Epistilbite: an acentric zeolite with domain structure

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Abstract. The refinement of the crystal structure of Theigarhorn epistilbite showed the presence of two tetrahedral configurations, as in Elba dachiardite. These two configurations, obtained by the rotation of two tetrahedra around one edge, have both $C2$ symmetry, with different frequency (82% and 18% respectively), thus the resulting space group is $C2$. The presence of these two acentric domains is interpreted as a tendency to avoid the $T-O-T$ angle of $180°$ present in the topological symmetry $C2/m$ of epistilbite. The amount of Al, obtained from the $T-O$ mean distance, has been corrected by a method which takes into account the influence of $T-O-T$ angles on the measured $T-O$ distance, and resulted in good accordance with Al content from the chemical analysis. A remarkable degree of ordering in the Si/Al distribution has been found. Two extraframework cation and six water molecule sites have been located. Both cation sites have a square antiprism coordination; these polyhedra form clusters of four antiprisms, which are linked together as in a chessboard.

Introduction

Epistilbite is a zeolite whose framework is related to that of mordenite. Kerr (1964) and Merlino (1965) proposed for epistilbite a structural model, which was confirmed by the refinements of Perrotta (1967) and Slaughter and Kane (1969). Both refinements however showed high discrepancy indices ($R = 0.15 - 0.16$), indicating basically correct but imprecise structure determinations. There is some evidence that the symmetry of epistilbite is lower than $C2/m$, proposed by Perrotta (1967). Actually

Table 1. Crystallographic and chemical data for the Theigarhorn epistilbite

$a = \quad 9.101(2)$ Å	Space group $C2$
$b = \quad 17.741(1)$ Å	$Z = 1$
$c = \quad 10.226(1)$ Å	Balance error $E = 1.0\%$
$\beta = \quad 124.66(2)°$	Chemical composition:
$V = 1358.2$ Å^3	$(Na_{0.79}K_{0.04}Ca_{2.56}Ba_{0.01})(Al_{6.02}Si_{18.00})O_{48}$
	$\cdot\ 15.64\ H_2O$
Number of electrons in	Number of electrons
extraframework cation sites:	in water sites:
chemical analysis 61	chemical analysis 125
structure refinement 67	structure refinement 128

Slaughter and Kane (1969) attributed to epistilbite a $C2/m$ symmetry with the exclusion of three framework oxygens and one water molecule which were considered to have a symmetry $C2$.

Vezzalini (1984) showed that in the structure of Elba dachiardite T − O − T angles of 180° are avoided through the formation of two opposite tetrahedral configurations, each with Cm symmetry and the same frequency, thus maintaining an average symmetry $C2/m$. In the epistilbite structure, which is very similar to that of dachiardite, some T − O − T angles of 180° are also present, consequently we cannot exclude that in epistilbite too opposite acentric domains are present.

The aim of this work is to determine the correct space group, to verify if two opposite configurations are present, to establish the Si/Al distribution and to better locate the water molecules and the extraframework cations.

Experimental

Electron microprobe analysis of the Theigarhorn epistilbite was carried out on an ARL-SEMQ instrument in the wavelength dispersive mode. The experimental conditions were: 15 kV, 20 nA beam current and defocused beam (spot size $\approx 20\ \mu m$) to minimize water loss. The instrument was operated in the automatic mode, with on-line data reduction, using the Ziebold and Ogilvie (1964) method and using Albee and Ray (1970) correction factors. The sample is chemically homogeneous and the analysis is in good agreement with that of Galli and Rinaldi (1974). The chemical analysis was normalized to 100% assuming the water content reported by Galli and Rinaldi (1974). The chemical formula is reported in Table 1.

