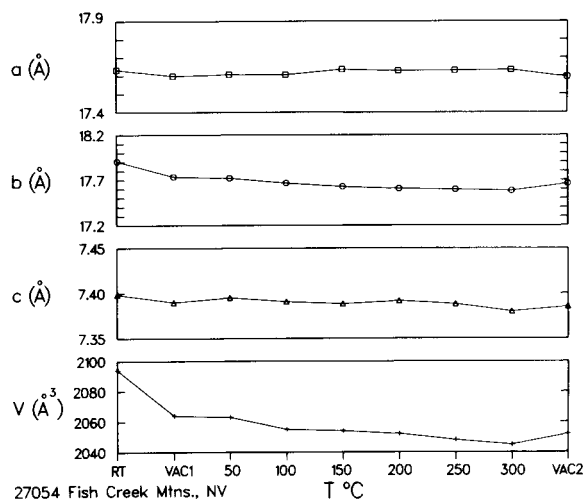


Figure 7. Unit-cell parameters of clinoptilolite 27054, Fish Creek Mountains, Nevada, as a function of temperature.

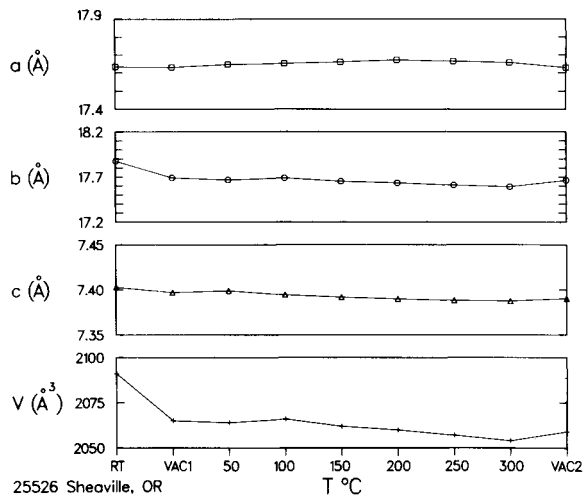


Figure 6. Unit-cell parameters of clinoptilolite 25526, Sheaville, Oregon, as a function of temperature.

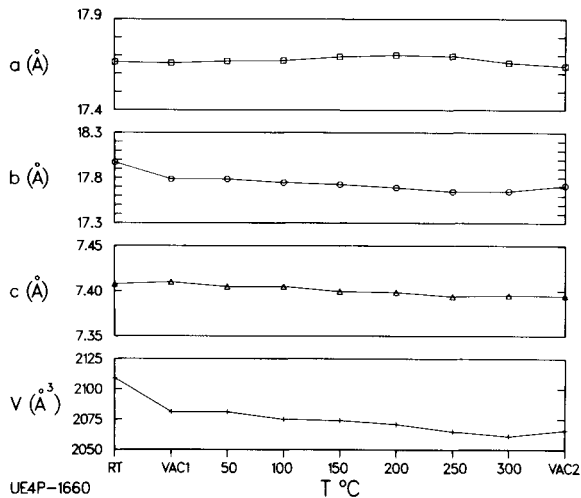


Figure 8. Unit-cell parameters of clinoptilolite UE4P-1660, Nevada Test Site, Nevada, as a function of temperature.

300°C; it did not re-expand at room temperature in a vacuum. The unit cells of the natural samples decreased mainly along b , the extent of the decrease being related to the nature of the exchangeable cation (samples 25524, 3.0%; 25525, 5.2%; 25526, 1.8%; 27054, 2.4%; UE4P, 2.3%; Agoura, 2.7%). The natural K-rich samples, 25526 and 27054, decreased least in volume. All of the natural samples re-expanded upon cooling in a vacuum. It is significant that, in addition to the lattice parameters, the peak intensities of these samples were sensitive to changes in relative humidity and temperature.

These high-temperature unit-cell data show consistent trends with temperature for all samples. Most importantly, the highest percentage decrease of cell dimensions of every clinoptilolite was along the b axis,

generally making up 80 to 90% of the total volume decrease. The change in the a axis was the smallest, usually <5%, although 26.5% of the contraction of the unit cell of the Na-exchanged 25525 clinoptilolite was along a . Clinoptilolite from Agoura and sample 25526, the two samples with the highest Si/Al ratios, actually expanded along a . The β angle for all samples except the K-exchanged clinoptilolite increased as the temperature was increased.

