Dehydration mechanism of clinoptilolite and heulandite: Single-crystal X-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K

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ABSTRACT

The crystal structure of clinoptilolite from Weitendorf, Styria, Austria \([a = 17.622(2), b = 17.895(2), c = 7.399(1) \text{ Å}, \beta = 116.45(2)^\circ, \text{space group } C2/m] \), \((\text{Mg}_{0.9}\text{Ca}_{1.0-\text{Sr}_{0.1}\text{Ba}_{0.3}\text{K}_{1.2}\text{Na}_{0.4}}\text{Al}_{5.2}\text{Si}_{7.8}\text{O}_{21.7}\cdot 25\text{H}_{2}\text{O})\), was studied by single-crystal X-ray diffraction. The structures of a fully hydrated form \((25 \text{H}_{2}\text{O})\) and three partially dehydrated forms with \(7-5 \text{H}_{2}\text{O}\) were refined at 100 K. The dehydration is accompanied by cation diffusion within the channel system. Four cation positions \((\text{Na}1, \text{Ca}2, \text{K}3, \text{Mg}4)\) were found in the channels of the highly hydrated form. With loss of \(\text{H}_{2}\text{O}\), cations migrate preferentially to site K3 at the center of a distorted eight-membered ring of tetrahedra, forming channels parallel to \(a\). In the \(5\text{H}_{2}\text{O}\) variant \([a = 17.61(1), b = 17.456(7), c = 7.360(7) \text{ Å}, \beta = 116.77(4)^\circ]\), \(\text{H}_{2}\text{O}\) is strongly disordered, but the framework remains expanded. With progressing dehydration, disorder in the tetrahedral framework is reflected in increasing atomic displacement parameters and decreased T-O distances.

The thermal stiffness of the heulandite-clinoptilolite framework is related to the \(\text{Al}\) concentration on \(T2\), which governs the bond strength between \(O1\) and \(\text{Ca}2\). A small \(\text{Al}\) concentration on \(T2\) enables cation diffusion to occur from \(\text{Ca}2\) to \(\text{K}3\) upon heating. High occupancies of large cations on \(\text{K}3\) prevent the structure from collapsing.

INTRODUCTION

Clinoptilolite and heulandite are monoclinic zeolite minerals characterized by large, intersecting open channels of ten- and eight-membered tetrahedral rings. The large ten-membered \(A\) ring and the smaller eight-membered \(B\) ring confine channels parallel to \(c\). Type \(C\) channels parallel to \(a\) are also formed by eight-membered rings and connect \(A\) and \(B\) channels (Merkle and Slaughter, 1968). The channels are occupied by cations and \(\text{H}_{2}\text{O}\).

It is well known that zeolites of the heulandite-clinoptilolite group react differently upon heating depending on their chemical composition (e.g., Alietti et al., 1974; Alberti and Vezzalini, 1983; Bish, 1984, 1988). This difference has even been used to distinguish clinoptilolite from heulandite (Mumpton, 1960; Boles, 1972). Bish (1984) reviewed the literature on dehydration of this mineral group and suggested that especially the low-temperature dehydration behavior is of interest because clinoptilolite-bearing tuffs at Yucca Mountain, Nevada, were being investigated as a potential repository for high-level radioactive wastes (Smyth, 1982). The \(\text{Na}, \text{K}, \) and \(\text{Ca}\) content of clinoptilolite-heulandite varies significantly in many deposits; thus dehydration must be investigated within the composition range of the natural material. Low-temperature dehydration was monitored in most previous experiments with X-ray powder diffraction, differential thermogravimetry (DTG), and differential thermoanaly-sis (DTA) techniques; thus only the change of cell dimension with \(\text{H}_{2}\text{O}\) loss was determined, and the exact mechanism of dehydration remains unclear.

In a previous single-crystal X-ray dehydration study (Armbruster and Gunter, 1991) clinoptilolite-heulandite, \((\text{Ca}_{2.9}\text{Mg}_{0.4}\text{Na}_{2.2}\text{K}_{0.8}\text{Al}_{5.0}\text{Si}_{7.4}\text{O}_{21.7}\cdot 25\text{H}_{2}\text{O})\), was stepwise dehydrated in a dry \(\text{N}_{2}\) atmosphere, and the structure was subsequently studied at 100 K. Annealing 1 h at 448 K in a dry atmosphere was sufficient to expel most of the \(\text{H}_{2}\text{O}\) and to produce a heat-collapsed structure with identical tetrahedral framework topology, but strongly altered T-O-T angles and decreased cell volume (1864 vs. 2097 Å).

