

Thermal stability of the stilbite-type framework: crystal structure of the dehydrated sodium/ammonium exchange form

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Abstract

The crystal structure of dehydrated Na/NH₄ exchanged stilbite, (NH₄)_{6.76}Na_{2.45}K_{0.15}Ca_{0.06}Al_{9.48}Si_{26.52}O₇₂ · xH₂O; $a = 13.57$, $b = 18.26$, $c = 11.32\text{Å}$, $\beta = 126.96^\circ$ has been refined in space group *C2/m*. The framework characteristics are consistent with those of the hydrated natural form and the dehydrated hydrogen form. Only slight displacements of the fundamental structural units exist, but 10% breaking of one of the T-O bonds of the T-O-T bridges between them occurs. The cations are located at the six-ring site and the flat eight-ring site, and residual water molecules at the boat-shaped eight-ring. The framework distortions are cation-induced and readily affect the cuboid polyhedron of the framework which is formed by joining adjacent structural units.

Introduction

Stilbite-type minerals are zeolites with a two-dimensional interconnected channel system. Ten-membered rings of (Si, Al) O₄ tetrahedra (free diameter 4.1 × 6.2Å, Meier and Olson, 1978) limit the pore size of the largest channels. These intersect with smaller channels with eight-ring apertures (free diameter 2.7 × 5.7Å, Meier and Olson, 1978). The inner surface should therefore be readily accessible to small molecules and these minerals could have a potential use as molecular sieves or catalysts. This would require an "activation" at elevated temperatures to remove the adsorbed water molecules. Unfortunately, in the presence of exchangeable cations, stilbite contracts on heating and the framework is destroyed (Passaglia, 1980). Contraction and destruction are related to the attractive force of the extra-framework cations. When a crystal of an isostructural phase, Nabarrerite is heated to 250°C (Alberti and Vezzolini, 1978), the framework is very much distorted and T-O-T bonds are broken. A similar behavior, but with a much smaller fraction of broken T-O-T bonds, occurs in dehydrated stellerite, the Ca variety of stilbite (Alberti *et al.*, 1978).

Jacobs *et al.*, (1979) characterized the hydrogen form as the most stable. This was confirmed by a structural study of the mineral after ammonium exchange and dehydration (Pearce *et al.*, 1980). Only very minor differences were found between the framework parameters of the hydrated form (Slaughter, 1970; Galli, 1971) and those of the dehydrated hydrogen form. By a reduction of the cation-framework interactions, which become progressively pronounced as the water ligands are removed, a collapse of the framework can be prevented. Not only

protons, but also cations such as K⁺ and Rb⁺ with a sufficiently low ionic potential (Passaglia, 1980) may "stabilize" the stilbite-type framework. The K and Rb forms do not undergo appreciable contraction and their destruction occurs only at fusion, *i.e.*, at about 1000°C.

As the dehydrated Ca-form exhibits a smaller fraction of broken T-O-T bonds (Alberti *et al.*, 1978) than the dehydrated Na-form (Alberti *et al.*, 1978), the number of cations might be an important parameter. A further reduction of the number of cations is attempted here in the study of a dehydrated Na-H-stilbite form. It will be shown that the framework-contraction and the framework-destruction steps can be separated.

Methods and results

Crystals of natural stilbite (STI) from the Faroe Islands (Denmark; Virginia Polytechnic Institute and State University Sample number B179) were exchanged in a 1N 1:1 NaCl:NH₄ Cl solution for five months. The exchange solution was renewed three times during this period. Electron microprobe analyses were made on crystals of the same batch. (The analysis was made at the Department of Geophysical Sciences, The University of Chicago under the following conditions: solid-state detector, Reed-Ware data reduction, beam current:100 nA, no corrections for water or Na loss, total wt.% between 80.2 and 82.3). Calibration factors for the different elements were determined using An₇₀ glass for Ca, Si, Na and Al, and asbestos microcline for K. Taken strictly at face value, when calculated to 72 oxygens with sufficient NH₄ added to balance the charges, the unit cell of Na-NH₄STI contains before dehydration:

