

Thermal stability of the heulandite-type framework: crystal structure of the calcium/ammonium form dehydrated at 483K

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Abstract

A crystal phase intermediate between the hydrated form of the natural zeolite heulandite and its heat-collapsed phase has been studied by single-crystal X-ray diffractometry. The crystal, $[(\text{NH}_4)_{1.2}\text{K}_{0.4}\text{Na}_{1.1}\text{Ca}_{2.8}\text{Si}_{27.7}\text{Al}_{8.3}\text{O}_{72} \cdot x\text{H}_2\text{O}]$, $a = 17.158$, $b = 17.433$, $c = 7.388\text{\AA}$, $\beta = 113.41^\circ$, $C2/m$ symmetry], was dehydrated at 483K. This temperature is lower than that required for the formation of the heat-collapsed phase (heulandite-B). However, some distortion of the fundamental polyhedral units in the direction known for the fully collapsed phase was noted in the present sample. The exchangeable cations are located in the framework eight-rings and are responsible for these distortions, which result in a decrease of the critical channel apertures.

Introduction

There are three sets of two-dimensional channels in hydrated zeolites of the heulandite-type with free dimensions of $4.0 \times 5.5\text{\AA}$ (eight-rings), $4.4 \times 7.2\text{\AA}$ (ten-rings) and $4.1 \times 4.7\text{\AA}$ (eight-rings) (Meier and Olson, 1978, p. 69). However, when this zeolite is dehydrated at 573–673K, a partial collapse of the framework occurs, yielding a new crystal phase, heulandite-B (Alberti, 1973; Gottardi *et al.*, 1973). As a result of this collapse, the two-dimensional channels are severely occluded, which renders them almost useless as industrial catalysts or dehydrating agents.

The collapse of the heulandite structure during dehydration is due to the presence of the exchangeable cations. When their water molecule ligands are removed, these cations must coordinate directly to the oxygens of the framework. Because of their high charge density, the cations can distort the framework to achieve the best coordination environment possible.

Framework distortions have previously been observed upon dehydration of stilbite-type zeolites, which are similar to heulandite in structure (Alberti and Vezzalini, 1978). Indeed, the distortion in stilbite was so severe that some of the bonds to tetrahedral atoms (Si or Al) were ruptured. However, when stilbite has no exchangeable cations (H-stilbite; Pearce *et al.*, 1980) or has only a limited number of cations

(Na/H-stilbite; Mortier, Smith and Pluth, in preparation), the degree of distortion is reduced and the open-channel system may be preserved.

This research establishes the structure of an activated (dehydrated) intermediate phase between hydrated heulandite and the heat-collapsed phase, heulandite-B. The work was undertaken to understand the structural distortions leading to the framework collapse. As with stilbite, it should be possible to stabilize the framework of heulandite and produce an industrially useful material by reducing the number of exchangeable cations. In fact, this should be somewhat easier to accomplish since heulandite is intrinsically more stable than stilbite. This is obvious from the observation that, even in the highly distorted phase (heulandite-B), all bonds to tetrahedral atoms remain intact.

Our sample is a single crystal of heulandite from which some of the calcium has been removed *via* ion exchange with the ammonium ion. An attempt to further stabilize this crystal was made by performing the dehydration under "deep bed" conditions. This simply means heating in the presence of the decomposition products, a procedure which is known to have a stabilizing effect on zeolite structures.

Experimental and results

Crystals of natural heulandite (Ca-HEU) from Lane County, Oregon (Virginia Polytechnic Institute

and State University sample #B323) were placed in a 1 M NH_4Cl solution for five months. The exchange solution was renewed three times during this period. Electron-microprobe analyses of the original sample (Ca-HEU) and the ion-exchanged form (Ca/ NH_4 -HEU) were performed using a solid-state detector, the Reed-Ware program and feldspar standards. This yielded the following unit cell compositions:



In the second formula, the value of y required for charge balance is 1.2. Only a limited exchange was achieved, probably due to the high selectivity of heulandite minerals for Ca^{2+} . In a related study of heulandite powders (Jacobs *et al.*, 1979), the maximum degree of exchange which could be achieved was 40%. Our sample shows an exchange of only 15%.

