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Crystal Structure of Mazzite Dehydrated at 600°C

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A single crystal of the new zeolite, mazzite, $\mathrm{Na}_{\sim 0\cdot 3}\mathrm{K}_{2\cdot 5}\mathrm{Ca}_{1\cdot 4}\mathrm{Mg}_{2\cdot 1}[\mathrm{Al}_{9\cdot 9}\mathrm{Si}_{26\cdot 5}\mathrm{O}_{72}].28\mathrm{H}_2\mathrm{O}$, was dehydrated at 600 ± 20°C and $\sim 10^{-5}$ Torr in a quartz capillary. Anisotropic least-squares refinement yielded $R = 0\cdot 62$ in $P6_3/mmc$. The cell dimensions change, upon dehydration, from $a = 18\cdot 384$ (1), $c = 7\cdot 639$ (1) to $a = 18\cdot 007$ (3), $c = 7\cdot 608$ (2) Å. The aluminosilicate framework consists of gmelinite-type cages staggered at $+\frac{1}{4}$ and $-\frac{1}{4}$ in z. Cross-linking results in 12-rings perpendicular to **c** which are connected uniquely to form isolated channels whose walls consist of alternating ladders of four- and five-rings. Four cation sites and two positions for approximately seven residual water molecules were located. The aluminosilicate framework undergoes only minor distortion upon dehydration, whereas the cations migrate in order to maintain a stable configuration. All the water present in the channels formed by the 12-rings was removed and 1·5K moved to the walls of the channel in square coordination with four framework oxygens. Magnesium is tetrahedrally coordinated to three framework oxygens and one water molecule within the gmelinite-type cages: each six-ring is blocked by 1 Mg. Calcium lies in the channels between adjacent cages and is octahedrally coordinated to four oxygens and two water molecules. These water molecules lie near the centers of boat-shaped eight-rings at the sides of the gmelinite cages. This site is also occupied by the remaining one K and by $\sim 2\mathrm{H}_2\mathrm{O}$ unbonded to Ca. The two cation sites assigned to K and Ca could actually be occupied by either cation or by a mixture of both, but the chemical environment favors the proposed distribution. No evidence of Si,Al ordering was found. The close similarity of the powder patterns of mazzite and synthetic zeolite Ω implies that they are probably isostructural, and that the earlier model for Ω may be incorrect.

Introduction

The new mineral mazzite was discovered in 1972 in a zeolitic assemblage at Mont Semiol, Montbrison, Loire, France. Preliminary X-ray and chemical work (Galli, Passaglia, Pongiluppi & Rinaldi, 1974) showed it to be a zeolite geometrically related to the natural phases offretite, erionite, chabazite, levyne and gmelinite and to the synthetic molecular sieves L and Ω (Barrer & Villiger, 1969*a,b*). The structure of hydrated mazzite was solved independently by Galli (1974) and of the dehydrated form by Rinaldi, Pluth & Smith (1974).

From the X-ray powder patterns, mazzite and synthetic zeolite Ω appear to be isostructural (Galli *et al.*, 1974). The first structure proposed for Ω (Barrer & Villiger, 1969*b*) was determined by powder data, and fits poorly with the measured intensities. Furthermore, the theoretical prediction of the possible structures that would fulfill the requirements of density, cell dimensions and sorption properties was incomplete and overlooked the present structure.

Experimental

A hexagonal needle $0\cdot 43 \times 0\cdot 05$ mm was inserted in a quartz capillary whose walls were approximately 0·02 mm thick. The capillary was evacuated at 10^{-5} Torr, kept at 600°C for 41 h, cooled and then sealed.