Table 1. Positional parameters, population factors and anisotropic thermal parameters for d-Na-H-STI

Atom	Equi-point	Popula-tion	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	8j	7.13(3)	0.99309(10)	0.19272(7)	0.25505(12)	327(11)	140(4)	454(15)	10(5)	272(10)	12(6)
T(2)	8j	7.19(3)	0.26117(10)	0.30682(7)	0.25557(11)	235(10)	139(4)	430(15)	1(5)	177(10)	-11(6)
T(3)	8j	8	0.20000(10)	0.08843(6)	0.49954(12)	465(10)	98(3)	769(15)	-17(5)	389(10)	-2(6)
T(4)	8j	8	0.11365(9)	0.31659(6)	0.50045(11)	334(9)	118(3)	609(13)	-12(5)	307(9)	-5(6)
T(5)	4g	4	0	0.25007(9)	0	348(13)	190(5)	497(182)	0	248(13)	0
O(1)	8j	8	0.9804(3)	0.1987(2)	0.1018(3)	100(3)	27(1)	100(4)	-18(2)	80(3)	-14(2)
O(2)	8j	8	0.1203(2)	0.3021(2)	0.1050(3)	42(2)	26(1)	95(4)	-4(1)	18(3)	12(2)
O(3)	8j	8	0.0617(3)	0.2668(2)	0.3557(3)	111(4)	27(1)	108(5)	-13(2)	73(4)	-21(2)
O(4)	8j	8	0.0693(3)	0.1189(2)	0.3500(3)	83(3)	25(1)	100(4)	12(2)	49(3)	15(2)
O(5)	8j	8	0.2927(3)	0.2525(2)	0.3535(3)	80(3)	26(1)	106(5)	8(2)	36(3)	21(2)
O(6)	8j	8	0.2812(3)	0.3790(2)	0.3521(3)	88(3)	26(1)	100(4)	-3(2)	54(3)	-17(2)
O(7)	8j	8	0.3513(3)	0.3123(2)	0.2054(3)	73(3)	51(2)	140(5)	-12(2)	70(4)	-23(2)
O(8)	8j	8	0.3182(3)	0.1103(2)	0.4996(3)	68(3)	19(1)	143(5)	-6(1)	71(3)	-2(2)
O(9)	4i	4	0.1871(4)	0	0.5028(5)	83(5)	15(1)	144(7)	0	76(5)	0
O(10)	4h	4	0	0.3460(2)	1/2	57(4)	25(1)	132(7)	0	65(4)	0
Na(1)	8j	1.45(4)	0.2323(12)	0.2780(7)	-0.0339(14)	6.1(4)****					
Na(2)	2d	1.74(4)	0	1/2	1/2	518(28)	65(5)	705(38)	0	367(27)	0
Na(3)	4i	2.78(4)	0.3860(7)	1/2	0.2702(8)	239(11)	65(3)	395(17)	0	198(11)	0
T(1)'	8j	0.62(3)	0.0960(12)	0.2039(8)	0.2918(14)	2.0(4)****					
T(2)'	8j	0.53(3)	0.1936(13)	0.2955(8)	0.2954(15)	1.2(4)****					

** estimated standard errors in parentheses refer to the last digit;
 *** anisotropic thermal parameters of T(1) to T(5) $\times 10^3$, others $\times 10^4$;
 **** thermal parameters of Na(1), T(1)' and T(2)'; isotropic: $B/\text{\AA}^2$.



This compares with the original sample composition (Pearce *et al.*, 1980) of



A single crystal of $\text{NaNH}_4\text{STI } 0.15 \times 0.3 \times 0.3 \text{ mm}^3$ in size was selected and mounted in a glass capillary. After evacuation of the capillary at room temperature ($P = 0.013 \times 10^{-6}$ bar), the temperature was raised to 383 K over a 3 hour period and maintained for 18 hours, subsequently raised to 603 K over a 2 1/2 hour period and after another 2 1/2 hour period at 603 K, sealed off and cooled to room temperature for data collection.