The relative changes in the lattice parameters of the clinoptilolites examined are similar to those found by Galli *et al.* (1983), Alberti (1973), and Alberti and Vezzalini (1983) for heulandites and are consistent with a distortion of the 10- and 8-member rings, as illustrated by Galli *et al.* Apparently, these distortions occurred at relatively low temperatures in some clinop-

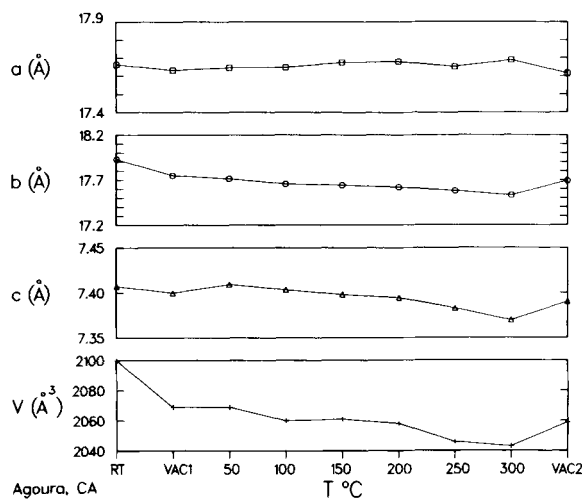


Figure 9. Unit-cell parameters of ground single crystals of clinoptilolite, Agoura, California, as a function of temperature.

tilolites and were brought on by a loss of water and by migration of exchangeable cations (Galli *et al.*, 1983). Distortions of the 10- and 8-member rings are also the likely cause of the significant changes in relative peak intensities noted when the samples were heated.

In the temperature range covered in this study, it appears that a combination of the size, amount, and charge of the exchangeable cations, and to a lesser extent the Si/Al ratio, governs the temperature of and the amount of volume decrease. The volume decrease noted in this study appears to be controlled, in large part, by the hydration energy of the cations; however, the high-temperature destruction (i.e., at $\sim 700^\circ\text{C}$) of the structure is related to the amount and size of the cations and the composition of the Al-Si framework (Alietti *et al.*, 1974). Na^+ dehydrates more easily than Ca^{2+} [enthalpy of hydration for $\text{Na}^+ = -400$ kJ/mole, $\text{Ca}^{2+} = -1580$ kJ/mole, $\text{K}^+ = -320$ kJ/mole (Barrow, 1973)]; hence the volume of Na-clinoptilolite decreased abruptly by 100°C . Higher temperatures are required to dehydrate Ca^{2+} , and the unit cell of Ca-clinoptilolite shrinks more than that of Na-clinoptilolite on heating to high temperatures (Alietti *et al.*, 1974), probably because only half as many cations are present in the former and because of the higher ionic potential of Ca^{2+} . The large K^+ ion is not highly hydrated, and because of its low ionic potential, K^+ dehydrates at relatively low temperatures. Even when dehydrated, K^+ is able to "prop" open the zeolite structure sufficiently to inhibit shrinkage even at high temperatures. In addition, there is evidence that K occupies a different site in the clinoptilolite structure than Na or Ca (Koyama and Takeuchi, 1977; Galabova, 1979) which may affect the thermal contraction behavior. In the present experiments, the ability of the clinoptilolites

to rehydrate upon cooling in a vacuum appears related to the presence of Ca^{2+} , an ion with a considerably greater hydration energy than that of K^+ or Na^+ . Apparently enough water molecules are present even in a 0.1-torr atmosphere to rehydrate heated clinoptilolite.

It is significant that a large part of the total volume contraction of many samples occurred on evacuation, demonstrating that the observed changes were due to water loss and not to a temperature-induced phase transformation as proposed by Knowlton *et al.* (1981). If the "external" water of Knowlton *et al.* (1981) were simply adsorbed on surfaces, the loss of this water should have no significant effect on unit-cell volume. That water loss on evacuation was considerable was evidenced by the violent "jumping" of the samples in the powder mounts unless the vacuum was applied very slowly. Inasmuch as the loss of water at room temperature produced such a significant volume effect, this low-temperature water should affect adsorption isotherms, as discussed by Knowlton *et al.* (1981).

