

Fig. 4. Packing diagram for molecule II illustrating the NH...O hydrogen bond.

the large values for the external C—C—C angles at the three-connected C atoms, *i.e.* C(12), C(15) and C(16): 126.0, 127.0 and 126.4°, respectively. In (II) the angular tertiary H atoms on C(14) and C(15) are *cis* to each other and consequently there is a *cis* junction between rings B and C which gives the molecule a folded rather than an extended conformation. As a consequence, the H atoms on C(1) and C(11) do not interfere with each other and the values for the external angles at C(15) and C(16) (113.7 and 121.5°, respectively) are smaller than the related angles in (I). For molecule I the average C—H distance is 1.05 Å. In (II) the N—H distance is 0.84 Å and the average C—H

distance is 0.95 Å. Angles involving the H atoms fall within normal ranges for both molecules.

The change in the environment at the N atom, from a CH₃ group in (I) to a H atom in (II), has an effect on the molecular packing. The methyl substituent in (I) precludes the possibility of any hydrogen bonding, and the molecules are held together in the unit cell solely by van der Waals forces, with the closest intermolecular approaches being C(8)...C(16) at 3.47 Å and C(11)...C(18) at 3.48 Å. In (II) the molecules are held together in pairs across a center of symmetry by a hydrogen bond extending from the imido group to the O of the lactam carbonyl, with an N...O distance of 2.86 Å and an NH...O angle of 168.7° (see Fig. 4). This hydrogen bond allows the molecules to pack more closely in the unit cell and accounts in part for the higher crystal density noted for (II).

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Dehydrated Natural Erionite with Stacking Faults of the Offretite Type

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Abstract. A single crystal of erionite, $\sim\text{Mg}_{0.7}\text{Na}_{0.9}\text{K}_{2.0}\text{Ca}_{2.4}\text{Al}_{9.1}\text{Si}_{26.9}\text{O}_{72} \cdot x\text{H}_2\text{O}$, from Mazé, Japan, was dehydrated in high vacuum at 300°C for 1 d, and the structure refined in $P6_3/mmc$ [$a = 13.252$ (4), $c = 14.810$ (7) Å] to a weighted R of 0.062. About 6% of the single six-membered rings are stacked AAB as in offretite instead of the $AABAAC$ stacking of erionite. In dehydrated erionite the center of the cancrinite cage is occupied by Ca with trigonal-prismatic coordination instead of K as in the hydrated

variety. This internal ion-exchange during dehydration results in K moving to a planar six-coordinated site at the center of an eight-membered ring. The Na, Mg and remaining Ca ions are bonded to three O atoms in the single six-membered rings at the ends of the erionite cages. The unusually long Ca—O distance of 2.73 Å may result from forces resisting further collapse of the cancrinite cage. Si,Al disorder is indicated by the near equality of the mean T —O distances for the two independent tetrahedra. The deviation of an individual

$T-O$ distance from the mean of its host tetrahedron correlates with $\sec(T-O-T)$ in accord with extended Hückel molecular-orbital calculations.

Introduction. Erionite is a fibrous, naturally occurring zeolite of complex chemical composition assigned to group 2 (Breck, 1974). It is relatively siliceous ($Si/Al = 3$) and has a rather high thermal stability. Unlike the relatively rare and topologically related offretite, erionite occurs naturally in huge amounts and may be commercially exploitable (Munson & Sheppard, 1974). Both the erionite and offretite structures can be viewed as consisting of columns of alternating $D6$ (double-six) rings and cancrinite or ϵ cages. In offretite successive ϵ cages have a parallel orientation so that the stacking sequence may be designated $\bar{\epsilon}-D6R-\bar{\epsilon}$ while successive cancrinite cages in erionite have undergone a relative rotation of 180° making the basic unit $\bar{\epsilon}-D6R-\epsilon'-D6R-\bar{\epsilon}$. This doubles the c length from offretite to erionite. Each ϵ cage is then linked to adjacent columns *via* $S6$ (single-six) rings. Particularly clear drawings of both arrangements are given by Gard & Tait (1971). See also Meier & Olson (1971) or Smith (1976) for drawings of the framework topology. Both structures may also be viewed as examples of an infinite family of framework structures based on sequential stackings of parallel $S6$ rings linked by pairs of $S4$ (single-four) rings. The stacking sequences of $S6$ rings in offretite and erionite may then be denoted by AAB and $AABAAC$ respectively (*e.g.* Smith, 1976).