A single crystal approximately $0.08 \times 0.15 \times 0.4$ mm was mounted in a glass capillary and pretreated as follows. After evacuation at room temperature under high vacuum (1.2×10^{-8} bar), 2.4×10^{-2} bar of water vapor was introduced to simulate the "deep bed" conditions. Next, the temperature was slowly raised by means of an external furnace to 483K, where it was held for five hours. Finally, the sample was evacuated at 483K for one hour. Attempts to use 573K as the pretreatment temperature resulted in badly fractured crystals, unsuitable for X-ray experiments.

A Syntex P2, diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069\text{\AA}$) was used to collect the intensity data. In total, 4757 reflections were measured up to $\sin\theta/\lambda = 0.65$. After intensity averaging, these yielded 2422 independent reflections, of which 1740 had $I > 3s$ in $C2/m$ symmetry. The unit-cell parameters were obtained by least-squares refinement of twenty intense reflections between 20° and 25° (2θ). This yielded $a = 17.158(4)$, $b = 17.433(6)$, $c = 7.388(2)\text{\AA}$; $\beta = 113.41(2)^\circ$. Data reduction was accomplished using the X-RAY-76 system (Steward *et al.*, 1976). The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were necessary ($\mu_{\text{MO}} = 7.48 \text{ cm}^{-1}$). The distribution of the normalized structure factors confirmed the choice of $C2/m$ as the space group, the same space group used in the refinement of the heulandite-B structure. Hydrated heulandite was found to have Cm symmetry. All three

structures, however, have an identical orientation of the mirror plane.

The framework parameters of natural heulandite did not give good agreement between the observed and calculated structure factors. The structure was therefore solved by direct methods. Triplets were generated with the SINGEN program (part of X-RAY-76) and the phases of 393 reflections were determined with the program PHASE (also part of X-RAY-76). A subsequent Fourier map showed 13 out of the 15 framework atoms, including all five of the T atoms (T = Si or Al). The remaining atoms were located by difference Fourier methods.

Data refinement was accomplished using the program NUCLS (a modified version of ORFLS; Busing *et al.*, 1962). Atomic scattering factors for Na^+ , Ca^{2+} , O^- , Si^{3+} , and Al^{2+} were utilized in this refinement. Anomalous scattering corrections were also applied (Cromer and Liberman, 1970). By including 2046 reflections having $|F| > 3\sigma$ and by incorporating anisotropic thermal parameters, the following agreement factors were attained.

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.086$$

$$wR = [(\Sigma w(|F_o| - |F_c|)^2)/\Sigma(|F_o|^2)]^{1/2} = 0.077$$

where $w = 1/\sigma_F^2$.

Residual electron density of $1.2 \text{ e}/\text{\AA}^3$ was found at the site denoted Ca(1). Residual density at other atomic sites did not exceed $0.75 \text{ e}/\text{\AA}^3$.

The final positional, population, and anisotropic thermal parameters are listed in Table 1, and selected interatomic distances and bond angles in Table 2.¹

Discussion

When zeolites exchanged with the ammonium ion are dehydrated at elevated temperatures, the NH_4^+ decomposes to H^+ and NH_3 . We therefore denote the present heulandite sample as d-Ca/H-HEU. In this discussion, the structure will be compared to those of hydrated heulandite (h-HEU) and heulandite-B (HEU-B). It will be demonstrated that d-Ca/H-HEU is more similar to the hydrated phase which is present prior to framework collapse and phase transformation to heulandite-B. That the crystal did not fracture during pretreatment at 483K supports this postulate.

¹To receive a copy of the observed and calculated structure factors, order Document AM-81-144 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 1. Positional, population and anisotropic thermal parameters for d-Ca/H-HEU