Koyama and Takéuchi (1977) suggested that \(\text{K}\) in \(\text{K}\)-rich clinoptilolite is positioned almost in the center of the \(C\) channel, thereby inhibiting collapse of the framework structure. This was confirmed by Galli et al. (1983), who studied a K-exchanged heulandite sample with single-crystal data up to 593 K and observed only a slight contraction of the framework structure [cell volume before heating: 2132(1) Å\(^3\); after heating excursion: 2012(2) Å\(^3\)]. However, the population of channel cations in this exchanged sample is much higher than those of most natural samples, which could also influence the stability of the expanded cavities. In the present study, clinoptilolite with a complex cation composition within the structural cavities was selected. The aim of this investigation is to understand the dehydration mechanism and the accompanying structural distortions.


**TABLE 1.** Data measurement and refinement parameters for clinoptilolite from Weitendorf, Styria, at 100 K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Natural</th>
<th>Dehyd1</th>
<th>Dehyd2</th>
<th>Dehyd3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan width (°)</td>
<td>1.5</td>
<td>1.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>a (Å)</td>
<td>17.622(2)</td>
<td>17.588(2)</td>
<td>17.619(6)</td>
<td>17.61(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.895(2)</td>
<td>17.572(4)</td>
<td>17.503(4)</td>
<td>17.456(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.399(1)</td>
<td>7.389(2)</td>
<td>7.371(3)</td>
<td>7.360(7)</td>
</tr>
<tr>
<td>β (°)</td>
<td>116.45(2)</td>
<td>116.77(2)</td>
<td>116.71(4)</td>
<td>116.77(4)</td>
</tr>
<tr>
<td>Max. θ (°)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>2333</td>
<td>2008</td>
<td>2003</td>
<td>2014</td>
</tr>
<tr>
<td>Observed unique reflections &gt;3σ(I)</td>
<td>1293</td>
<td>1293</td>
<td>1293</td>
<td>1293</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>209</td>
<td>184</td>
<td>184</td>
<td>184</td>
</tr>
<tr>
<td>R (%)</td>
<td>3.33</td>
<td>3.97</td>
<td>4.29</td>
<td>4.31</td>
</tr>
<tr>
<td>R(1%)</td>
<td>4.64</td>
<td>5.79</td>
<td>5.42</td>
<td>5.31</td>
</tr>
</tbody>
</table>

Note: \( R = \frac{\sum |F_{o} - F_{c}|}{\sum |F_{o}|} \), \( R_{w} = \frac{\sum w |F_{o} - F_{c}|}{\sum w |F_{o}|} \).

**EXPERIMENTAL PROCEDURE**

The clinoptilolite sample is from the basalt at Weitendorf, Styria, Austria (Armbruster et al., 1991). The composition, \( \text{Mg}_{0.9} \text{Ca}_{1.8} \text{Sr}_{0.9} \text{Ba}_{0.1} \text{K}_{1.2} \text{Na}_{0.1} \text{Al}_{1.0} \text{Si}_{2.5} \text{O}_{1.7} \cdot 25 \text{H}_{2} \text{O} \), was determined with an ARL-EMX-SM electron microprobe operating at 15 kV and 20 nA with a defocused beam (20 μm). With Na + K > Ca and Si/Al = 4.14, the sample fulfills both definitions of a clinoptilolite (Mason and Sand, 1960; Boles, 1972). The \( \text{H}_{2} \text{O} \) content was estimated from structure refinements described below.