A crystal of irregular shape of approximately $2 \times 10^{-6}\ cm^3$, was used for the data collection. Cell parameters (see Table 1) and intensities were collected on a Philips PW1100 automatic single crystal diffractometer (Mo$K\alpha$ radiation). Intensities were corrected for absorption by a combination of the semi-empirical method proposed by North et al. (1968) with the

absorption correction for the spherical shape ($\mu = 9$ cm^{-1}, r $= 0.008$ cm). 3960 reflections were collected in the $C\bar{1}$ space group. The statistical analysis of the hkl and $h\bar{k}l$ intensities clearly indicated the monoclinic symmetry for epistilbite. The number of independent reflections, after averaging symmetrically equivalent reflections, was 2049, of these 1473 with $I > 3\,\sigma(I)$ were used in the refinement.

Structure refinement

The unit cell of epistilbite, monoclinic C, can be described by two similar systems of axes, being the framework pseudoorthorhombic F. One was used by Slaughter and Kane (1969), the other by Perrotta (1967); we used the unit cell of Perrotta (1967), because it is that usually assumed in the literature. The transformation matrix between the two unit cells is: $100/0\bar{1}0/\bar{1}0\bar{1}$. Besides, the origin of Slaughter's unit cell is translated by $1/2\ a$ and $1/2\ c$ in respect to that one of Perrotta.

Extinction and anomalous-scattering corrections were not applied; atomic scattering factors for neutral atoms were used in the structure refinement.

At first the refinement was carried out in the $C2/m$ space group. Starting coordinates for the framework atoms were from Perrotta (1967). The extra-framework sites were located from three-dimensional electron density syntheses. Although all the extraframework ions had been localized and the anisotropic thermal factors had been used for the tetrahedral cations, the refinement gave a discrepancy index R as high as 0.17. Therefore we supposed that the symmetry was lower than $C2/m$ and that, as in dachiardite, the avoidance of $T-O-T$ angles of 180° was the cause of the shift of framework oxygens away from the $\bar{1}$ position with a consequent lowering of symmetry. Assuming that the shift of the framework atoms was similar to that found in dachiardite, the more probable space group was $C2$. At the end of the anisotropic refinement in $C2$ s.g. the R value was 6%. The Fourier synthesis however showed still residual maxima near to the T2, T2P, T3, T3P, O7, O8, O8P and O9 atoms, thus indicating the presence of two possible configurations (called A and B configurations from now on), analogous to those of dachiardite (Vezzalini, 1984). The refinement in $C2$ space group, assuming isotropic temperature factors for the split sites and anisotropic temperature factors for the other ones, gave occupancy factors of 82% and 18% for the tetrahedra of the A and B configuration, respectively. The final R and R_w values were 5.5 and 4.6 respectively. Positional and thermal parameters are reported in Table 2, interatomic distances and angles in Tables 3 and 4[1].

Figure 1 shows A(...) and B(---) configurations.

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[1] The list of structure factors and thermal parameters may be obtained from the authors upon request

Table 2. Atomic coordinates, occupancy factors and isotropic temperature factors or equivalent isotropic thermal parameters for epistilbite [Å^2]. [$B_{eq} = 8\,\pi^2\,(U_{11} + U_{22}\sin^2\beta + U_{33} + 2\,U_{31}\cos\beta)/3\,(1-\cos^2\beta)$]