Weissenberg photographs, taken before and after dehydration, showed no change of space group. The extinction condition of $hh\overline{2h}l$ with $l = 2n$ indicates that $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$ are possible space groups. The cell dimensions changed from $a = 18\cdot 384$ (1), $c = 7\cdot 639$ (1) to $a = 18\cdot 007$ (3), $c = 7\cdot 608$ (2) Å with a 4·4% volume reduction. They were determined by least-squares refinement of 20 high 2θ values (Burnham, 1962) measured on a Picker FACS-1 diffractometer at room temperature by averaging four half-height-peak settings (plus and minus 2θ).

Electron microprobe analysis and TGA determination of water (Galli *et al.*, 1974) gave $\mathrm{Na}_{0\cdot 03}\mathrm{K}_{1\cdot 9}\mathrm{Ca}_{1\cdot 35}\mathrm{Mg}_{2\cdot 0}[\mathrm{Al}_{9\cdot 8}\mathrm{Si}_{26\cdot 5}\mathrm{O}_{72}].28\mathrm{H}_2\mathrm{O}$. New electron microprobe data showed that the earlier data were somewhat incorrect, probably because Na and K had volatilized. The new analyses were reproducible and did not change after repetition on the same spot. The conditions were 15 kV, beam current 0·05 μA, spot size 20 μm, solid-state detector using a Reed–Ware correction procedure calibrated by I. M. Steele and checked against feldspar standards. The new analyses yielded $\mathrm{Na}_{\sim 0\cdot 3}\mathrm{K}_{2\cdot 5}\mathrm{Ca}_{1\cdot 4}\mathrm{Mg}_{2\cdot 1}[\mathrm{Al}_{9\cdot 9}\mathrm{Si}_{26\cdot 5}\mathrm{O}_{72}]$ with an oxide total of 85·4 wt.%: the deficiency corresponds to residual water. On the basis of population refinement of the two positions occupied by water, the chemical formula for the dehydrated form at 600°C has seven water molecules out of the original 28.

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Intensity data were collected at room temperature on a Picker FACS-1 automated single-crystal diffractometer with θ–2θ scans (1° min^{-1}); 1300 diffractions (four equivalent sets) were measured [$(\sin\theta/\lambda)_{\max}=0{\cdot}497$] using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). After averaging, the resulting 353 independent diffractions with $F\le 2\sigma_F$ were used in the refinement.

The estimated errors in the intensities (σ_I) were calculated using: $\sigma_I=[S+t^2B+k^2(S+tB)^2]^{1/2}$ where $S=$ peak scan counts, $B=$ total background counts, $t=$ ratio of peak to background observation times, $k=$ instability constant (0·01).

Equivalent diffractions were averaged using: $\bar{I}=\sum_i(I_i/\sigma_i^2)/\sum_i(1/\sigma_i^2)$, $\bar{\sigma}_I=[1/\sum_i(1/\sigma_i^2)]^{1/2}$ where I_i and σ_i are the intensity and the standard deviation of the ith equivalent diffraction. The intensity data were corrected for Lorentz and polarization effects and an absorption correction was applied assuming the shape of a hexagonal prism (crystal plus capillary) with dimensions $0{\cdot}05\times0{\cdot}43$ mm and a mass absorption coefficient (μ) of 90·4 cm^{-1} averaged for mazzite and quartz.

The $\bar{\sigma}_I$'s were converted to the estimated errors in the relative structure factors (σ_F) by $\sigma_F=[(F^2+\sigma_{F2})]^{1/2}-F$.

Structure refinement

The hypothetical model for zeolite Ω (Barrer & Villiger, 1969*b*) does not satisfy the *c* glide plane. Assuming that the general structural features of mazzite are similar to those of the hypothetical model for zeolite Ω, a framework model for mazzite was built in which the gmelinite-type cages of the Ω model were staggered at $+\frac{1}{4}$ and $-\frac{1}{4}$ in *c* to satisfy the *c* glide plane. This model has maximum symmetry of $P6_3/mmc$. The structure was refined by Fourier and least-squares techniques. The final cycle of least-squares refinement minimized $\sum w||F_o|-|F_c||^2$ with $w=(1/\sigma_F)^2$ and yielded $R=0{\cdot}062$, $R_w=0{\cdot}026$, $S=1{\cdot}94$ where

$$R=\sum||F_o|-|F_c||/\sum|F_o|,$$
$$R_w=[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2},$$
$$S=[\sum w||F_o|-|F_c||^2/(n_o-n_v)]^{1/2},$$

with $n_o=$ number of diffractions, $n_v=$ number of parameters. The maximum shifts ($\sim0{\cdot}4\sigma$) appeared in the thermal parameters of Ca and *W*(1).

