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 \([a = 17.622(2), b = 17.895(2), c = 7.399(1) \text{ Å}, \beta = 116.45(2)^\circ, \text{space group } C2/m]\), \((\text{Mg}_{0.9}\text{Ca}_{1.4-}
\text{Sr}_{0.3}\text{Ba}_{0.2}\text{K}_{1.2}\text{Na}_{0.4})\text{Al}_{1.0}\text{Si}_{2.9}\text{O}_{7\times-25}\text{H}_2\text{O}\), 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 \((\text{Na}1, \text{Ca2, K3, Mg4})\) were found in the channels of the highly hydrated form. With loss of \text{H}_2\text{O}, cations migrate preferentially to site \text{K3} at the center of a distorted eight-membered ring of tetrahedra, forming channels parallel to \text{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 Al concentration on T2, which governs the bond strength between O1 and Ca2. A small Al concentration on T2 enables cation diffusion to occur from Ca2 to K3 upon heating. High occupancies of large cations on K3 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 Na, K, and 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 thermodogradimetry (DTG), and differential thermoanalysis (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 (Armbuster and Gunter, 1991) clinoptilolite-heulandite, \(\text{Ca}_{2.3}\text{Mg}_{0.9}\text{Na}_{2.3}\text{K}_{0.8}\text{Al}_{1.0}\text{Si}_{2.3}\text{O}_{7\times-25}\text{H}_2\text{O}\), was stepwise dehydrated in a dry N2 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 \((1864 \text{ vs. } 2097 \text{ Å}^3)\). Koyama and Takéuchi (1977) suggested that K in 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 \([\text{cell volume before heating: } 2132(1) \text{ Å}^3; \text{after heating excursion: } 2012(2) \text{ Å}^3]\). 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.
Experimental procedure

The clinoptilolite sample is from the basalt at Weitendorf, Styria, Austria (Armbruster et al., 1991). The composition, \((\text{Mg}_{0.9}\text{Ca}_{1.6}\text{Sr}_{0.1}\text{Ba}_{0.2}\text{K}_{0.3}\text{Na}_{0.9})\text{Al}_{2}\text{Si}_{2}\text{O}_{7}\cdot 2\text{H}_{2}\text{O}\), was determined with an ARL-EMX-SM electron microprobe operating at 15 kV and 20 nA with a defocused beam (20 pm). With Na + K (1.6) > Ca (1.4) and Si/Al = 4.14, the sample fulfills both definitions of a clinoptilolite (Mason and Sand, 1960; Boles, 1972). The H₂O 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-N₂ cooling device. Experimental details were described by Armbruster and Gunter (1991) and are summarized in Table 1. The natural crystal was immersed in H₂O 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 N₂ 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 \(15° > \theta > 10°\). With progressive dehydration the X-ray reflections became streaked along the \(\omega\) direction, and the scan angle had to be varied to be within the various data sets (Table 1). Absorption was tested by \(\psi\) 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 \(\chi^2\) 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 Takeuchi (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 \(\pm 0.7\) e/Å³.