| Atom | Type | Population | x/a | y/b | z/c | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|------|------------|-----------|-----------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| T(1) | 8j | 8 | 0.3200(1) | 0.1632(1) | 0.2343(3) | 139(5) | 288(9) | 863(42) | 15(6) | 109(11) | 56(16) |
| T(2) | 8j | 8 | 0.0668(1) | 0.2137(1) | 0.2154(3) | 193(6) | 258(9) | 897(44) | 47(6) | 152(13) | 24(16) |
| T(3) | 8j | 8 | 0.2162(1) | 0.3145(1) | 0.2018(3) | 265(6) | 255(9) | 923(46) | 4(6) | 223(14) | 8(16) |
| T(4) | 8j | 8 | 0.2020(1) | 0.0895(1) | 0.4121(3) | 276(7) | 155(8) | 1193(48) | 8(6) | 244(14) | 7(16) |
| T(5) | 4h | 4 | 0.0 | 0.2956(2) | 0.5 | 155(8) | 240(12) | 1016(62) | 0 | 191(17) | 0 |
| O(1) | 8j | 8 | 0.4190(2) | 0.1504(3) | 0.3841(8) | 19(1) | 30(2) | 189(14) | 1(2) | -3(4) | 6(5) |
| O(2) | 8j | 8 | 0.2906(3) | 0.2513(3) | 0.2421(7) | 32(2) | 31(2) | 149(13) | 10(2) | 17(4) | 6(5) |
| O(3) | 8j | 8 | 0.3068(3) | 0.1409(4) | 0.0091(8) | 43(2) | 49(3) | 128(13) | 11(2) | 33(4) | 6(5) |
| O(4) | 8j | 8 | 0.0170(3) | 0.2408(4) | 0.3462(10) | 52(3) | 46(3) | 347(20) | -8(2) | 89(6) | -54(6) |
| O(5) | 8j | 8 | 0.2627(3) | 0.1018(4) | 0.2909(9) | 32(2) | 47(3) | 271(18) | -7(2) | 49(5) | 22(6) |
| O(6) | 8j | 8 | 0.1117(3) | 0.1337(4) | 0.3046(10) | 43(2) | 41(3) | 401(23) | 15(2) | 57(6) | 33(7) |
| O(7) | 8j | 8 | 0.2520(4) | 0.3862(5) | 0.3558(9) | 68(3) | 65(4) | 160(17) | 5(3) | 14(6) | -34(7) |
| O(8) | 8j | 8 | 0.1345(4) | 0.2768(4) | 0.2172(11) | 54(3) | 45(3) | 522(27) | -2(3) | 117(8) | 30(8) |
| O(9) | 4i | 4 | 0.1765(6) | 0.0 | 0.4095(17) | 71(5) | 20(4) | 580(42) | 0 | 144(13) | 0 |
| O(10) | 4g | 4 | 0.0 | 0.1948(7) | 0.0 | 109(7) | 70(7) | 87(22) | 0 | -39(10) | 0 |
| Ca(1) | 4i | 2.41(5) | 0.2591(6) | 0.5 | 0.0820(14) | 137(6) | 44(4) | 664(39) | 0 | 82(12) | 0 |
| Ca(2) | 4i | 0.76(3) | 0.0326(9) | 0.0 | 0.2901(29) | 52(7) | 37(8) | 504(68) | 0 | 92(18) | 0 |

** parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 0.3200(1) indicates an esd of 0.0001.

*** anisotropic thermal parameters $\times 10^4$, for T(1) to T(5) $\times 10^5$.

Framework

The heulandite-type framework is built from the fundamental polyhedral unit (FPU) depicted schematically in Figure 1. The apices in this drawing represent tetrahedral or T atoms (T = Si or Al). The oxygen atoms which form a bridge between the T atoms are depicted as straight lines. Each FPU consists of two four-membered rings which face each other across the unit and four adjacent five-membered rings. The heulandite lattice can be visualized as follows. The FPU's are first joined through the T5 atoms to form long chains. These chains are next linked laterally through the T1, T2, and T3 atoms to

produce dense silicate layers. Finally, parallel layers are joined through the T4 atoms to form the three-dimensional crystal framework which encloses the system of two-dimensional channels.

The stereodrawings of skeletal models in Figure 2 are the simplest way to illustrate the gradual changes in the heulandite structure during dehydration. The three drawings in the figure are: 2a, natural (hydrated) heulandite (Merkle and Slaughter, 1968); 2b, the present structure; 2c, heulandite-B (Alberti, 1973). Qualitatively, it is easy to see that these three structures are all different. The FPU's twist and rotate during the transition h-HEU to HEU-B.