Atom	x	y	z	Occupancy	B^* or B_{eq}
T1	0.0025(5)	0.0887	0.1600(4)	1.00[a]	1.0
T1P	0.0047(5)	−0.0889(2)	0.1593(4)	1.00	1.1
T2A	0.3013(7)	0.2067(4)	0.3768(7)	0.82(1)	1.2(1)*
T2PA	0.2923(6)	−0.2082(4)	0.4078(7)	0.82	1.3(1)*
T2B	0.2862(31)	0.2101(15)	0.3958(31)	0.18(1)	0.6(4)*
T2PB	0.2945(23)	−0.2126(11)	0.3742(25)	0.18	0.1(3)*
T3A	0.7093(6)	0.1936(4)	0.1169(7)	0.82	1.3(1)*
T3PA	0.7080(5)	−0.1999(3)	0.0772(7)	0.82	0.9(1)*
T3B	0.6954(30)	0.1899(14)	0.0640(34)	0.18	2.0(5)*
T3PB	0.7170(22)	−0.1994(11)	0.1277(26)	0.18	0.1(3)*
O1	0.0248(7)	−0.0042(7)	0.2188(6)	1.00	1.7
O2	0	0.0969(10)	0	1.00	2.8
O2P	0	−0.0985(10)	0	1.00	2.3
O3	0.8099(15)	0.1163(6)	0.1364(14)	1.00	2.2
O3P	0.8156(15)	−0.1155(7)	0.1260(13)	1.00	2.3
O4	0.1730(16)	0.1333(6)	0.3171(13)	1.00	2.3
O4P	0.1662(14)	−0.1342(6)	0.3059(13)	1.00	2.9
O5	$\frac{1}{2}$	0.1736(11)	0	1.00	3.5
O5P	$\frac{1}{2}$	−0.1796(10)	0	1.00	2.9
O6	$\frac{1}{2}$	0.1737(10)	$\frac{1}{2}$	1.00	2.2
O6P	$\frac{1}{2}$	−0.1819(10)	$\frac{1}{2}$	1.00	2.9
O7A	0.7819(16)	0.2614(7)	0.0607(16)	0.82	2.1(2)*
O7B	0.7160(98)	0.2331(40)	−0.0450(99)	0.18	5.6(17)*
O8A	0.2585(14)	−0.2824(7)	0.2957(13)	0.82	3.0(2)*
O8PA	0.3036(15)	0.2473(8)	0.2391(14)	0.82	3.3(3)*
O8B	0.2677(53)	−0.2471(23)	0.2241(48)	0.18	0.1(7)*
O8PB	0.2158(49)	0.2805(23)	0.2740(43)	0.18	1.0(7)*
O9A	0.2530(14)	0.2705(6)	0.4610(11)	0.82	2.2(2)*
O9B	0.2048(45)	0.2467(26)	0.4733(49)	0.18	1.5(7)*
C1	0.7598(5)	−0.0035(5)	0.2513(5)	0.60(1)[b]	3.0
C2	0.7443(12)	0.0081(8)	0.4990(10)	0.35(1)[b]	5.1
W1	$\frac{1}{2}$	−0.0118(15)	$\frac{1}{2}$	1.00	6.4
W2	0	0.0772(12)	$\frac{1}{2}$	1.00	5.3
W2P	0	−0.0863(14)	$\frac{1}{2}$	1.00	11.9
W3	0.5861(34)	0.0752(9)	0.2997(22)	1.00	11.8
W3P	0.5656(22)	−0.0828(9)	0.2806(21)	1.00	6.7
W4	0	−0.0046(15)	0	1.00	3.7

[a] The occupancy refers to a scattering curve of Si 75% and Al 25%
[b] The occupancy refers to a scattering curve of Ca 75% and Na 25%