Results

Dehydration was accompanied by a change in cell dimensions, which is most pronounced along \(b\) (Table 1). Based on site-occupancy refinements, H₂O in the natural sample amounts to 25 H₂O pfu. Flushing the crystal with dry N₂ at 373 K reduced the H₂O content to 7 H₂O (dehyd1), and in dehyd3 only 5 H₂O 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 Takeuchi (1977) and Armbruster and Gunter (1991), four cation sites (Na1, Ca2, K3, Mg4) were resolved in the fully hydrated sample within the channel system (Fig. 1). Na1 is 2.08 Å from K3 and 2.25 Å from Mg4; thus these sites are too close to one another to be occupied simultaneously. Na1 (oc-
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 x O2 (2.83 Å) and 2 x O3 (3.10 Å) of the tetrahedral framework and five H$_2$O molecules O16' (2.48 Å), O11 (2.74 Å), and 2 x O15 (2.91, 3.00 Å). O16' and O15 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 x O10 (2.75 Å), 1 x O1 (2.55 Å) of the framework, and five H$_2$O molecules [4 x O13 (2 x 2.42, 2 x 2.57 Å), and 1 x O14 (3.07 Å)]. K3 (occupancy 0.08 Ba, 0.07 K, 0.03 Sr) is coordinated by six framework O atoms [2 x O2 (3.18 Å), 2 x O3 (2.98 Å), 2 x O4 (3.07 Å)]. The coordination is completed by two H$_2$O molecules at O13 (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 x O15 (1.91 Å), 2 x O12 (2.03 Å), 2 x O16' (2.16 Å)] centered in the ten-membered ring of tetrahedra defining the A channels. The disorder is caused by the split character of O15 and O16'. The above assignments leave O16 and O19 as H$_2$O molecules that are not coordinated by cations. The refined position O12, which has large and strongly anisotropic displacement parameters (Table 4), is a mixture of the H$_2$O sites O12 and O12'. These positions are only 0.7 Å apart (Hambley and Taylor, 1984). O12 is coordinated to K3 and Mg4, whereas O12' is a H$_2$O molecule not bonded to channel cations. The contribution of O12' 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 x O2 (2.58 Å), 2 x O3 (2.76 Å), and H$_2$O on O12 (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 $\rightarrow$ K3 diffusion, the population of K3 increased [0.33(K,Ca)] but its position and O coordination were unchanged. K3 became coordinated by two satellite positions (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 O18. 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 O12 (2.33 Å) and O18 (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 O13 (occupancy 0.37) is significantly disordered and coordinates K3. The high displacement parameter $U_{32}$ indicating that this O13 is a mixture of O13 (general position) and O13' (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 x O13 (2.79 Å), 1 x O14 (2.10 Å), 2 x O10 (2.61 Å), and 1 x O1 (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
were localized in the corresponding Weitendorf sample.

were almost identical to those yielding dehyd in this
be responsible for shortened T-O distances. H_{14}, bonded
content of the Succor and Coonabarabran sample main-
kJ/mol) known for Ca (Barrow, 1973). The higher Ca
agreement with the high enthalpy of hydration (-1580
ural state and after treatment in vacuum at 343 K. After
Na, oAl, ,Sir, , Or'.nHrO from Coonabarabran in its nat-
Also similar to these investigations are the neutron dif-
(dehyd3) 14 HrO pfu were founJ, whereas only 7 HrO
persists.

strains due to formation of a heat-collapsed variant,
observed T4-O5 change. The influence of channel cations
and after treatment in vacuum at 343 K. After
Ca2 will be situated in the neighborhood of O1 along a). The increase of R values (Table 1) from
the natural sample to dehyd3, B_{eq} of O1 and O5 increased by factors of 3.1 and 3.3, respectively, indicating that rigid rotational disorder of TO\textsubscript{4} units is largely responsible for T-O shortening. There is a general and continuous increase of B_{eq} for framework atoms with dehydration reflecting this increasing disorder. A similar but less pronounced increase of B_{eq} was observed for partially dehydrated (dehyd3) Succor clinoptilolite-heulandite (Armbruster and Gunter, 1991).

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, Ca\textsubscript{2},Mg\textsubscript{0.5}Na\textsubscript{1.5}K\textsubscript{0.3}Al\textsubscript{1.6}Si\textsubscript{28.5}O\textsubscript{72}·nH\textsubscript{2}O (Armbruster and Gunter, 1991), leading to sample dehyd3 were almost identical to those yielding dehyd1 in this study (373 K, dry N\textsubscript{2}). However, in the Succor sample (dehyd3) 14 H\textsubscript{2}O pfu were found, whereas only 7 H\textsubscript{2}O 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 Ba\textsubscript{0.9}Sr\textsubscript{0.1}Ca\textsubscript{2.2}Na\textsubscript{4}Al\textsubscript{1.1}Si\textsubscript{28.5}O\textsubscript{72}·nH\textsubscript{2}O from Coonabarabran in its natural state and after treatment in vacuum at 343 K. After these moderate dehydration conditions, the H\textsubscript{2}O 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 H\textsubscript{2}O coordination number, which is available at Na1. Only depletion of H\textsubscript{2}O 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 Takeuchi (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 Takeuchi, 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 clinoptilolite, cations on Ca2 may easily diffuse to other channel positions, such as K3, as observed in the present investigation. Koyama and Takeuchi (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. 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 Ca$_2$ population.

REFERENCES CITED