A single near-cylindrical crystal of erionite from Mazé, Japan (0.04×0.55 mm elongated along c) was sealed in a silica capillary under 10^{-5} Torr and cooled to room temperature after being dehydrated for 1 d at $300^\circ C$. Oscillation photographs about c showed only

sharp Bragg diffraction maxima on l -even layer lines, but diffuse diffraction maxima on l -odd layer lines indicated randomly distributed offretite stacking sequences. The crystal was transferred to a Picker FACS-1 automated diffractometer [$\theta-2\theta$ scan at 2° min^{-1} , $\sin \theta/\lambda(\text{max}) = 0.65 \text{ \AA}^{-1}$, Mo $K\alpha$ radiation] and 7064 diffraction intensities were collected and averaged to yield 642 independent intensities with a magnitude greater than 3σ in $P6_3/mmc$. No absorption correction was applied ($\mu = 7.9 \text{ cm}^{-1}$).

Four crystals were mounted in epoxy cement and analyzed with an ARL-EMX electron microprobe using a solid-state detector, the Reed-Ware program, silicate standards, 15 kV, $0.1 \mu\text{A}$ beam current and 0.01 mm spot size. The range of analyses is $\text{Na}_{0.8-0.9}\text{Mg}_{0.5-0.8}\text{K}_{1.9-2.0}\text{Ca}_{2.3-2.6}\text{Al}_{9.5-9.8}\text{Si}_{26.4-26.7}\text{O}_{72}$. Unlike the analysis quoted by Sheppard & Gude (1969, Table 1, No. 2) no Fe was found at the 0.2 wt% detection level. The crystal structure refinement could be explained (see later) by 2 K and 2 Ca atoms, respectively, in the K and Ca sites and mixed (Na, Mg, Ca) in the (Na, Mg) site. We shall assume that the chemical composition of the crystal used for structure refinement is near $(\text{Na}_{0.9}\text{Mg}_{0.7}\text{Ca}_{0.4})\text{K}_{2.0}\text{Ca}_{2.0}\text{Al}_{9.1}\text{Si}_{26.9}\text{O}_{72}$.

Refinement was started from the framework coordinates for hydrated erionite (Gard & Tait, 1973) and cation positions were determined from difference-Fourier maps. Instead of the population factors for the B and C rings being one-half of those for the A rings, they were about 6% smaller. The remaining electron density occurred in B' and C' rings displaced $c/2$ from the B and C rings, which corresponds to stacking errors of AAB (or AAC) in the $AABAAC$ stacking. Refinement used p as the fractional occupancies of the $T(2)$,

Table 1. Atomic coordinates ($\times 10^4$) and populations

The standard error in parentheses is to the same significance level as the last digit. Values without errors are symmetry fixed.

	Type	Population	x	y	z
Si, Al(1)	24(<i>l</i>)	24	0 (1)	2304 (2)	1071 (1)
Si, Al(2)	12(<i>j</i>)	11.3 (1)	938 (2)	4256 (2)	2500
O(1)	24(<i>l</i>)	22.6	338 (5)	3501 (4)	1593 (3)
O(2)	12(<i>k</i>)	12	930 (3)	2x	1346 (5)
O(3)	12(<i>k</i>)	12	1258 (4)	2x	6410 (5)
O(4)	12(<i>i</i>)	12	2523 (5)	0	0
O(5)	6(<i>h</i>)	5.7	2363 (5)	2x	2500
O(6)	6(<i>h</i>)	5.7	4552 (6)	2x	2500
Ca	2(<i>b</i>)	2	0	0	2500
K	6(<i>g</i>)	1.60 (7)	5000	0	0
Na, Mg(1)	2(<i>c</i>)	1.9	3333	6666	2500
<i>B'C'</i> ring					
Si, Al(3)	12(<i>j</i>)	0.7	938	4256	7500
O(7)	24(<i>l</i>)	1.4	338	3501	6593
O(8)	6(<i>h</i>)	0.3	2363	2x	7500
O(9)	6(<i>h</i>)	0.3	4552	2x	7500
Na, Mg(2)	2(<i>d</i>)	0.1	3333	6666	7500

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$)