As derived from Weissenberg photographs, the systematic absences were consistent with the space group $C2/m$. Using graphite-monochromatized $\text{MoK}\alpha$ radiation, 5158 reflections were measured on a Syntex P2₁ single crystal diffractometer in the omega scan mode up to $\sin\theta/\lambda = 0.65$, yielding 2521 independent reflections of which 1793 were larger than $3\sigma_I$ after averaging and were considered as observed. The unit cell parameters were obtained by least-squares refinement of 25 intense reflections having $2\theta = 21^\circ - 33^\circ$, yielding $a = 13.571(4)$, $b = 18.264(2)$, $c = 11.323(4)\text{\AA}$ and $\beta = 126.96(2)^\circ$. Data reduction was performed using the X-ray 76 system (Stewart *et al.*, 1976). The intensities were corrected for Lorentz-polarization effects, but no absorption corrections were applied ($\mu_{\text{MoK}\alpha} = 5.9 \text{ cm}^{-1}$). With the starting parameters from d-H-STI (Pearce *et al.*, 1980), the structure was refined using the program NUCLS, a modified version of ORFLS (Busing *et al.*, 1962) to final agreement factors for the observed reflections of $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.055$ and $wR = [\sum (w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.043$. Electron density due to non-framework electrons was located by difference Fourier methods and assigned to Na^+ . The electron

density at each of the T(1) and T(2) sites was split into separate peaks, T(1) and T(1)', and T(2) and T(2)' respectively, and their population factors were allowed to vary independently. The T(1) + T(1)' and T(2) + T(2)' populations sum to 7.75 and 7.72 respectively, instead of 8. This deficiency is significant and might be an indication of partial dealumination, as it frequently occurs during heat treatment of NH_4 -exchanged zeolites (McDaniel and Maher, 1976). The residual electron density at the completion of the refinement did not exceed $1e/\text{\AA}^3$ with the exception of peaks near the centers of Na(2) and $2e/\text{\AA}^3$ and Na(1) ($1.6e/\text{\AA}^3$). A previous anisotropic refinement of Na(1), with its position fixed at the center of the six-ring, had not converged and yielded very elongated thermal ellipsoids. While a position displaced from the center converged if refined isotropically, the residual electron density at the center of the peak might also be an indication of a mixed occupancy. This latter could also be true for the eight-ring site Na(2). Residual water molecules, K^{3+} or Ca^{2+} ions or even Al^{3+} extracted from the framework could also be located at these sites (see discussion). Although the T(1) and T(2) sites are split, no indication was found for split oxygen sites (see also discussion).

Atomic scattering factors (*International Tables for X-ray Crystallography*, vol. III, 1968) for Na^+ , O^{1-} , Al^{2+} and Si^{3+} were used. Anomalous scattering corrections were applied to all atoms (Cromer and Liberman, 1970).

The positional parameters, population factors and the anisotropic thermal parameters are given in Table 1 and the interatomic distances and bond angles in Table 2.¹

¹ To receive a copy of the observed and calculated structure factors, order Document AM-83-218 from the Business Office Mineralogical Society of America, 8000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 for the microfiche.