Atomic scattering factors (Mann, 1968) were used for Mg^{2+}, K^+, Ca^{2+} and $[\frac{1}{4}Al^+ + \frac{3}{4}Si^{2+}]$ (for which Al^+ was interpolated between Al and Al^{3+} and Si^{2+} between Si and Si^{4+}). Anomalous scattering corrections (Cromer & Liberman, 1970) were applied to all atoms. The final model was checked by difference-Fourier synthesis. Some residual electron density (maximum height 0·75 e Å^{-3}) appeared near O(1).

The zero-moment test of Howells, Phillips & Rogers (1950) plotted along the centric curve. Effectively the symmetry of the space group assumed in the refinement must be at least locally violated by the incomplete

Table 1. *Positional thermal and population parameters*

		x/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)*	Population
T(1)	12(*j*)	0·1572 (2)	0·4908 (2)	$-\frac{1}{4}$	3·2 (2)	12
T(2)	24(*l*)	0·0934 (2)	0·3565 (2)	0·0472 (3)	3·3 (1)	24
O(1)	6(*h*)	0·2628 (4)	0·5256	$-\frac{1}{4}$	4·4 (6)	6
O(2)	6(*h*)	−0·4225 (5)	−0·8450	$\frac{1}{4}$	7·4 (7)	6
O(3)	12(*j*)	0·0985 (5)	0·3875 (5)	$\frac{1}{4}$	3·7 (4)	12
O(4)	24(*l*)	0·1104 (3)	0·4379 (3)	−0·0730 (6)	5·3 (3)	24
O(5)	12(*k*)	0·1640 (2)	0·3280	0·0054 (8)	5·1 (5)	12
O(6)	12(*i*)	0·0	0·2761 (4)	0·0	5·7 (5)	12
K	12(*j*)	−0·0773 (13)	0·1473 (13)	$\frac{1}{4}$	4 (1)	1·48 (5)
Ca	6(*g*)	0·0	$\frac{1}{2}$	0·0	16 (4)	1·65 (18)
Mg	4(*f*)	$-\frac{1}{3}$	$\frac{1}{3}$	0·1681 (23)	6 (1)	1·90 (6)
W(1)	6(*h*)	0·4426 (12)	0·8852	$\frac{1}{4}$	15 (2)	6·55 (34)
W(2)	4(*f*)	$-\frac{1}{3}$	$\frac{1}{3}$	−0·1453 (31)	7 (2)	2·27 (8)

* *B*'s from last cycle of isotropic refinement.

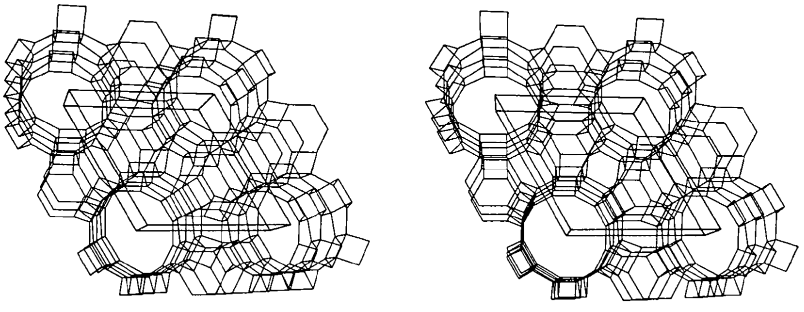

Fig. 1. Framework structure of mazzite looking down **c**. The intersections of lines represent tetrahedral atoms; oxygen atoms lie approximately at the midpoints of the lines (*ORTEP*, Johnson, 1965).

statistical occupancy of the cations and water molecules.