Tetrahedra			
$T(1)-O(1)$	1.613 (5)	$2T(2)-O(1)$	1.626 (5)
$-O(2)$	1.660 (4)	$-O(5)$	1.667 (5)
$-O(3)$	1.626 (4)	$-O(6)$	1.607 (3)
$-O(4)$	1.613 (2)		
Mean	1.628	Mean	1.632
$O(1)-T(1)-O(2)$	109.9 (3)	$O(1)-T(2)-O(1)$	111.5 (4)
$-O(3)$	110.7 (4)	$2 \times -O(5)$	110.1 (3)
$-O(4)$	108.6 (3)	$2 \times -O(6)$	111.0 (3)
$O(2)-T(1)-O(3)$	104.4 (4)	$O(5)-T(2)-O(6)$	102.8 (6)
$-O(4)$	111.8 (3)		
$O(3)-T(1)-O(4)$	111.4 (3)		
Oxygen bond angles			
$T(1)-O(1)-T(2)$	144.2 (3)	$T(1)-O(4)-T(1)$	159.3 (5)
$T(1)-O(2)-T(1)$	133.8 (5)	$T(2)-O(5)-T(2)$	142.2 (7)
$T(1)-O(3)-T(1)$	139.9 (5)	$T(2)-O(6)-T(2)$	176 (1)
Cations			
$6 \times \text{Ca}-O(2)$	2.735 (8)	$4 \times \text{K}-O(1)$	3.256 (5)
$3 \times \text{Na, Mg}-O(5)$	2.23 (1)	$2 \times \text{K}-O(4)$	3.282 (7)
$3 \times \text{Na, Mg}-O(6)$	2.80 (1)		

O(1), O(5) and O(6) sites and $1 - p$ for $T(3)$, O(7), O(8) and O(9), where p refined to 0.94. Similarly, the occupancies of Na, Mg(1) and Na, Mg(2) were fixed at p and $1 - p$. In theory, the x , y and z coordinates of the faulted positions could have been refined independently, but in practice the electron density peaks were too weak, and the coordinates in Table 1 are related to those for the unfaulted positions by adding 0.5 to z .

Refinement was carried out with the Ibers *NUCLS* program using half-ionized scattering factors and anomalous-scattering corrections (Ibers & Hamilton, 1974). It was assumed that the K and Ca sites were occupied only by K and Ca atoms respectively. The (Na,Mg) site was approximated by full occupancy of Mg whose scattering factor is close to that expected for partial occupancy by Na, Mg and Ca. Procedures for data reduction and the structure refinement were similar to those of mazzite (Rinaldi, Pluth & Smith, 1975) and the final values of R , R_w and S were 0.062, 0.061 and 4.2. Table 1 gives positional and occupancy parameters for both parts of the framework. Table 2 contains selected interatomic distances and angles calculated using *ORFFE* (Busing, Martin & Levy, 1964).*

Discussion. Fig. 1 shows the framework geometry and cation positions for dehydrated erionite. It is unnecessary to mention the stacking faults because the cation positions have the same first-neighbour coordination whatever the stacking sequence. These faults convert a certain fraction of the erionite cages into smaller cancrinite cages while simultaneously creating long open sections which are actually segments of the open channel present in offretite.

The near equality of mean T -O distances in the $T(1)$ and $T(2)$ tetrahedra indicates random Si,Al occupancy, as in hydrated erionite (Gard & Tait, 1973), unless the space-group symmetry is actually lower than $P6_3/mmc$.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32794 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Strictly speaking, the locations of the cations cannot be determined uniquely from the structure refinement because K and Ca have similar scattering factors. However, crystal-chemical considerations lead to a highly probable distribution. There are three cation sites: (a) at the centre of the cancrinite cage inside a trigonal prism of O atoms at 2.73 Å, (b) at the center of one-third of the *S*8 boat-shaped rings which form the walls of the erionite cages, with planar coordination to six framework O atoms, four at 3.26 and two at 3.28 Å, and (c) at the center of the *S*6 rings at the ends of the erionite cage with planar coordination to three framework O atoms at 2.23 Å. The (c) site must be occupied by the small Mg and Na cations with additional Ca cations to bring the occupancy up to 1. In dehydrated offretite, the equivalent site was essentially fully occupied by Mg at 2.08 Å to the three O atoms, and the substitution of larger Na and Ca cations in the erionite site should raise the distance by about 0.2 Å. Because K-O distances are usually ~0.3–0.5 Å longer than Ca-O distances, site (a) was filled with Ca ions even though the cation-oxygen distance of 2.73 Å is ~0.3 Å larger than normally found for Ca. The 2 K ions were then placed in the sixfold site (b), and the large distances of 3.26–3.28 Å might be explained by an average of shorter distances when K is present and longer ones when it is absent. These assignments are the same as those in dehydrated offretite, except for the substitution of Na and Ca in the Mg site. The population refinements suggest that there is no significant substitution of Na in the Ca site.

In both dehydrated erionite and dehydrated offretite the centers of the cancrinite cages are occupied by Ca^{2+} ions, in direct contrast to the hydrated structures where the K ion occupies this position. In hydrated offretite and erionite the K ion cannot be removed from the structure *via* ion exchange in aqueous solution (Gard & Tait, 1971), and the K ion was therefore said to be 'locked' into the cancrinite cage. The present study and that of Mortier, Pluth & Smith (1976) have shown that in both erionite and offretite the Ca drives the K ion from its position in the cancrinite cage during the dehydration process. This phenomenon was termed 'internal ion exchange' and is the basis of US Patent 3 640 680 (Kokotailo & Lawton, 1972).