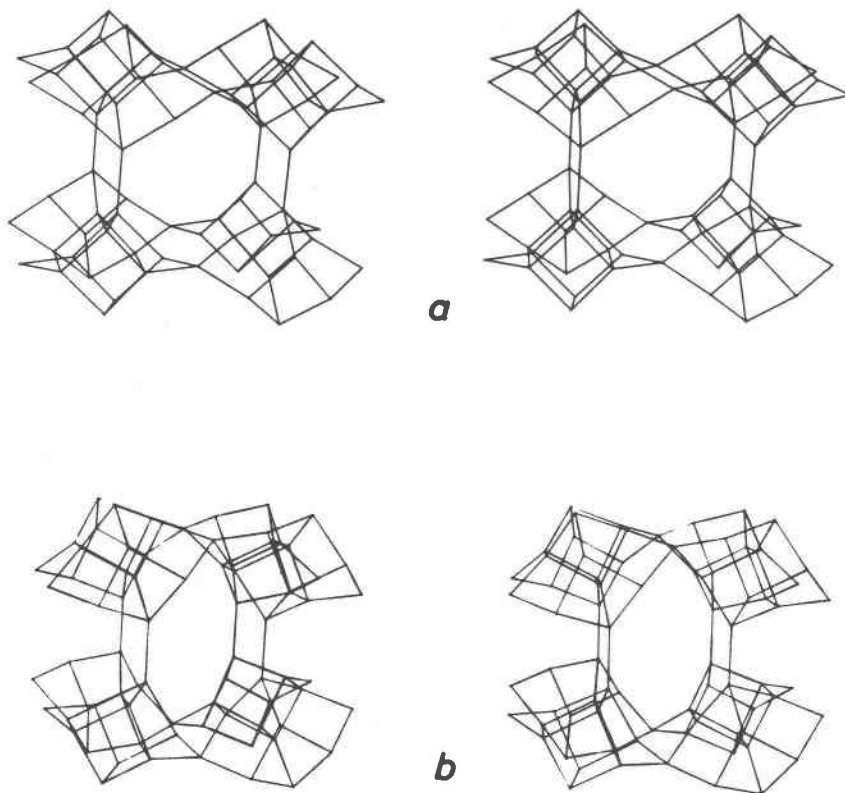


Fig. 1. Stereo drawings of the skeletal models showing the 4-connected nets formed by the tetrahedral atoms for (a) d-Na-H-STI and (b) d-Na-STI.

Discussion

The framework

As clearly shown by Passaglia (1980), contraction and destruction of the stilbite-type framework are related to the interaction with the exchangeable cations. The framework is indeed stable as the hydrogen form (Pearce *et al.*, 1980) or in the presence of cations with a sufficiently low ionic potential such as K^+ or Rb^+ (Passaglia, 1980). The structural parameters of d-H-STI (Pearce *et al.*, 1980) indicated that the framework was very similar to the hydrated natural form, and no destruction of the framework could be detected. For the collapsed phases (Barerite-B, *i.e.*, d-Na-STI, Alberti and Vezzalini, 1978; and stellerite-B, *i.e.*, d-Ca-STI, Alberti *et al.*, 1978) contraction of the framework was accompanied by breaking of T-O-T bonds. This suggests that introduction of considerable stress into the framework causes damage.

An instructive way of illustrating the framework, is with skeletal models which show only the tetrahedral atoms (T = Si, Al). A comparison of d-Na-H-STI (present work) with d-Na-STI (Alberti and Vezzalini, 1978) can be seen in Figures 1a and 1b. A visual inspection of d-Na-H-STI, and d-H-STI (figure not shown) indicates that these structures are very similar

and that they are characterized by the complete absence of any framework contraction caused by a rotation of the 4-4-1 secondary building units (Meier and Olson, 1978) as is evident for d-Na-STI in Figure 1b.

Polyhedral building units (PU, not secondary building unit since this requires the framework to be entirely made up of one type only) can be defined as in Figure 2. These PU's consist of two four-rings joined at two opposite corners (T(3) and T(4)) through two O-T(5)-O bridges. Each of these T(5) atoms is then shared by two neighbouring PU's to form "chains" (see Fig. 1 showing skeletal models consisting of 8 PU's each). These "chains" are joined laterally by oxygen bridges at three of the four T-atoms in the four-rings of the PU's to form a "dense silicate layer". These layers are further stacked in a parallel way and linked at the fourth T-atom of the PU four-rings.