Attempts to refine the structure in a space group of lower symmetry failed because of the large correlation coefficients. Nevertheless it is likely that the Mg atoms consistently occupy one of the two possible positions near the six-rings thereby giving a polar space group $P6_3mc$, at least in domains and perhaps throughout the whole crystal. The final data are given for the non-polar space group $P6_3/mmc$.

The results of the refinement are given in Table 1 (positional and population parameters), Table 2* (structure factors), Table 3 (anisotropic thermal parameters), Table 4* (r.m.s. components and directions of thermal displacements), Tables 5 and 6 (interatomic distances and angles). Interatomic distances and angles were calculated using the computer program *ORFFE* (Busing, Martin & Levy, 1964).

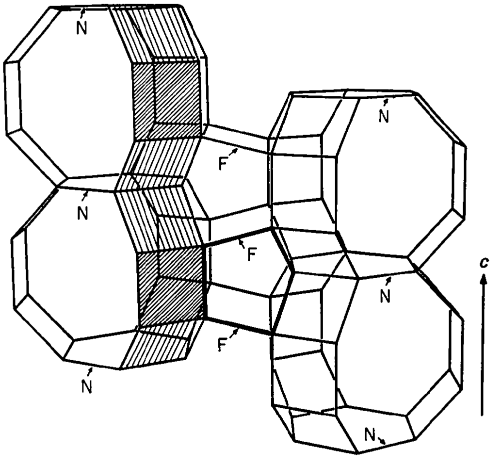

Fig. 2. Framework structure of mazzite and FFN scheme of the chains of tetrahedra. The intersections of lines represent tetrahedral atoms: oxygen atoms lie approximately at the midpoints of the lines.

Table 3. *Anisotropic thermal parameters*

The anisotropic temperature factor is in the form of $\exp\left[-\sum_{j=1}^{3}\sum_{i=1}^{3}\beta_{ij}h_ih_j\right]$. The β values are multiplied by 10^4.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	51 (3)	37 (2)	122 (8)	25 (2)	0	0
T(2)	34 (1)	54 (2)	89 (4)	22 (1)	3 (2)	8 (3)
O(1)	67 (6)	78 (9)	211 (32)	39	0	0
O(2)	58 (6)	200 (16)	356 (42)	100	0	0
O(3)	49 (5)	79 (6)	94 (14)	34 (5)	0	0
O(4)	60 (4)	69 (4)	167 (11)	30 (3)	8 (7)	25 (7)
O(5)	45 (3)	87 (6)	211 (22)	44	−34 (21)	−17
O(6)	39 (4)	77 (10)	238 (27)	39	−12 (8)	−6
Ca	394 (86)	97 (25)	3835 (920)	49	871 (229)	436
Mg	52 (8)	52	354 (62)	26	0	0
K	61 (15)	44 (15)	126 (48)	13 (13)	0	0
W(1)	89 (12)	222 (29)	647 (64)	111	0	0
W(2)	79 (14)	79	526 (132)	40	0	0

Table 5. *Framework* T–O *distances* (Å) *and angles* (°)

T designates tetrahedral sites occupied by Si or Al.