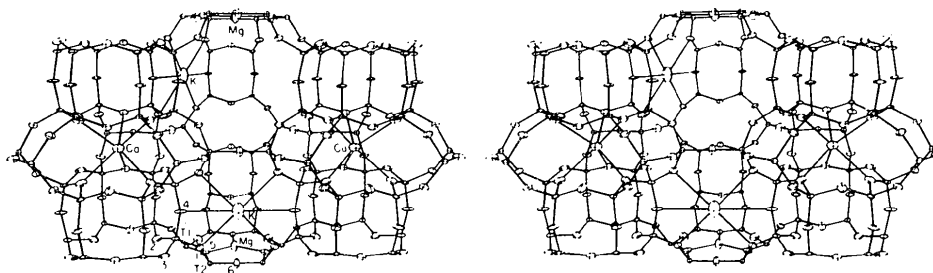


Fig. 1. Stereoplot of the crystal structure of dehydrated erionite viewed perpendicular to c (*ORTEP*, Johnson, 1965). Displacement ellipsoids are at the 30% probability level.

The presence of the highly charged Ca ion inside the cancrinite cage causes considerable contraction in the cage, and this is primarily responsible for the 0.24 Å decrease in the length of the c axis of erionite on dehydration. A similar contraction of 0.24 Å occurred when offretite was dehydrated. In spite of the contraction, the Ca–O distances in both dehydrated offretite and erionite are very large, presumably because any further contraction of the cancrinite cage would result in unfavourable T –O– T angles in the silicate framework. The contraction reduces the cation–oxygen distances in the cancrinite cages from 2.96 and 2.92 Å to 2.62 and 2.73 Å respectively for offretite and erionite during dehydration. There is no obvious explanation why erionite has a smaller contraction than offretite (0.19 vs 0.34 Å in the cation–oxygen distance, and 0.12 vs 0.24 Å in the height of the ϵ cage), but the effect of the stacking sequence on the flexibility of the framework is a possible factor.

The first coordination polyhedra for cations in dehydrated offretite and erionite are the same, and there is no need for detailed discussion here.

As reviewed by Gibbs, Meagher, Smith & Pluth (1977), EHMO theory applied to T_5O_{16} clusters predicts a linear correlation between $-\sec(T-O-T)$ and $\Delta(T-O)$, the deviation of an individual $T-O$ distance from the mean of its host tetrahedron, and an excellent correlation was found for several varieties of mordenite, especially dehydrated H-mordenite. A moderate correlation was also found for dehydrated brewsterite (Schlenker, Pluth & Smith, 1977). In dehydrated erionite (Fig. 2), there is a moderate correlation coefficient of 0.79. Omission of the datum for O(5), which is bonded strongly to the three-coordinated (Na, Mg, Ca) ion, would improve the correlation coefficient to 0.92. The regression equations are:

$$\Delta(T-O) = -0.149 - 0.124 \sec(T-O-T)$$

for all oxygens and

$$\Delta(T-O) = -0.140 - 0.112 \sec(T-O-T)$$

omitting O(5). EHMO theory also predicts that the

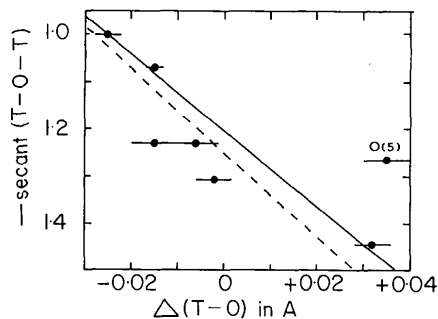


Fig. 2. Relation between $\Delta(T-O)$ and $-\sec(T-O-T)$ for dehydrated erionite: solid line, all data; dashed line, O(5) omitted.

coefficient of the $\sec(T-O-T)$ term should increase as the average electronegativity of the tetrahedral sites increases, and this implies an increase with increasing Si/Al ratio. Although the spread of data for both erionite and brewsterite is large, there is a trend in accordance with EHMO theory (brewsterite, Si/Al 2.9, coefficient 0.057; dehydrated erionite, 3.0, 0.124 or 0.112; dehydrated H-mordenite, 5.2, 0.132). However, until further structure determinations of ion-exchanged forms of brewsterite and erionite, and of other zeolites with different Si/Al ratios have been made, the above observational trend is very highly tentative.

In conclusion, the results of this and the previous study of dehydrated offretite show that internal ion exchange occurs in both erionite and offretite on being dehydrated in high vacuum at elevated temperatures. Various experiments to determine the conditions for internal ion exchange are planned, and these include rehydration at low temperature.

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