The degree of distortion of the structure may be quantified in a number of ways, the first of which is by considering the orientation of the FPU's with respect to their neighbors. To do this, we imagine a vector between the two T5 atoms in one FPU, depicted as a dashed line in Figure 1. The angle be-

Table 2. Selected interatomic distances (Å) and bond angles ($^\circ$) for d-Ca/H-HEU

| | | | |
|--------------|----------|-----------------|----------|
| T(1)-O(1) | 1.633(7) | T(4)-O(5) | 1.635(6) |
| O(2) | 1.625(7) | O(6) | 1.626(8) |
| O(3) | 1.635(6) | O(7) | 1.634(8) |
| O(5) | 1.617(7) | O(9) | 1.618(4) |
| mean | 1.627 | mean | 1.628 |
| T(2)-O(4) | 1.595(6) | T(5)-2 O(1) | 1.614(8) |
| O(6) | 1.602(8) | -2 O(4) | 1.597(7) |
| O(8) | 1.596(8) | mean | 1.605 |
| O(10) | 1.582(6) | | |
| mean | 1.594 | | |
| T(3)-O(2) | 1.620(8) | T(1)-O(1)-T(5) | 136.3(4) |
| O(3) | 1.643(7) | T(1)-O(2)-T(3) | 150.3(4) |
| O(7) | 1.637(9) | T(1)-O(3)-T(3) | 137.5(4) |
| O(8) | 1.592(7) | T(2)-O(4)-T(5) | 154.4(4) |
| mean | 1.623 | T(1)-O(5)-T(4) | 144.4(5) |
| | | T(2)-O(6)-T(4) | 145.3(5) |
| Ca(1)-2 O(3) | 2.68(1) | T(3)-O(7)-T(4) | 145.0(6) |
| -2 O(7) | 2.87(1) | T(2)-O(8)-T(3) | 160.4(5) |
| | | T(4)-O(9)-T(4) | 149.2(6) |
| Ca(2)-2 O(6) | 2.68(1) | T(2)-O(10)-T(2) | 156.0(9) |
| O(9) | 2.27(2) | | |

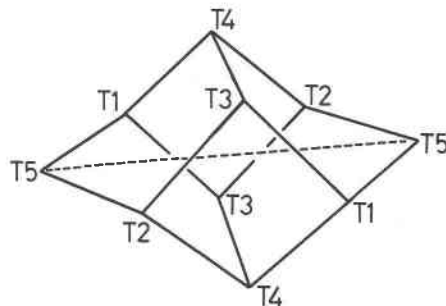


Fig. 1. Schematic drawing of the Fundamental Polyhedral Unit (FPU).