It is most convenient to quantify the distortion of the framework using vectors describing the relative orientations and cross distances of the polyhedral units. Three vectors across the PU's will be considered (see Fig. 2): V_1 , a vector in the direction of the chains; V_2 , between two corners of opposite four-rings more or less perpendicular to the dense silicate layer, *i.e.*, between the top and bottom nodes by which the layers are connected; and

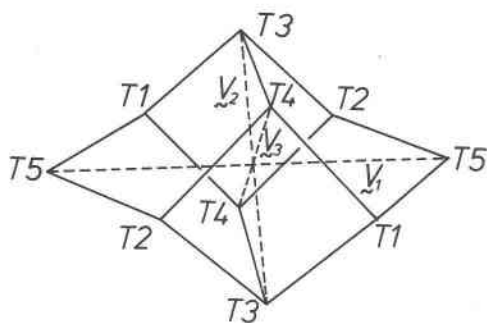


Fig. 2. Schematic drawing of the polyhedral unit indicating the vectors V_1 , V_2 and V_3 .

V_3 , between the two other corners of the four-rings, but in the dense silicate layer. The following angles between these vectors can then be taken into account:

(1) the angle between V_2 , and V_3 in the PU must express the deformation of the PU; (2) the angle between two adjacent V_1 vectors quantifies the zig-zag formation of the "chains", and (3) the angles between two V_2 and (4) two V_3 vectors are related to the relative tilt of the PU's across and in the dense silicate layer respectively. The lengths of these vectors and the angles between them are given in Table 3.

The order in which the zig-zag in the chains varies, as expressed by the angles between the V_1 vectors of two adjacent PU's is: d-Na-H-STI, d-H-STI, d-Ca-STI and d-Na-STI. It is remarkable that the behavior of the partially exchanged sample (d-Na-H-STI), is different from that of the fully Ca and Na exchanged samples, in that the zig-zag in the chains decreases for d-Na-H-STI, but increases for d-Na-STI and d-Ca-STI with respect to d-H-STI. This could be an indication of the existence of several cation-framework interaction centers, all affecting the framework in a distinct way.

In the present structure, three different extra-framework sites were found. Only one of these has sufficiently short coordination distances to the framework oxygens, *i.e.*, site (1) with Na(1)-O(7) distances of 2.24 and 2.27 Å. The closest approach from the center of the flat eight-ring to the framework oxygens (2 oxygens O(10) is 2.81 Å, *i.e.*, about 0.46 Å in excess of the sum of the effective ionic radii of Na^+ and O^{2-} (Shannon and Prewitt, 1969). The Na(3)-O(4) distances of 3.00 Å and Na(3)-O(6) distances of 3.05 Å make it very unlikely that Na-ions are located at this site at all.

The interaction of these sites with the framework will be different for each site as can be derived from the positioning of the cations in the framework, shown in Figure 3. The electrostatic interaction of exchangeable cations in site 3 with the framework oxygens may be responsible for the zig-zag of the "chains" found in d-Na-STI (Alberti and Vezzalini, 1978) and in d-Ca-STI (Alberti *et al.*, 1978). This interaction occurs together with a shortening of the cation coordination distances

from $2 \times 3.00 \text{ \AA}$, $2 \times 3.05 \text{ \AA}$ and $2 \times 3.27 \text{ \AA}$ to $4 \times 2.43 \text{ \AA}$ and $2 \times 2.63 \text{ \AA}$ for d-Na-STI and to $4 \times 2.58 \text{ \AA}$ and $2 \times 2.61 \text{ \AA}$ for d-Ca-STI respectively. In this way, favorable coordination distances for cations at site 3 can be obtained. Site 3 is the highest occupied site both for d-Na-STI and for d-Ca-STI. Because of the absence of any zig-zag in the chains and because of the excessively long coordination distances at site 3, it is most probable that this site in d-Na-H-STI is occupied only by residual water molecules.