T(1)–O(1)	1·679 (5)	O(1)–T(1)–O(2)	102·3 (7)
T(1)–O(2)	1·582 (4)	2O(1)–T(1)–O(4)	112·2 (3)
2T(1)–O(4)	1·621 (5)	2O(2)–T(1)–O(4)	108·6 (4)
Ave. T–O	1·626	O(4)–T(1)–O(4)	112·4 (4)
T(2)–O(3)	1·628 (3)	O(3)–T(2)–O(4)	105·8 (4)
T(2)–O(4)	1·621 (5)	O(3)–T(2)–O(5)	112·0 (4)
T(2)–O(5)	1·622 (3)	O(3)–T(2)–O(6)	111·8 (3)
T(2)–O(6)	1·618 (3)	O(4)–T(2)–O(5)	110·6 (3)
Ave. T–O	1·622	O(4)–T(2)–O(6)	109·0 (3)
		O(5)–T(2)–O(6)	107·6 (4)

Table 6. *Cation coordination and water oxygen distances* (Å) *and angles* (°)

4Ca—O(4)	2·782 (5)	2O(4)–Ca—O(4)	81·2 (2)
2Ca—*W*(1)	2·612 (25)	2O(4)–Ca—O(4)	98·8 (2)
2Ca—O(2)	3·076 (12)	2O(4)–Ca—O(4)	180
		4O(4)–Ca—*W*(1)	73·8 (4)
		4O(4)–Ca—*W*(1)	106·2 (4)
		W(1)–Ca—*W*(1)	180
3Mg—O(1)	2·286 (12)	3O(1)–Mg—O(1)	112·9 (4)
1Mg—*W*(2)	2·385 (27)	3O(1)–Mg—*W*(2)	105·8 (4)
2K—O(5)	2·603 (16)	O(5)–K—O(5)	96·6 (8)
2K—O(6)	2·776 (14)	2O(5)–K—O(6)	58·1 (3)
		2O(5)–K—O(6)	119·6 (8)
		O(6)–K—O(6)	86·5 (5)
2*W*(1)–O(3)	2·924 (8)	2O(3)–*W*(1)–O(3)	170·0 (15)

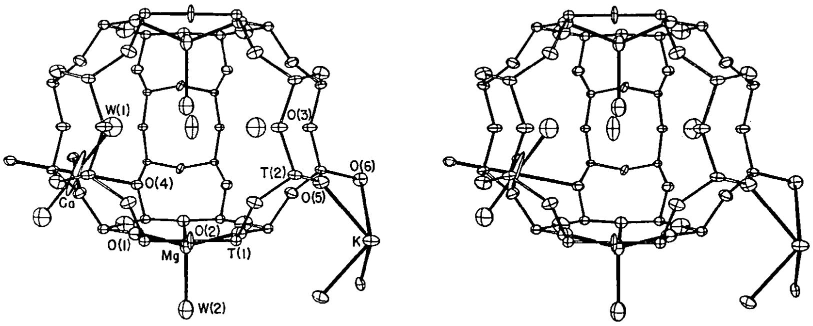

Fig. 3. Distribution of the cations relative to one complete gmelinite-type cage in dehydrated mazzite. The distribution and relative positions of the cations represent a close approximation to the actual statistical configuration; 15% ellipsoids of displacement (*ORTEP*, Johnson, 1965).

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* Tables 2 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30902 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

Framework

The basic building block is the gmelinite unit with two opposing six-rings linked by three triplets of four-rings and three boat-shaped eight-rings. In mazzite, infinite columns are produced by sharing hexagonal faces of gmelinite units (Fig. 1). Each column has three infinite ladders of inclined four-rings. Only in one way do the columns fit into a framework which obeys the space group, $P6_3/mmc$, and the unit-cell shape of mazzite. Alternate columns are staggered $+\frac{1}{4}$ and $-\frac{1}{4}$ along **c**, and the cross linkages are formed by ladders of non-planar five-rings.

The framework has near-cylindrical channels bounded by 12-rings of minimum 'free' diameter of 7·2 Å, O(6) to O(6), assuming the effective radius of oxygen to be 1·35 Å. These channels are walled by the ladders of four-rings and non-planar five-rings which should be impenetrable by molecules under normal conditions.