**Single-crystal data collection**

Single-crystal X-ray data were obtained at 100 K with an Enraf-Nonius CAD-4 diffractometer (graphite-monochromatized MoKα radiation) using a conventional liquid-N\(_2\) cooling device. Experimental details were described by Armbruster and Gunter (1991) and are summarized in Table 1. The natural crystal was immersed in H\(_2\)O for several weeks and subsequently quenched to 100 K on the diffractometer (sample: natural). After data measurement the same crystal was kept on the diffractometer, flushed for 2.5 h with dry N\(_2\) at 373 K and quenched to 100 K for data measurement (sample: dehyd1). This procedure was repeated after flushing 4 h at 413 K (sample: dehyd2) and 1 h at 473 K (sample: dehyd3). Cell dimensions were determined for all samples with reflections 15° > θ > 10°. With progressive dehydration the X-ray reflections became streaked along the c direction, and the scan angle had to be varied within the various data sets (Table 1). Absorption was tested by ψ scans, but the effect was considered insignificant, and the correction was not applied. The program SHELX76 (Sheldrick, 1976) was used for structure refinement with a \( 1/σ^2 \) weighting scheme. The populations of the channel cation sites Na1, Ca2, K3, and Mg4 were refined with Na, Ca, K, and Mg scattering factors. In addition, all Ba found by electron microprobe analyses was constrained to occupy K3. For estimates of site occupancies of various species, it was assumed that Ca and K have about twice and Sr four times as many electrons as Na. Resulting T-O distances were used to estimate Si/(Al + Si) for each site, using the same method as Koyama and Takéuchi (1977). Corresponding Si, Al scattering factors were introduced for the tetrahedral cations in the subsequent refinement cycles. For additional details and nomenclature of atomic sites see Armbruster and Gunter (1991). Final difference Fourier maps of all samples showed maximum peaks and minima of about ±0.7 e/Å\(^3\).

**RESULTS**

Dehydration was accompanied by a change in cell dimensions, which is most pronounced along b (Table 1). Based on site-occupancy refinements, H\(_2\)O in the natural sample amounts to 25 H\(_2\)O pfu. Flushing the crystal with dry N\(_2\) at 373 K reduced the H\(_2\)O content to 7 H\(_2\)O (dehyd1), and in dehyd3 only 5 H\(_2\)O pfu were detected (Fig. 1). The dehydration within the investigated temperature range does not lead to formation of a heat-collapsed phase (e.g., Armbruster and Gunter, 1991). Observed and calculated structure factors for all structures are given in Table 2; positional parameters and occupancies are summarized in Table 3; and anisotropic displacement parameters are listed in Table 4. Table 5 shows T-O distances, T-O-T angles, and M-O distances for channel cations.

**Natural sample**

In agreement with Koyama and Takéuchi (1977) and Armbruster and Gunter (1991), four cation sites (Na1, Ca2, K3, Mg4) were resolved in the fully hydrated sample (Fig. 1). Na1, Ca2, K3, and Mg4 were refined with Na, Ca, K, and Mg scattering factors. In addition, all Ba found by electron microprobe analyses was constrained to occupy K3. For estimates of site occupancies of various species, it was assumed that Ca and K have about twice and Sr four times as many electrons as Na. Resulting T-O distances were used to estimate Si/(Al + Si) for each site, using the same method as Koyama and Takéuchi (1977). Corresponding Si, Al scattering factors were introduced for the tetrahedral cations in the subsequent refinement cycles. For additional details and nomenclature of atomic sites see Armbruster and Gunter (1991). Final difference Fourier maps of all samples showed maximum peaks and minima of about ±0.7 e/Å\(^3\).

1 A copy of Tables 2, 3, 4, and 5 may be ordered as Document AM-93-517 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
Fig. 1. Projection along [001], displaying the large A channel confined by ten tetrahedra and the B channel by eight-membered rings. Thin lines connect channel cations with coordinating framework O, thick bonds are drawn between channel cations and H$_2$O. (Left) sample natural; (right) sample dehyd3.