Table 3. Bond distances (Å), percent of Al and angles (°) for the tetrahedra

T1 –O1	= 1.726(12) Å	T1P –O1	= 1.593(12)	T2B –O4	= 1.62(3)	T2PB –O4P	= 1.69(2)
–O2	= 1.630(4)	–O2P	= 1.614(4)	–O6	= 1.73(3)	–O6P	= 1.65(2)
–O3	= 1.700(11)	–O3P	= 1.623(12)	–O8PB	= 1.62(4)	–O8B	= 1.54(4)
–O4	= 1.667(10)	–O4P	= 1.596(11)	–O9B	= 1.51(4)	–O9B	= 1.72(4)
Mean 1.681	Al% 50ᵃ	Mean 1.607	Al% 6	Mean 1.62		Mean 1.65	
T2A –O4	= 1.619(10)	T2PA –O4P	= 1.663(12)	T3B –O3	= 1.57(3)	T3PB –O3P	= 1.74(2)
–O6	= 1.615(8)	–O6P	= 1.628(7)	–O5	= 1.53(3)	–O5P	= 1.67(2)
–O8PA	= 1.592(13)	–O8A	= 1.656(12)	–O7B	= 1.45(4)	–O7B	= 1.76(4)
–O9A	= 1.626(10)	–O9A	= 1.656(10)	–O8B	= 1.77(4)	–O8PB	= 1.54(4)
Mean 1.613	Al% 9	Mean 1.651	Al% 35	Mean 1.58		Mean 1.68	
T3A –O3	= 1.597(11)	T3PA –O3P	= 1.702(12)	T2A–T2B	= 0.30(3)	T3A–T3B	= 0.49(3)
–O5	= 1.610(6)	–O5P	= 1.623(6)	T2PA–T2PB	= 0.36(3)	T3PA–T3PB	= 0.47(3)
–O7A	= 1.627(13)	–O7A	= 1.617(12)	O7A–O7B	= 1.02(4)	O8A–O8B	= 1.00(4)
–O8A	= 1.672(12)	–O8PA	= 1.655(12)	O8PA–O8PB	= 1.20(4)	O9A–O9B	= 0.67(4)
Mean 1.627	Al% 19	Mean 1.649	Al% 34				

T1–O2–T1	= 170°ᵇ	T1–O1–T1P	= 143
T1–O4–T2A	= 145	T1–O3–T3A	= 137
T1P–O2P–T1P	= 168	T1P–O4P–T2PA	= 158
T1P–O3P–T3PA	= 133	T2A–O6–T2A	= 138
T2A–O9A–T2PA	= 149	T2A–O8PA–T3PA	= 151
T2PA–O6P–T2PA	= 147	T2PA–O8A–T3A	= 142
T3A–O5–T3A	= 155	T3A–O7A–T3PA	= 149
T3PA–O5P–T3PA	= 155		

ᵃ Values calculated according to Alberti and Gottardi (1985) method
ᵇ Standard deviation on the T–O–T angles = 1°

Table 4. Cation, oxygen and water molecules distances less than 3.10 Å

C1–O1	= 2.62(1)	C2–O1	= 2.43(1)	W1–O6P	= 3.02(3)
C1–O3	= 2.59(1)	C2–O4	= 2.73(1)	W1–W3	= 3.00(2)
C1–O3P	= 2.57(1)	C2–O4P	= 3.03(1)	W1–W3P	= 2.92(2)
C1–C2	= 2.62(1)	C2–W1	= 2.26(1)	W2–W2P	= 2.90(2)
C1–W4	= 2.30(1)	C2–W2	= 2.63(1)	W3–O8A	= 2.99(2)
C1–W2	= 2.64(1)	C2–W2P	= 2.86(2)	W3–W3P	= 2.81(1)
C1–W2P	= 2.66(2)	C2–W3	= 2.08(2)	W3–W4	= 3.05(2)
C1–W3	= 2.36(2)	C2–W3P	= 2.47(2)	W4–O3P	= 3.09(2)
C1–W3P	= 2.41(2)			W4–W3P	= 2.93(2)
				W3P–O8PB	= 2.80(3)
				W3P–O9	= 3.08(2)
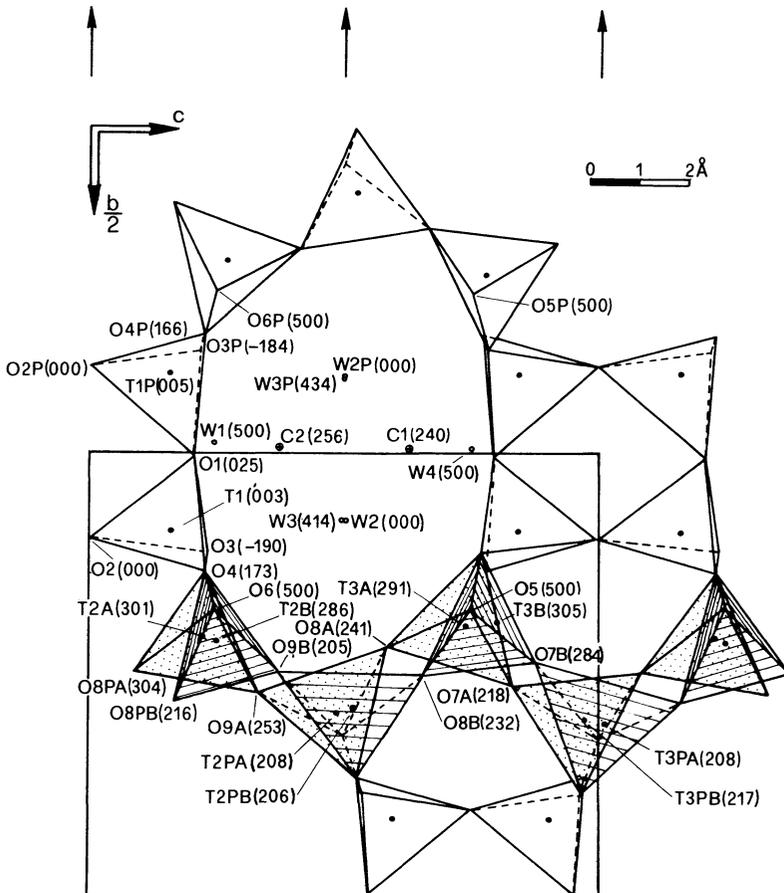
Fig. 1. Projection of the epistilbite structure onto the (100) plane. The dotted tetrahedra (. . . .) indicate the A configuration, the dashed tetrahedra (————) the B configuration