Consideration of similar electrostatic interactions suggests that the site 2 cations may be responsible for a rotation of the PU's. A shortening of the O(10)-O(10) distances should cause a decrease of the angle between the V_2 vectors and of that between two V_3 vectors. Site 2 is unoccupied for d-Na-STI and only 10% occupied in d-Ca-STI. A direct comparison of the angles between two vectors V_2 and two vectors V_3 for the collapsed d-Na-STI and d-Ca-STI frameworks with the open d-H-STI and d-Na-H-STI samples is however not possible because of the large difference in zig-zag of the chains which also affects these angles. Despite the 5° decrease in zig-zag from d-H-STI to d-Na-H-STI, and the concomitant increase in the angle between the two V_2 vectors, the slightly smaller angle between the two V_3 vectors could support a partial occupancy of site 2 by cations.

The second most important site in d-Ca-STI is the six-ring site (site 1). This site is unoccupied in d-Na-STI and d-H-STI. Because of the short site 1-framework distances, there is also no doubt that, for the present structure, this site is occupied by small cationic species such as Na^+ , Ca^{2+} or Al^{3+} extracted from the framework. The dimensions of the six-ring are already small, and it may be anticipated that the cations at this site do not significantly contribute to the framework distortions. It is therefore obvious that the cations at site 3 are principally responsible for the contraction of the framework in d-Ca-STI and d-Na-STI.

Table 3. Stilbite-framework analysis

	d-Na-H-STI**	d-H-STI***	d-Ca-STI†	d-Na-STI††
1. Length of the vectors (Å)				
V_1 [T(5)-T(5)]	9.045	9.013	8.701	8.402
V_2 [T(3)-T(3)]	6.049	6.017	5.979	5.861
V_3 [T(4)-T(4)]	4.428	4.467	4.506	4.680
2. Angles in the PU (°)				
(1) V_2/V_3	69.6	71.10	71.2	74.0
3. Angles between two adjacent PU's (°)				
(2) V_1/V_1	180.0	174.9	146.9	145.1
(3) V_2/V_2	154.2	151.8	134.9	138.5
(4) V_3/V_3	113.4	114.4	114.8	124.7

** present structure; *** Pearce *et al.*, 1980; † Stellerite-B, Alberti *et al.*, 1978; †† Barrerite-B, Alberti and Vezzalini, 1978.

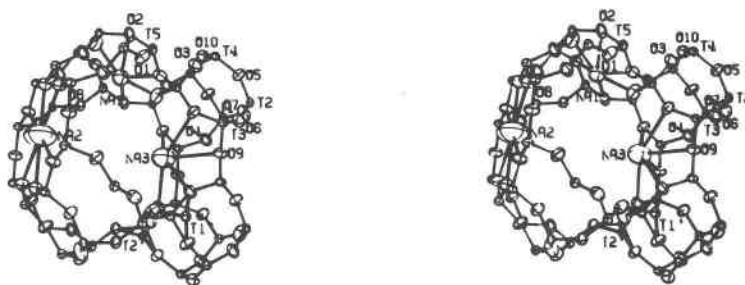


Fig. 3. Stereo drawing of the d-Na-H-STI framework and cation positions. Thermal ellipsoids shown at 50% probability.