occupancy 0.1 Na and 0.19 K) is coordinated by $2 \times O_2$ (2.83 Å) and $2 \times O_3$ (3.10 Å) of the tetrahedral framework and five H$_2$O molecules $O_16'$ (2.48 Å), $O_{11}$ (2.74 Å), and $2 \times O_{15}$ (2.91, 3.00 Å). $O_{16}'$ and $O_{15}$ were highly disordered and refined as split positions. Assignment of additional K to the Na1 position is justified by the refined population (greater than the analyzed Na content) and by the long Na1-O distances. The maximum occupancy of Ca2 is 0.5 because its symmetry-equivalent at $-x, -y, -z$ is too close to permit occupancy of both sites. Ca2 (occupancy 0.35 Ca and 0.04 K) is eightfold-coordinated with $2 \times O_{10}$ (2.75 Å), $1 \times O_1$ (2.55 Å) of the framework, and five H$_2$O molecules [$4 \times O_{13}$ (2.24, 2.2 × 2.57 Å), and $1 \times O_{14}$ (3.07 Å)]. K3 (occupancy 0.08 Ba, 0.07 K, 0.03 Sr) is coordinated by six framework O atoms [$2 \times O_2$ (3.18 Å), $2 \times O_3$ (2.98 Å), $2 \times O_4$ (3.07 Å)]. The coordination is completed by two H$_2$O molecules at $O_{13}$ (3.08 Å). Mg4 (occupancy 0.36 Mg) is not bonded to any framework O but the coordination can be described as a disordered octahedral [Mg(H$_2$O)$_6$]$^{2+}$ ion [$2 \times O_{15}$ (1.91 Å), $2 \times O_{12}$ (2.03 Å), $2 \times O_{16'}$ (2.16 Å)] centered in the ten-membered ring of tetrahedra defining the A channels. The disorder is caused by the split character of $O_{15}$ and $O_{16'}$. The above assignments leave $O_{16}$ and $O_{19}$ as H$_2$O molecules that are not coordinated by cations. The refined position $O_{12}$, which has large and strongly anisotropic displacement parameters (Table 4), is a mixture of the H$_2$O sites $O_{12}$ and $O_{12}'$. These positions are only 0.7 Å apart (Hambley and Taylor, 1984). $O_{12}$ is coordinated to K3 and Mg4, whereas $O_{12}'$ is a H$_2$O molecule not bonded to channel cations. The contribution of $O_{12}'$ is lost upon dehydration, and the displacement parameters become more isotropic. The disordered character of O12 is also responsible for the short Na1-O12 and K3-O12 distances.

Sample dehyd1 (2.5 h at 373 K)

O16 and O19 became vacant, and the populations of all other H$_2$O positions decreased significantly. Position Na1 approached site K3 (Fig. 1). The distance Na1-K3 decreased to 1.3 Å. The electron density at Na1 decreased significantly, with Na1-O distances becoming shorter, suggesting that K diffused from Na1 to K3 (K3 increased in population). The new Na1 site (occupancy 0.10 Na and 0.09 K) is coordinated by $2 \times O_2$ (2.58 Å), $2 \times O_3$ (2.76 Å), and H$_2$O on $O_{12}$ (2.47 Å). Cations on Ca2 moved preferentially to K3; in turn the electron density at Ca2 was reduced by 50%, leading to a Ca population of 0.22. The Ca2-O distances became significantly shorter compared with those of the fully hydrated sample. As a consequence of the Ca2 → K3 diffusion, the population of K3 increased [0.33(K-Ca)] but its position and O coordination were unchanged. K3 became coordinated by two eight-membered rings (K3 and K3) with small populations. K3 has two distances to framework O4 of about 1.97 Å and one of 1.93 Å to H$_2$O at $O_{18}$. It is very likely that Mg moved to K3, because the electron density at Mg4 was no longer detectable. K3 has four distances to framework O of about 2.7 Å and is also coordinated by $O_{12}$ (2.33 Å) and $O_{18}$ (2.80 Å). The low population and characteristic distances thus suggest that this site is mainly occupied by Sr.

Samples dehyd2 and dehyd3

Both samples are very similar and therefore are discussed together. The populations of O atoms related to H$_2$O agree within 3σ for both samples, which both contain approximately 5 H$_2$O pfu. However, displacement parameters are significantly greater for dehyd3. The populations of Na1 and Ca2 further had decreased, and those for K3 increased. Satellite position K3, could no longer be resolved. Residual H$_2$O on $O_{13}$ (occupancy 0.37) is significantly disordered and coordinates K3. The high displacement parameter $U_{22}$ indicating that this $O_{13}$ is a mixture of $O_{13}$ (general position) and $O_{13}'$ (on the mirror plane), as refined by Hambley and Taylor (1984) and Armbruster and Gunter (1991), is striking. Splitting into two sites was not considered for this sample because of low occupancy. Ca2 possesses sixfold coordination [$2 \times O_{13}$ (2.79 Å), $1 \times O_{14}$ (2.10 Å), $2 \times O_{10}$ (2.61 Å), and $1 \times O_1$ (2.20 Å)]. The largest changes in corresponding T-O-T angles between the fully hydrated sample and dehyd3 were observed for T1-O3-T3, which decreased 6.5°, and T4-O5-T4, which increased 5.4° with dehydration.