The significant reduction in low-angle scattering of every sample on evacuation is noteworthy and is illustrated in Figures 10a and 10b, the XRD patterns of the Agoura clinoptilolite at 22.5°C and 30% relative humidity and under a vacuum at 21.5°C . The clinoptilolite 110 reflection at $7.45^\circ 2\theta$ was significantly enhanced after evacuation and was noted in the XRD patterns of all samples after evacuation, including ground single crystals of the Agoura clinoptilolite. This reflection is weakly present in the XRD patterns of some clinoptilolite-rich samples under room conditions and may be mistaken as evidence of the presence of erionite. The 110 clinoptilolite reflection, however, is at $7.48 \pm 0.04^\circ 2\theta$ (average of 11 natural clinoptilolites), whereas the 100 erionite reflection is at $\sim 7.75 \pm 0.02^\circ 2\theta$ (average of three natural erionites). Thus, with care, a distinction can be made between these two zeolites based on this difference in peak position if enough erionite is present.

CONCLUSIONS

These XRD data on natural and cation-exchanged clinoptilolites demonstrate that decreases in the unit-cell volume on heating and the ability of samples to rehydrate depend strongly on the amount and nature of the exchangeable cation. The unit cells of the clinoptilolites examined contracted between 1.6 and 8.4%; most of which occurred along the *b* axis. Clinoptilolites in the tuffs at Yucca Mountain, Nevada, are variable in composition (Bish *et al.*, 1982; Caporuscio *et al.*, 1982). Thus, the variation in degree of contraction as a function of exchangeable cation composition found in the present study explains the variability in macroscopic behavior of clinoptilolite-bearing tuffs from Yucca Mountain found by Lappin (1982) (*vide supra*).

The unit-cell volume of clinoptilolite is also sensitive to changes in relative humidity and temperature.

