

A refinement of Elba dachiardite: Opposite acentric domains simulating a centric structure

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Abstract. The crystal structure of Elba dachiardite shows an unusual rotation of two tetrahedra around one edge. This rotation gives rise to two configurations which have the same frequency thus maintaining the statistical symmetry $C2/m$. The most probable distribution of ions indicates the presence of two cation sites and five water molecules. One cation site is at the crossing of the two systems of channels and is 8-fold coordinated, the other is in the channel parallel to c and is 2-fold coordinated. The extraframework sites are not affected by the rotation within the framework, coordinating only the fixed framework oxygens.

Introduction

Dachiardite was first found in S. Piero in Campo, Elba, Italy (D'Achiardi, 1906). No additional occurrences has been noted until 1964, when Minato announced the second occurrence of Dachiardite from Onoyama gold mine, Kagoshima, Japan. Subsequently other authors (Alberti, 1975; Wise and Tshernich, 1978; Nishido and Otsuka, 1981 and related literature) described several occurrences of this zeolite. All these samples however differ from the Elba dachiardite as they lack the characteristic beaker-like twins (Berman, 1925; De Angelis, 1925), and have a different paragenesis and chemical composition. In fact the Elba dachiardite is unique in that it is Cs bearing (D'Achiardi, 1906; Bonardi, 1979); this Cs content can be correlated with the unusual origin (hydrothermal deposition in a pegmatite with Cs minerals) of this dachiardite. Furthermore Elba dachiardite does not show the disorder in the lattice observed in the Alpe di Siusi sample (Alberti, 1975) and the twinning and faulting found in svetlozarite (Gellens et al., 1982), re-interpreted as a multiply-twinned and highly-faulted dachiardite.

Table 1. Crystallographic and chemical data for the Elba dachiardite

$a = 18.676 \text{ \AA}$	Space group: $C2/m$
$b = 7.518 \text{ \AA}$	$Z = 1$
$c = 10.246 \text{ \AA}$	Balance error $E = +1.9 \%$ (Passaglia, 1970)
$\beta = 107.87^\circ$	
$V = 1369.20 \text{ \AA}^3$	
Chemical composition:	
$(\text{Na}_{0.42}\text{K}_{0.92}\text{Cs}_{0.11}\text{Ca}_{1.54}\text{Sr}_{0.12}\text{Ba}_{0.01})(\text{Fe}_{0.02}\text{Al}_{4.86}\text{Si}_{18.96})\text{O}_{48} \cdot 12.56 \text{ H}_2\text{O}$	
Number of electrons in extraframework cation sites:	Number of electrons in water sites:
chemical analysis = 64.6	chemical analysis = 100.5
structure refinement = 67.1	structure refinement = 96.0

The structure of Elba dachiardite was solved in 1963 by Gottardi and Meier. Gottardi (1972) reported a structural model by Merlino (private communication) concerning the framework of the Na-exchanged Elba dachiardite at -140°C . According to Merlino the real structure is acentric Bm , instead of $B2/m$ (Gottardi and Meier, 1963) and the framework is formed from alternating sheets with different orientations of the T1 and T2 tetrahedra.

The aim of this work is to confirm this structural model, to establish a possible ordered distribution of Si and Al and to better locate the water molecules and the extraframework cations.

Experimental

Electron microprobe analysis of the Elba dachiardite 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 $\sim 20 \mu\text{m}$) 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. Nine analyses showed high chemical homogeneity of the sample and good agreement with the analyses of Gottardi (1960) and Bonardi (1979) for the same Elba dachiardite. The chemical analysis was normalized to 100% assuming the water content reported by Gottardi (1960); the chemical formula is reported in Table 1.