**Discussion**

Dehydration of the Weitendorf sample leads to an apparent decrease of T-O distances (up to 0.03 Å). This decrease cannot be related to changes in T-O-T angles...
(e.g., Hill and Gibbs, 1979). As an example, T4-O5-T4 increases because of dehydration from 143.9(3)° to 149.3(6)°; however, T4-O5 distances become shorter by 0.03 Å (corresponding to 10%). The influence of broken H bridges as a consequence of dehydration cannot also be responsible for shortened T-O distances. H14, bonded to O14 (fully occupied in the natural sample), was localized by Hambley and Taylor (1984) by neutron diffraction for natural heulandite. Judging from bond valence calculations for O5, which has a O5-H14 distance of ca. 2.3 Å, this H bond is by far too weak to cause the observed T4-O5 change. The influence of channel cations must also be ruled out because O5 has none in its neighborhood. However, from sample natural to dehyd3, Beq of O1 and O5 increased by factors of 3.1 and 3.3, respectively, indicating that rigid rotational disorder of TO4 units is largely responsible for T-O shortening. There is a general and continuous increase of Beq for framework atoms with dehydration reflecting this increasing disorder. A similar but less pronounced increase of Beq was observed for partially dehydrated (dehyd3) Succor clinoptilolite-heulandite (Armbruster and Gunter, 1991).

With additional dehydration, displacement parameters of various critical O positions (e.g., O1) even decreased in the heat-collapsed Succor structure (dehyd4). This suggests that Succor dehyd3 and Weitendorf dehyd3 represent strongly strained structures where heat-collapsed domains may already exist. This is also confirmed by the anisotropy of O1 displacement parameters, for which the largest increase was parallel to a upon dehydration (the heat-collapsed structure is characterized by a large shift of O1 along a). The increase of R values (Table 1) from the natural sample to dehyd3 indicates that a harmonic vibrational model is not sufficient to simulate this disorder. Additional dehydration (dehyd4) of the Succor sample (Armbruster and Gunter, 1991) led to release of strain due to formation of a heat-collapsed variant, whereas in the Weitendorf sample the strained variant persists.

The dehydration conditions of clinoptilolite-heulandite from Succor Creek, Ca2,Mg0.3Na2,K0.29Al1.6Si28.5O72.nH2O (Armbruster and Gunter, 1991), leading to sample dehyd3 were almost identical to those yielding dehyd1 in this study (373 K, dry N2). However, in the Succor sample (dehyd3) 14 H2O pfu were found, whereas only 7 H2O were localized in the corresponding Weitendorf sample. Also similar to these investigations are the neutron diffraction experiments by Hambley and Taylor (1984), who studied a sample with the composition Ba0.1Sr0.1Ca2.2Na2.4Al1.2Si28.5O72.nH2O from Coonabarabran in its natural state and after treatment in vacuum at 343 K. After these moderate dehydration conditions, the H2O content is mainly related to the Ca concentration. This is also in agreement with the high enthalpy of hydration (−1580 kJ/mol) known for Ca (Barrow, 1973). The higher Ca content of the Succor and Coonabarabran sample maintains higher O13 and O14 (coordinated to site Ca2) populations at this dehydration level, whereas reduced populations are observed in this study for a sample with smaller Ca content.

At first glance it may appear surprising that, in spite of its high K content, a low K3 occupancy was found for the natural Weitendorf sample. However, framework O2 and O3 are coordinated similarly to both K3 and Na1. In the fully hydrated sample, K prefers a large H2O coordination number, which is available at Na1. Only depletion of H2O forces K to move to K3. The partial dehydration of K is promoted by its low enthalpy of hydration of −320 kJ/mol (Barrow, 1973). In contrast, the K-rich clinoptilolite studied by Koyama and Takéuchi (1977) was also rich in Na; thus the Na1 site was preferred by Na, and all K was placed in K3.