The remainder of the volume consists of the staggered pores of the gmelinite cages and the narrow rectangular channels bounded by strongly non-planar eight-rings. Access between the gmelinite cages is obtained *via* the boat-shaped eight-rings or the near-circular six-rings, both of which are very much more restrictive than the 12-rings (assuming no blocking by cations: see below). This interconnected system of gmelinite cages and rectangular channels is three-dimensional, in contrast to the one-dimensional system of cylindrical channels.

There is no simple way of introducing stacking faults into the mazzite structure, and no subsidiary diffractions were observed.

Barrer & Villiger (1969*a*) developed a family of hypothetical zeolites based on a ladder of four-rings found in zeolite *L* (this is the same as the ladders in Fig. 1). In this family, all six-rings lie at the same height along *z*, whereas in mazzite the six-rings are staggered to obey the glide plane. In the notation of Barrer and Villiger, mazzite would have an *FFN* chain [*F*=far, *N*=near] and belong to the *not shared*, *not facing* type (Fig. 2). One ladder is emphasized by using heavy stipple for the vertical four-rings and light stipple for the pairs of tilted four-rings. The symbols *N* and *F* refer to the oxygen bridges which link the ladder to neighboring ladders, either *near* to or *far* from the reference axis which passes in mazzite through the gmelinite cages. Barrer & Villiger built structures in which the *F* links were *horizontal* and the ladders were *not* staggered along **c**. In mazzite, the *F* links are tilted thereby producing five-rings (one of which is emphasized in Fig. 2). To complete the description, the ladders of four-rings are *not shared* and do *not face* each other. The notation of Barrer & Villiger is insufficient, and a further element is needed to describe the type of cross linkage.

The mean T–O distances of dehydrated mazzite are consistent with Si, Al disorder (Table 5) but a lower space group could permit ordering. The long distance to O(1) is explained by the bonding of Mg to this oxygen (see below).

Cation location and bonding

When three exchangeable cations are present, some uncertainty in placement is to be expected. The proposed distribution provides the simplest explanation on the assumptions that (*a*) the cations tend strongly to occupy only one site, and (*b*) the coordination depends on ionic size and charge.

Every gmelinite cage (Fig. 3) contains one Mg in tetrahedral coordination with three O(1) from a six-ring at 2·29 Å and a residual *W*(2) at 2·39 Å (or perhaps OH^-: see below). In the hydrated form, Mg occupies the center of every gmelinite cage where it is surrounded by water molecules (Galli, 1974): this hydration complex may form a template which stabilizes the gmelinite unit during crystallization. Upon dehydration, Mg moves to the top or bottom of the cage thereby adopting a position of lower symmetry with an occupancy of one-half. The tetrahedral coordination with three framework oxygens and one residual water molecule provides a much more satisfactory environment for the Mg than a hypothetical coordination to just three framework oxygens pulled in from a six-ring. The bonding of O(1) to Mg distorts the six-ring which leads to perturbations on the remainder of the framework.

Although there are two sites in each cage for the Mg atom, Mg atoms should not bond to the same O(1) atom because of electrostatic repulsion. Mathematically this requires that the Mg atoms occupy either all the upper positions or all the lower positions thereby giving a polar symmetry. Of course, Mg disorder could permit the formation of positive and negative domains. All six-rings are blocked by Mg, thereby stopping diffusion between adjacent gmelinite cages unless Mg atoms migrate.

No sites for water molecules were found in the cylindrical channels, which is not surprising because of the high temperature of dehydration and the weak crystal field in these large channels. A 12-fold site with one-sided coordination to four framework oxygens was assigned to 1·5 K atoms (Fig. 3). The distances of 2·60 and 2·78 Å to two O(5) and two O(6), respectively, are reasonable. Potassium ions in silicates are normally surrounded by six to 12 oxygen ions in an irregular coordination: however, in zeolites dehydrated at high temperatures the usual crystal-chemical rules need not be obeyed. Yanagida, Amaro & Seff (1973) found a similar one-sided coordination for type 3 sodium ions in dehydrated Na_{12}-Type *A* zeolite: here the coordination consisted of two O(3) at 2·47 (7) Å and two O(1) at 2·51 (7) Å. Dehydrated Na–X also has some Na atoms on the walls of the supercage (Hseu, 1972). Because the revised electron microprobe analysis shows 2·5 K atoms per cell of mazzite, one K must lie elsewhere.