The differences in length of the vectors V_1 , V_2 and V_3 between the d-H-STI and d-Na-H-STI structures are less than 0.04\AA . The values for these two structures are very different from those of d-Na-STI and d-Ca-STI. The dimensions of V_1 and V_2 decrease, and those of V_3 increase in the order d-Na-H-STI, d-H-STI, d-Ca-STI and d-Na-STI. This is the sequence in which the zig-zag of the chains increases. This may also be related to the broken bonds in the framework. Concomitant with the contraction of the framework, oxygen bridges between T-atoms of the four-rings of the PU's were broken to an extent of 10% for stellerite-B (Alberti *et al.*, 1978) and to about 50% for barrerite-B (Alberti and Vezzalini, 1978). The destruction mechanism is obviously different in the case of the present structure. Instead of a contraction of the framework with respect to d-H-STI and natural stilbite, the reverse is observed. From the splitting of the T(1) and T(2) tetrahedral sites, and their population factors, it can be estimated that about 10% of the T-O(7) bonds linking two adjacent PU's are broken. However, no electron density deficiency at the O(7) oxygens could be detected. If the positions of the framework oxygens are not affected, this would suggest that at these sites, an inverted tetrahedron is formed (see Fig. 3), but with one oxygen missing. The O-T-O angles at the T(1)' and T(2)' tetrahedra are: O(3)-T(1)'-O(3): 108° ; O(3)-T(1)'-O(4): 106° ; O(1)-T(1)'-O(4): 100° ; O(2)-T(2)'-O(5): 106° ; O(5)-T(2)'-O(6): 104° and O(2)-T(2)'-O(6): 98° . The breaking of a T-O bond is most likely to occur when T is Al. The weakening of the Al-O bond will certainly be enhanced by protonation of the Al-O-Si bond during decomposition of NH_4^+ to H^+ and NH_3 in the dehydration step. Since T(1) and T(2) will not be simultaneously occupied by Al, only one side of the T-O-T bridge should be broken. Al^{3+} may then behave merely as an exchangeable cation and can be located at an exchange site (the population deficiency of T(1) + T(1)' and T(2) + T(2)' is an indication of this), or at a three-coordinated site formed by three of the four oxygens of the original tetrahedron. It should be emphasized here, that in this case, neither the $\equiv\text{Si-O(7)-H}$ bond nor the $(\equiv\text{Si-O})_3\text{Al}^{3+}$ group carries any residual charge. An inversion-type mechanism for the topotactic transformation of the zeo-

lite EAB to a sodalite type structure was proposed by Meier and Groner (1981). The defects at the T(1)' and T(2)' positions could be an indication of a similar process.

The mechanism of breaking the link between two adjacent "chains" of PU's and the decrease of the zig-zag in the chains, is clearly different from the observations for d-Na-STI (Alberti and Vezzalini, 1978) and d-Ca-STI (Alberti *et al.*, 1978). In all cases however, the cuboid polyhedron in the framework formed by two four-rings of two adjacent PU's which are joined at three of the four corners by oxygen bridges, constitutes the weakest link, and is invariably affected. Broken bonds were not observed for the heulandite-type framework after collapse (Alberti, 1973) although it contains the same PU's. Chains formed by identical PU's are also joined laterally, but through a sequence of one four-ring and two five-rings, instead of through a sequence of two four-rings and one six-ring. Apparently, this arrangement has considerably more flexibility.

The channel apertures have changed only slightly as compared to d-H-STI. The dimensions of the eight-ring at site 2 are 8.52\AA [O(9)-O(9)] and 5.62\AA [O(10)-O(10)] vs. 8.66\AA and 5.49\AA for d-Na-H-STI and d-H-STI respectively. The O(9)-O(9) distance across the boat-shaped eight-ring at site 3 is 5.03\AA vs. 4.93\AA for d-H-STI, and the O(9)-O(9) distances across the ten-membered ring 9.16\AA and 9.27\AA vs. 9.07\AA and 9.32\AA .

Cations

The localization of the cations has already been partly discussed in association with the distortion of the framework. It is highly improbable that cations were located at site 3. Residual water molecules will certainly be present in the structure, considering the relatively low dehydration temperature of 603 K. About 2.8 H_2O molecules (or OH^-) can therefore be located at site 3. A total residual electron density ($\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}$ as shown by the chemical analysis and Al^{3+} from the deficient T(1) + T(1)' and T(2) + T(2)' sites) of 3.36 Na^+ equivalents should be located at the other two exchange sites. At sites 1 + 2, 3.2 Na^+ equivalents were located, certainly within the limit of the chemical analysis. Both sites probably have a mixed occupancy.

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