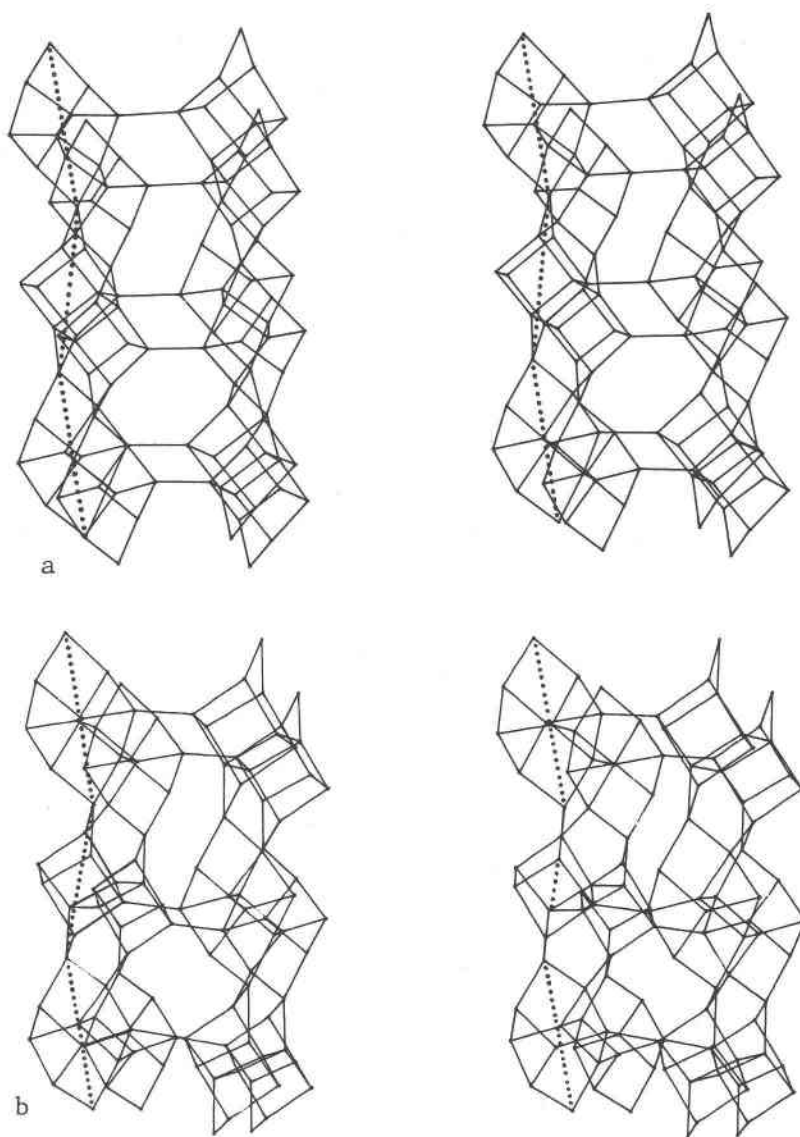


Fig. 2.

tween this vector and the identical vector in the adjacent FPU will indicate how much they are twisted relative to one another. These vectors are also included in the stereodrawings of Figure 2, and it is obvious that the degree of twist or distortion of the FPU's increases steadily from hydrated heulandite to the collapsed phase, heulandite-B. In particular, the angles between the vectors are 163.70° for h-HEU, 159.00° for the present sample (d-Ca/H-HEU), and 146.58° for HEU-B. From this evidence alone, it can be deduced that the present structure is, indeed, an intermediate between the hydrated and collapsed phases. Furthermore, since the relevant angle in the present structure is much closer to that of hydrated

heulandite than that of heulandite-B, we conclude that the degree of structural distortion is quite modest in this crystal.

Any number of vectors may be constructed in the manner described above to illustrate the framework. While it is too difficult to describe them using the simplified drawings in this text, we have examined a variety of such vectors. In all cases, the results are the same, *i.e.*, the present sample is shown to be an intermediate between the hydrated and collapsed heulandite phases. In addition, d-Ca/H-HEU more closely resembles the structure of the hydrated form.

Another indication of the structural distortion which occurs in going from h-HEU to HEU-B is

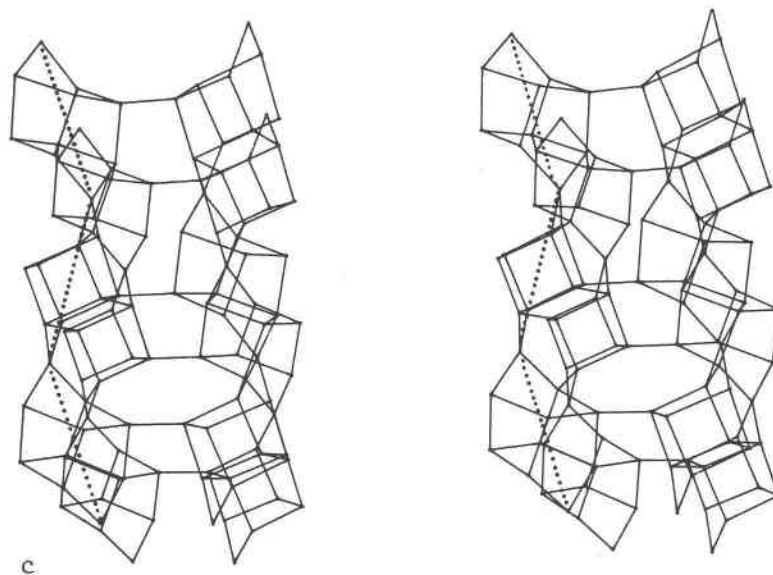


Fig. 2. Stereodrawings showing skeletal models of the heulandite-type frameworks: (a) hydrated natural heulandite (h-HEU); (b) dehydrated Ca/NH₄-heulandite (d-Ca/H-HEU); (c) heulandite-B (HEU-B).

found in the unit-cell parameters and volumes, which are tabulated below for the three structures of interest (a , b , c in Å; β ; V):