Discussion

Tetrahedral framework

A building block, which allows an easy description of epistilbite framework, is a cage formed by 4 pentagonal rings (see Merlino, 1976). The different connection of these cages generates the related frameworks of epistilbite, dachiardite and mordenite. A detailed description of these structures can be found in Gottardi and Galli (1985) and an exhaustive study on the possible structures obtainable by the connection of this building block is given by Merlino (1976).

In epistilbite, as in dachiardite, if we assume the $C2/m$ symmetry, two oxygens (O7 and O9) are on $\bar{1}$ position, consequently $T-O-T$ angles of $180°$ are present; to avoid this situation O7 and O9 atoms shift away from this site, thus reducing the symmetry to $C2$. In Theigarhorn epistilbite these oxygens are split into two positions about 1Å apart. This oxygen splitting causes an analogous splitting of the T-sites T2, T2P, T3 and T3P, which in turn gives rise to the splitting of O8 and O8P, the oxygens linking them together (see Fig. 1). The A and B configurations can be obtained by the rotation of the T2, T2P, T3 and T3P tetrahedra around the $O4-O6$, $O4P-O6P$, $O4-O5$ and $O4P-O5P$ edges, respectively.

The most remarkable difference between this epistilbite and Elba dachiardite is that in this structure the A configuration occurs in 82% of the cases and the B configuration in the remaining 18% of the cases, whereas in dachiardite both configurations have the same probability to be present. As a consequence Elba dachiardite maintains the statistical symmetry $C2/m$, whereas in epistilbite the symmetry is definitely $C2$.

The $T-O$ distances are rather regular for the tetrahedra of the A configuration, quite irregular for those of the B configuration (see Table 3), a result justified by the low probability of this last configuration.