The electron density at a sixfold equipoint in the narrow channels between the gmelinite cage was assigned to 1·7 (2) Ca (Fig. 3). This site coordinates to four O(4) at 2·78 Å and two water *W*(1) at 2·61 Å in a near-octahedral coordination. These distances are rather long for a Ca ion (2·4 Å is more usual), but the distances cannot be accurate because of atomic disorder. Both the original and revised analyses showed 1·4 Ca, and the extra electron density may result either from experimental error or occupancy by Na or K atoms.

Each Ca atom could bond to only 2*W*(1), but the observed electron density ($6{\cdot}6H_2O$) is greater than the maximum of $3{\cdot}4H_2O$ for calcium-bonded water. In addition the Mg, K and Ca sites cannot account for all the cations from the electron-probe analysis (*viz* ~0·3Na, 2·5 K, 1·4 Ca and 2·1 Mg). The simplest solution is that some K cations occupy the *W*(1) site, which could provide fairly suitable bond distances to framework oxygens of the eight-ring. We suggest the following assignment of cations and water molecules:

Mg site 2·0 Mg, K site 1·5 K
Ca site 1·4 Ca + 0·3 Na + 0·1 Mg,
W(1) site, 1·0 K + $\sim 4H_2O$.

In this model, the Mg site is completely occupied and one water molecule (or hydroxyl) is bonded to each Mg atom. The Ca site takes all the Ca and Na plus the residual 0·1 Mg. Each of these atoms lies in a near-octahedron and is bonded to $2H_2O$ giving a total of $3{\cdot}6H_2O$ in the *W*(1) site. The residual 1·0 K also occupies the *W*(1) site and its scattering power is approximately equivalent to that from 2 to $3H_2O$. The combined scattering power for *W*(1) would be consistent with the experimental data. Obviously there is considerable tolerance in these values when account is taken of experimental error. The large *B* values for the Ca and *W*(1) sites would be explained largely by occupancy of positions about 0·5 Å apart. For this model, cations must not occupy adjacent Ca and *W*(1) sites since both sites are sixfold and the cation contents are only 1·8 and 1·0, respectively. Since each occupied site should restrict occupancy by cations of two adjacent sites, the combined cation content of 2·8 requires that the cations have short-range order along the zigzag chain of Ca and *W*(1) sites.

All atoms in mazzite show large *B* values (Table 1). This is unusual for framework atoms, and cannot reasonably be ascribed to thermal vibration. Probably the true symmetry of mazzite is lower than $P6_3/mmc$, but satisfactory refinement in a lower space group was not achieved.

In hydrated mazzite (Galli, 1974), the Ca atoms were assigned to hydration complexes in the large cylindrical cavities, and the K atoms to the present Ca site. If this and the present assignment for the dehydrated variety are correct, the Ca and some of the K must diffuse through the walls during dehydration, presumably through the five-rings rather than the four-rings. At high temperatures, this should be relatively easy, but at low temperature diffusion might be rather sluggish. Perhaps a metastable form of hydrated mazzite could be produced in which the dehydrated form is rapidly cooled thereby trapping the Ca in the narrower channels.

The structures of hydrated erionite and offretite have been determined (Gard & Tait, 1972, 1973), but those of the dehydrated forms are still unknown. By analogy with mazzite, predictions can be made.