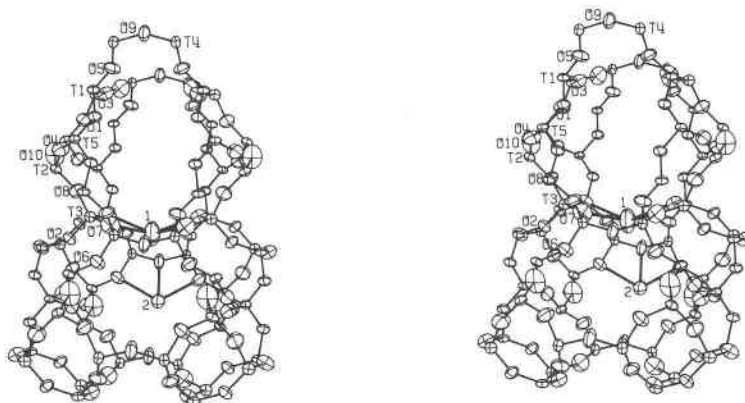
| | | | | | |
|---------|-------|-------|------|-------|------|
| h-HEU: | 17.73 | 17.82 | 7.43 | 116.3 | 2105 |
| d-Ca/H: | 17.16 | 17.43 | 7.39 | 113.4 | 2029 |
| HEU-B: | 16.95 | 16.42 | 7.28 | 117.8 | 1792 |

All three axial lengths and the volumes decrease monotonically in the transition from h-HEU to HEU-B. Unfortunately, there is no trend in the β angles.

The mechanism of framework distortion is related to the presence of calcium cations in the heulandite channels. In the present structure, calcium has been

located at two sites [denoted Ca(1) and Ca(2)] which are shown in the stereodrawing of Figure 3. Both sites are in eight-membered rings. The cations at Ca(2) do not seem to induce important changes in the framework structure, consistent with their low occupancy and their coordination which is not suited for a strong cation-framework interaction. The Ca(1) cations, however, do exert a strongly attractive force on the framework oxygens, drawing them closer to achieve the best possible coordination environment. A distortion of the framework is the result.

An important implication of framework distortion is that the critical apertures of the heulandite channels are markedly decreased. Restriction of



the apertures is evident from the dimensions of the eight-membered rings at the sites Ca(1) and Ca(2), tabulated below for the three heulandite structures.

| | Ca(1) eight-ring | Ca(2) eight-ring |
|--------|--------------------------------|--------------------------------|
| h-HEU | $5.61 \times 7.43 \text{ \AA}$ | $6.79 \times 7.59 \text{ \AA}$ |
| d-Ca/H | $4.91 \times 7.39 \text{ \AA}$ | $5.99 \times 7.30 \text{ \AA}$ |
| HEU-B | $4.23 \times 7.32 \text{ \AA}$ | $4.80 \times 7.32 \text{ \AA}$ |

The dehydration of Ca-stilbite, which is constructed from the same FPU as is heulandite, resulted in the rupture of some framework bonds. However, exchanging the Ca^{2+} with NH_4^+ prior to dehydration caused all framework bonds in the resultant H-stilbite to remain intact. The obvious manifestation of bond rupture is that the dimensions of the FPU's will change as they collapse. We can follow the changes in these dimensions by defining a "pseudo-volume" of the FPU as the product of three distances across the FPU, *i.e.*, $(T3-T3) \times (T4-T4) \times (T5-T5)$. A significant decrease in this "volume" will suggest FPU collapse. This is nicely demonstrated by comparing the FPU volumes for d-H-stilbite and d-Ca-stilbite, which are 242 \AA^3 and 230 \AA^3 , respectively. An indication of the greater stability of the heulandite-type structure is evident from the observations that its FPU volume is remarkably constant during dehydration, *i.e.*, 236 \AA^3 for h-HEU, 237 \AA^3 for d-Ca/H-HEU, and 236 \AA^3 for HEU-B.

Cations

The chemical analysis of the present sample yielded a Ca^{2+} concentration of 3.8 ions per unit cell, agreeing very well with the number of cations (3.7) located by least-squares refinement. The small difference is within the error of microprobe analysis. The small thermal displacement ellipsoids show that the cation sites are well defined with relatively good coordination distances.

Conclusions

Because of the distortion of the heulandite framework upon dehydration, an open channel system is probably only possible in the presence of a limited number of exchangeable cations. However, even when such distortion is evident, the integrity of the heulandite framework is preserved, since none of the framework bonds are ruptured as has been observed for stilbite.

By reducing the number of exchangeable cations and by employing a moderate dehydration temperature (483K), we have succeeded in producing a heu-

landite sample which is intermediate between hydrated heulandite and its heat-collapsed phase, heulandite-B. A further reduction of the cation content should produce samples which are more suitable for adsorptive and catalytic studies on activated heulandite zeolites.

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