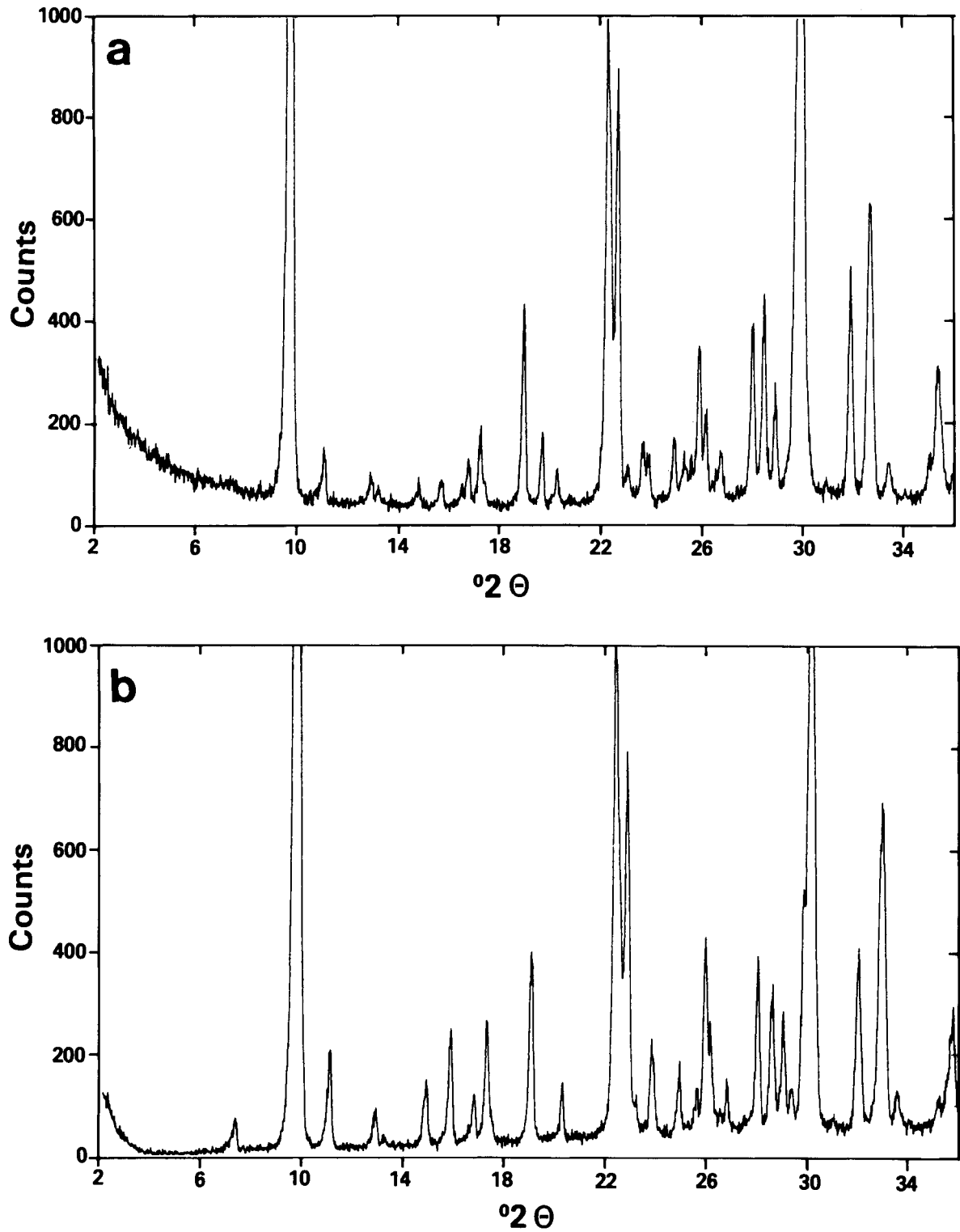


Figure 10. X-ray powder diffraction pattern of Agoura clinoptilolite at (a) 22.5°C and 30% relative humidity and (b) 21.5°C under a vacuum, $\text{CuK}\alpha$ radiation.

Therefore, significant modifications in the unit-cell volumes of clinoptilolites (as much as 8%) in rocks could occur in a repository where temperatures may approach 100°C, particularly if the clinoptilolites occurred in unsaturated, dehydrated rock. According to Knowlton *et al.* (1981), a vacuum causes water loss in clinoptilolite at ~50°C lower than when in a nitrogen atmosphere, so dehydration in partially water-saturated rocks should occur at higher temperatures than found in the present study. Further experiments will address the effects of heating clinoptilolite in a humid atmosphere and the effects of unit-cell volume changes on rock permeabilities and mechanical properties.

The sensitivity of clinoptilolite to relative humidity has important implications for quantitative X-ray powder diffraction analyses of clinoptilolite-bearing rocks. Because the relative intensities of clinoptilolite diffraction peaks vary with relative humidity, it is imperative that the analysis of standards and unknowns be performed under identical conditions of relative humidity. In addition, the XRD intensity changes imply that the structure (probably the 10- and 8-member rings) can vary (or flex) significantly with minor additions or subtractions of water at room temperature.

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Резюме—Параметры решетки шести природных и трех катионо-обменных (Ca, K, Na) клиноптилолитов исследовались как функции температуры для лучшего объяснения и предсказания эффектов термального пульса, вызванного хранимыми отходами на породы, содержащие клиноптилолит. Образцы исследовались при комнатной температуре, в вакууме и при 50°C увеличениях температуры до 300°C при использовании высоко-температурного рентгеновского порошкового дифрактометра. В случае всех образцов элементарная ячейка уменьшалась по объему в диапазоне температур между 20° и 300°C; для Na-насыщенного клиноптилолита, уменьшение объема было самое большое (8,4%), а для K-насыщенного клиноптилолита—самое маленькое (1,6%) из всех исследованных клиноп-

тилолитов. Уменьшение объема Са-насыщенного клиноптилолита было равно 3,6%. Самое большое процентное уменьшение для каждого образца происходило вдоль оси *b*, в основном составляло 80–90% полного уменьшения объема. Изменение вдоль оси *a* было самое маленькое и его величина была <5%, хотя 26,5% уменьшения Na-насыщенного клиноптилолита происходило вдоль оси *a*. Большинство случаев уменьшения объема многих образцов происходило во время обезвоживания при комнатной температуре указывая на то, что эти наблюдаемые изменения были результатом потери воды, а не температурного изменения структуры. Рассеяние по малой величине угла уменьшалось значительно после обезвоживания для каждого образца, и отражение от плоскости 100 клиноптилолита при 2θ равным $7,45^\circ$ являлось тогда очевидным в противоположность необработанным образцам.

Эти данные указывают на то, что эффекты нагревания на объем элементарной ячейки клиноптилолита зависят сильно от содержания обмениваемого катиона. Значительные уменьшения объемов элементарных ячеек натуральных смешанных Na-K-Ca клиноптилолитов могут происходить в породах в условиях хранилища, особенно если клиноптилолиты находятся в ненасыщенной, дегидратированной породе. Однако, значения объема клиноптилолитов в частично насыщенных породах при температурах ниже 100°C не должны уменьшаться значительно. [E.G.]