X-ray data collection and determination of the cell parameters (see Table 1) were carried out on an irregular prismatic crystal ($0.1 \times 0.2 \times 0.3 \text{ mm}$) using a Philips PW 1100 diffractometer with $\text{MoK}\alpha$ radiation. Intensities were corrected for absorption by a combination of the semiempirical method proposed by North et al. (1968) with the absorption correction for

the spherical shape ($\mu = 30 \text{ cm}^{-1}$, $r = 0.002$). 3994 reflections were collected in the $C\bar{1}$ space group; the statistical analysis of the $(hk\bar{l})$ and $(\bar{h}kl)$ intensities clearly indicates monoclinic symmetry. The number of independent reflections, after averaging the symmetrically equivalent ones, is 2142; of these 1229 with $I_0 > 3\sigma(I_0)$ were used in the refinement.

Structure refinement

The refinement was carried out in space group $C2/m$; this choice of cell dimensions was used by Alberti (1975) and differs from $B2/m$ used by Gottardi and Meier (1963). Atomic scattering factors for neutral atoms were used in the structure refinement. Extinction and anomalous-scattering corrections were not applied. Starting coordinates, for the framework atoms, were from Gottardi and Meier (1963). The dachiardite structure was refined using a combination of three-dimensional electron density synthesis (to locate extraframework sites) and full matrix least-squares techniques; care was taken to refine strongly correlated variables separately. After some cycles of isotropic refinement all extraframework sites were determined. The final R and R_w indices, obtained from anisotropic refinement, were 6.99 and 6.37 respectively.

At this point the Fourier synthesis showed very elongated maxima for the O(3), O(7), and O(8) oxygens and the largest semiaxis of the anisotropic thermal factors of these atoms had the elongation direction of the Fourier maxima. Gottardi and Meier (1963) had already noted that "the somewhat elongated peaks of O(7) and O(8) might indicate some local departures from centrosymmetry rather than thermal anisotropy". Therefore, according to Gottardi (1972) it was preferred to split the O(3), O(7), and O(8) sites and consequently the tetrahedral sites T(1) and T(2). The two configurations are named A (. . . .) and B (----) and are shown in Figure 1. The A and B configurations can be obtained by rotation of the T(1) and T(2) tetrahedra around the O(1)–O(6) and O(2)–O(5) edges respectively. The isotropic refinement of the split atoms gives values for R and R_w of 6.85 and 6.32 respectively, they are very similar to those of the anisotropic refinement as can be expected because the number of variables is similar in both cases.

The Harker $h0l$ section and $0k0$ line of the Patterson function were examined to verify, if the structure became acentric for the prevalence of one of the two (A or B) configurations. In this way however it was impossible to decide whether the $C2$ or Cm space group was more probable. Nevertheless, as all the displacements of the atoms affected by the rotation were nearly parallel to (010) , the Cm space group was assumed as more probable than $C2$. The refinement in Cm gave the same values of occupancy for the atoms in both A and B configurations, consequently the refinement was finished in $C2/m$ assuming isotropic temperature factors for the split sites and aniso-

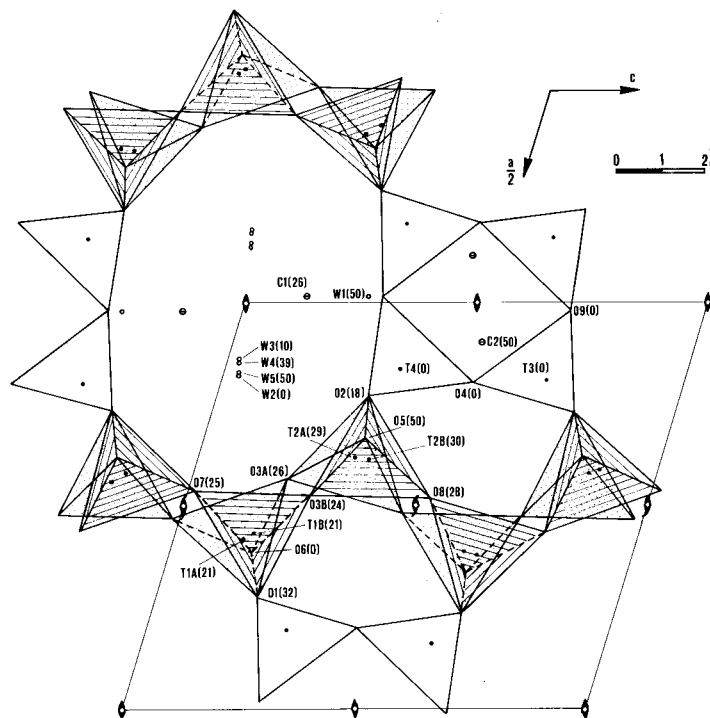


Fig. 1. Projection of the dachiardite structure onto the (010) plane. The dotted tetrahedra (...) indicate the A configuration, the dashed tetrahedra (----) the B configuration