These new data support the conclusions summarized by Hambley and Taylor (1984); channel occupation of various cations and substitution of Al for Si play an interrelated role in determining the thermal stability of these zeolites. In all minerals of the heulandite-clinoptilolite group, T2 is preferentially occupied by Al, as T2-O are the longest T-O distances within the structure (e.g., Koyama and Takéuchi, 1977; Alberti, 1975; Hambley and Taylor, 1984; Smyth et al., 1990; Armbruster and Gunter, 1991). A key to understanding the thermal stability of this mineral group is in the manner in which O1 links the two T2 tetrahedra. Considering only the framework structure, O1 is underbonded, owing to relatively large Al content on T2 (30% in the Weitendorf sample). In addition, O1 is coordinated to the channel site Ca2. Thus the bond strength between Ca2 and O1 will be dependent on the Al population on T2. In heulandite samples with high Al contents Ca2 will be situated in the neighborhood of O1 (Hambley and Taylor, 1984; Armbruster and Gunter, 1991). As an example, the population of Ca2 of Succor sample dehyd3 was only slightly smaller (occupancy 0.33) than that of the fully hydrated sample (occupancy 0.37). In Al-poor clinoptilolites, cations on Ca2 may easily diffuse to other channel positions, such as K3, as observed in the present investigation. Koyama and Takéuchi (1977) suggested that large cations on K3 plug the C channel (Fig. 2), which prevents the structure from collapsing. This also explains why the framework structure of the K-poor, Al-rich Succor sample collapsed during heating to 448 K, whereas the K-rich, Al-poor Weitendorf sample did not collapse on heating to 473 K.

Based on the above observations of complex natural samples, the dehydration experiments of Alietti et al. (1974) on cation-exchanged (Na,K,Ca) clinoptilolite (their no. 23) and heulandite (their no. 24) can be better understood. For both framework compositions, the K-exchanged variants did not collapse with heating up to 1073 K. Galli et al. (1983) showed for a K-exchanged heulandite (9.3 Al pfu) that three types of K channel positions exist: (1) a ten-membered ring site, (2) a channel wall site (corresponding to K3), and (3) an eight-membered ring site (corresponding to Ca2). At 573 K the site in the eight-membered ring (bonded to O1) was 65% occupied by K; the site at the channel wall (K3) had a K occupancy of
confined by eight-membered rings, which are plugged by cations. (Left) sample Weitendorf dehyd3; (right) heat-collapsed structure dehyd4 from Succor (Armbruster and Gunter, 1991).

70%. Thus both criteria are fulfilled, O1 (underbonded because of significant Al on T2) is coordinated to K, and occupancy of K3 is large, preventing the structure from collapsing (Fig. 2). In addition, the K position in the ten-membered ring has K-O distances to framework O4 and O6 of 2.8–3.1 Å, which reduces compression. Structural data for K-exchanged clinoptilolite do not exist, but we may assume from these experiments and those of Koyama and Takéuchi (1977) that with increasing dehydration, K moves to K3, which keeps the channels expanded (Fig. 2). In contrast to heulandite, the small Al population of T2 allows very low occupancies of Ca2.

Both Na exchanged heulandite and clinoptilolite collapse below 473 K (Alietti et al., 1974). In both minerals cation sites Na1 and Ca2 are occupied by Na. In heulandite site Ca2 is expected to be preferred by Na because of the coordination to the underbonded O1 atom. With progressive dehydration Na will migrate from Na1 to a site closer to the channel wall position (K3). However, Na is too small to maintain expansion of the channels (Fig. 2), and the structure must collapse.

Ca-exchanged clinoptilolite and heulandite collapse (Alietti et al., 1974). The concentration of divalent Ca is only half those of Na or K for a given Al substitution in the framework. Ca in heulandite is concentrated at Ca2 neighboring O1. Excess Ca is located at Na1. Ca is too small to keep the channels open even if it diffuses to K3. Furthermore, occupation of K3′ (Armbruster and Gunter, 1991) in the center of the ten-membered ring (at 000) of a collapsed cavity is a preferred site for Ca, with 4 (K3′-O) of 2.15 Å. The collapse of the Ca-exchanged clinoptilolite (no. 23) of Alietti et al. (1974) is much more pronounced than that of Ca-exchanged clinoptilolite from Castle Creek, Idaho, of Bish (1984), which is related to the higher stabilizing (not exchanged) K content of the latter sample.

The complex dehydration behavior of natural clinoptilolite and heulandite depends on the concentration of large cations, such as K, Cs, and Ba, and the Al concentration in the framework, which governs the Ca2 population.

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