In offretite, 0·82 of the gmelinite cages are occupied by $Mg(H_2O)_5$, and the 0·82 Mg might lose four H_2O and migrate to a six-ring and assume a tetrahedral coordination as in mazzite. Alternatively, it might occupy the center of a hexagonal prism but this is unlikely because very strong distortion would be needed to attain the short Mg–O distances, and because Ca atoms should tend to occupy this site. The 1·1 Ca and 1·1 K in dehydrated offretite should tend to occupy the hexagonal prism sites and the centers of the cancrinite cages. There is one prism site and one cancrinite center per unit cell, of which the latter is larger. Probably the prism site tends to be occupied by Ca by analogy with dehydrated chabazite (Smith, 1962), while K occupies the center of the cancrinite cage.

In erionite, there were 2·0 K, 1·9 Na, 1·2 Ca and 0·6 Mg per cell. In the dehydrated variety, the Mg probably forms a tetrahedral coordination near a six-ring of a supercage, thereby freeing the cancrinite–hexagonal prism complex for the other cations. There are two cancrinite cages and two hexagonal prisms per cell, and the total of four sites is not sufficient to account for the 2·0 K, 1·9 Na and 1·2 Ca. Perhaps the 1·2 Ca enters the hexagonal prism along with some monovalent ions while the other monovalent ions occupy several different positions. Obviously detailed analyses are needed to check these proposals.

Returning to dehydrated mazzite, the interatomic distances and angles require little comment. It is not possible to decide from the Mg–*W*(2) distance of 2·38 (3) Å whether *W*(2) is occupied by H_2O or OH^-. Polarization of H_2O into OH^- plus H^+ should lead to a framework OH^- by condensation of the proton with an oxide ion. Such a process has been demonstrated in faujasite-type zeolites (Breck, 1974). At first sight the long T(1)–O(1) distance of 1·679 (5) might be ascribed to O(1) being a hydroxyl. However, this long distance is to be expected because of the bonding of Mg only to O(1): the bonding effects of the other cations should be relatively low. Furthermore, it would be unreasonable electrostatically to assign a proton to a framework oxygen bonded to 2 Si and 1 Mg. All the other T–O distances are short, and give no indication of the presence of hydroxyl. Unfortunately, not enough mazzite was available for infrared study.

Conclusion

The present structure indicates the strong tenacity of highly polarizing cations for residual water molecules, as has been noticed for other zeolites. Further progress in understanding cation assignments requires analysis of mono- or dicationic varieties, and appropriate studies are planned. Detailed analysis of Ω is needed to test whether it has the same framework as mazzite.

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Studies in Molecular Structure, Symmetry and Conformation. XI. The Crystal and Molecular Structure of Glycyl-DL-threonine Monohydrate*

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The title compound is orthorhombic, space group $Pca2_1$, with $a=16{\cdot}26$ (1), $b=4{\cdot}87$ (1), $c=23{\cdot}24$ (1) Å, $Z=8$. The structure was solved by direct methods with visual X-ray intensities. The asymmetric unit contains two molecules which are related by an approximate centre of inversion. The dimensions of the peptide group are in agreement with the weighted mean values of Marsh & Donohue [*Advanc. Protein Chem.* (1967). **22**, 235–256]. The peptide chain is in the extended conformation. The conformation of the threonine side group is different from that in free threonine.

Introduction

In earlier parts of this series (parts VIII, IX and X: Swaminathan & Srinivasan, 1975*a*,*b*,*c*) we discussed the structural and conformational aspects of allothreonine and its derivatives. This paper deals with the structure determination of glycyl-DL-threonine monohydrate.

Experimental

Single crystals of glycyl-DL-threonine monohydrate were grown by evaporation of an aqueous solution. Preliminary photographs showed the crystals to be orthorhombic, space group $Pca2_1$ (or $Pcam$). The density was determined by flotation in a mixture of benzene and bromoform.

Crystal data

$C_6H_{12}N_2O_4.H_2O$. Orthorhombic, $a=16{\cdot}26$ (1), $b=4{\cdot}87$ (1), $c=23{\cdot}24$ (1) Å; systematic absences $0kl$, $l=$

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