Owing to the low occupancy of the tetrahedra and to the high standard deviations on the $T-O$ distances in the B configuration, the $Si-Al$ distribution is evaluted from the distances of the tetrahedra of the A configuration only. According to the $T-O$ mean distance, the Jones relationship (1968) gives for the Theigarhorn epistilbite an Al content of 22% against an Al content of 25% given by the chemical analysis. This underestimation is common in the disordered zeolites; Alberti and Gottardi (1985) showed that it occurs because the position of the atoms given by the X-ray refinement, do not correspond, when disorder is present, to the true position of the atoms, but to the centre of gravity of the sites occupied by the ions in the different unit cells. The Al underestimation in a tetrahedron depends on the $T-O-T$ angles and on the Al content in this tetrahedron and in the adjacent ones. A computer program (Alberti and Gottardi, private communication), which takes into account these factors, indicated that in epistilbite the Al underestimation is of 3%. The consequent Al content
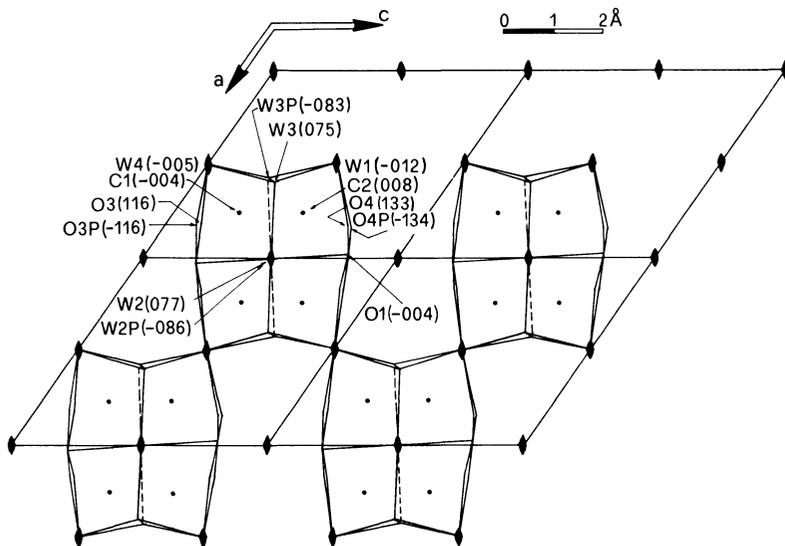
Fig. 2. Clusters of extraframework cation polyhedra projected on (010) plane

(25%) is in good agreement with the chemical data. The range of variation of the corrected Al percentage in each tetrahedron is rather large (from 50% to 6%, see Table 3). The value of 50% of Al in T1 is the highest value possible for this tetrahedron if we accept the Loewenstein rule (Loewenstein, 1954). If we average the Al content of the $C2/m$ pseudosymmetric tetrahedra (T1 – T1P; T2A – T2PA; T3A – T3PA) we obtain values quite similar (29%, 22%, 26% respectively), indicating a not remarkable enrichment of Al in one tetrahedron.

Extraframework sites

In epistilbite eight extraframework sites have been found and the good agreement with the chemical analysis warrants that all extraframework ions have been located (see Table 1).

Comparing our data with those of Slaughter and Kane (1969), we found in C2 site 6.2 e⁻ against their 4.2 e⁻, besides the occupancies of W(1) are 100% and 50% respectively. At last in the refinement of Slaughter and Kane (1969) there is a water site at $0,0,\frac{1}{2}$ [HOH(6) in their notation] with low occupancy, which we found empty; in return, the near sites W4 and W4P have higher occupancies. Perrotta (1967) found empty our W1 site and attributed our C2 site to a water molecule.

In epistilbite there is only one set of eight-membered channels parallel to c. The other set of channels orthogonal to this, present in mordenite and

in dachiardite, is here closed by four-membered rings of tetrahedra, thus forming large cages. Both C sites are eight-coordinated with three non-split framework oxygens and five water molecules to form an irregular square antiprism. As shown in Figure 2, the C1 and C2 polyhedra share one of the square faces. This couple of polyhedra is joint to a symmetrically equivalent couple through the sharing of a diamond-shaped face obtained from two triangular faces, one for each antiprism, thus forming a cluster of four polyhedra. Given the occupancies of C1 and C2 sites and the cation-cation distances (see Tables 2 and 4) only two tetrahedra of the group of four can be simultaneously occupied. Each cluster shares four vertices with four other clusters, thus forming a two-dimensional chessboard of polyhedra parallel to (010) plane. The short coordination distance C2 — W3 of 2.08 Å can be explained with the high and strongly anisotropic thermal parameters of W3 ($B_{eq} = 12$ Å^2).

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