Resümee—Um die Auswirkungen einer thermischen Beeinflussung, verursacht durch eine Lagerung radioaktiven Abfalls, auf Klinoptilolith-führende Gesteine zu verstehen und vorauszusagen, wurden die Gitterparameter von 6 natürlichen und 3 kationenausgetauschten (Ca, K, Na)-Klinoptilolithen in Abhängigkeit von der Temperatur untersucht. Die Proben wurden bei Raumtemperatur unter Vakuum und bei einer Temperaturzunahme von 50°C auf 300°C untersucht, wobei ein Hochtemperatur-Röntgenpulverdiffraktometer verwendet wurde. Die Elementarzelle aller Proben zeigte zwischen 20° und 300°C eine Volumensabnahme; Na-gesättigter Klinoptilolith zeigte die größte Abnahme (8,4%) und K-gesättigter Klinoptilolith die kleinste (1,6%) der untersuchten Klinoptilolithe. Die Volumensabnahme von Ca-gesättigtem Klinoptilolith war 3,6%. Die größte prozentuelle Abnahme war bei jeder Probe in Richtung der *b*-Achse, im allgemeinen 80–90% der gesamten Volumensabnahme. Die Veränderung in Richtung der *a*-Achse war am kleinsten und betrug im allgemeinen <5%; obwohl 26,5% der Kontraktion bei Na-ausgetauschtem Klinoptilolith in Richtung *a* war. Der Hauptanteil der Volumensverminderung vieler Proben geschah während der Evakuierung bei Raumtemperatur, was darauf hindeutet, daß die beobachteten Veränderungen durch Wasserverlust verursacht werden und nicht durch Temperatur-bedingte strukturelle Veränderungen. Die Kleinwinkelstreuung wurde durch das Evakuieren bei jeder Probe beträchtlich verringert und der 110 Reflex von Klinoptilolith bei $7,45^\circ 2\theta$ wurde sichtbar, was bei unbehandelten Proben nicht der Fall war.

Diese Ergebnisse zeigen, daß die Auswirkungen der Erwärmung auf das Volumen der Elementarzelle von Klinoptilolith sehr stark vom Gehalt an austauschbaren Kationen abhängt. Beachtliche Verkleinerungen des Elementarzellvolumens von natürlichen gemischten Na-K-Ca-Klinoptilolithen können in Gesteinen in der Umgebung von Ablagerungsplätzen stattfinden, vor allem wenn die Klinoptilolithe in einem ungesättigten, dehydratisierten Gestein auftreten. Die Volumen der Elementarzelle von Klinoptilolithen in teilweise gesättigten Gesteinen sollten jedoch bei Temperaturen unter 100°C nicht bemerkenswert abnehmen. [U.W.]

Résumé—Pour comprendre et prédire les effets d'une pulsation thermique induite par un répositoire de déchets radioactifs sur des roches contenant de la clinoptilolite, les paramètres de l'édifice cristallin de 6 clinoptilolites naturelles et 3 clinoptilolites à cations échangés (Ca, K, Na) ont été étudiés en fonction de la température. Les échantillons ont été examinés à température ambiante, sous le vide, et par accroissements de 50°C jusqu'à 300°C , utilisant un diffractomètre de rayons-X à haute température. La maille de tous les échantillons a diminué de volume entre 20° et 300°C ; de toutes les clinoptilolites étudiées, le volume de la clinoptilolite saturée de Na a diminué le plus (8,4%), et celui de la clinoptilolite saturée de K a le moins diminué (1,6%). La diminution de volume de la clinoptilolite saturée de Ca était 3,6%. Le pourcentage de diminution le plus élevé pour chaque échantillon était le long de l'axe *b*, généralement de 80 à 90% de la diminution de volume totale. Le changement de l'axe *a* était le plus petit et d'habitude <5%, quoique 26,5% de la contraction de la clinoptilolite échangée avec Na était le long de l'axe *a*. La majorité de la contraction de volume de beaucoup d'échantillons s'est passée lors de l'évacuation à température ambiante, démontrant que les changements observés étaient dus à une perte d'eau et non à des changements structuraux induits par la température. L'éparpillement d'angles aigus était réduit de manière significative pour chaque échantillon et la réflexion 110 de la clinoptilolite à $7,45^\circ 2\theta$ est devenue évidente alors qu'elle ne l'était pas dans les échantillons non-traités.

Ces données montrent que les effets de l'échauffement sur le volume de la maille de clinoptilolite dépendent fortement du contenu en cations échangeables. Des réductions significatives des volumes des mailles de clinoptilolites mélangées Na-K-Ca naturelles pourraient se passer dans les roches dans un environnement de répositoire, particulièrement si les clinoptilolites se trouvaient dans de la roche déshydratée, nonsaturée. Les volumes des mailles dans des roches partiellement saturées à des températures en dessous de 100°C , cependant, ne devraient pas diminuer de manière significative. [D.J.]