tropic temperature factors for the other framework atoms and for the C(1) and W(1) extraframework atoms.

Positional and thermal parameters are reported in Table 2, interatomic distances and angles for the framework are reported in Table 3 and distances $< 3 \text{ \AA}$ for extraframework sites in Table 4¹.

Discussion

The tetrahedral framework

The dachiardite framework was described by Gottardi and Meier (1963) and can be interpreted as cages of four pentagonal rings connected to build up the so called mordenite chains or mordenite columns. In the Elba dachiardite however an interesting feature was noted: the splitting of the O(7) and O(8) oxygens from the $\bar{1}$ position reported for these atoms by Gottardi and Meier (1963). In this way the T–O–T angles of 180° around these oxygens are avoided. This oxygens' splitting causes an analogous splitting of the

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

Table 2. Atomic coordinates, occupancy factors and isotropic temperature factors or equivalent isotropic thermal parameters for dachiardite [\AA^2].

$$(B_{\text{eq}} = 8\pi^2(U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{31}\cos\beta)/3(1-\cos^2\beta))$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>B</i> * or <i>B</i> _{eq}
T(1)A	0.2905(4)	0.2084(11)	0.1496(7)	0.50	1.2(1)*
T(1)B	0.2846(4)	0.2053(10)	0.1660(7)	0.50	1.1(1)*
T(2)A	0.1914(3)	0.2901(8)	0.3371(5)	0.50	1.3(1)*
T(2)B	0.1929(3)	0.2978(7)	0.3714(5)	0.50	1.0(1)*
T(3)	0.0964(1)	0	0.7007(3)	1.00	1.1
T(4)	0.0816(1)	0	0.3793(3)	1.00	1.2
O(1)	0.3636(3)	0.3239(7)	0.2168(6)	1.00	3.3
O(2)	0.1162(3)	0.1770(7)	0.3265(5)	1.00	3.1
O(3)A	0.2188(6)	0.2642(16)	0.2070(12)	0.500	2.4(2)*
O(3)B	0.2382(7)	0.2370(19)	0.2652(14)	0.500	4.3(3)*
O(4)	0.1002(4)	0	0.5457(8)	1.00	4.3
O(5)	0.1688(5)	1/2	0.3487(9)	1.00	4.0
O(6)	0.3098(5)	0	0.1759(8)	1.00	3.5
O(7)	0.2335(6)	0.2452(19)	0.0131(13)	0.500	3.2(3)*
O(8)	0.2427(7)	0.2777(17)	0.5249(12)	0.500	2.9(2)*
O(9)	0.0103(3)	0	0.7080(7)	1.00	1.9
C(1) ^a	-0.0091(4)	0.2598(11)	0.1297(9)	0.345(4) ^b	7.8
C(2)	0.0456(17)	1/2	0.5374(35)	0.156(3) ^c	10.3(9)*
W(1) ^a	-0.0084(4)	1/2	0.2668(11)	1.00	5.4
W(2)	0.0884(15)	0	0.0330(30)	0.500	6.7(6)*
W(3) ^a	0.0694(19)	0.1037(46)	0.0261(40)	0.250	7.5(9)*
W(4) ^a	0.0724(18)	0.3931(42)	0.0258(38)	0.250	6.5(7)*
W(5)	0.0860(14)	1/2	0.0310(29)	0.500	6.0(6)*

^a C(1) correspond to the first extraframework site of Gottardi and Meier (1963), W(1) to the fourth, W(3) to the third and W(4) to the second

^b The occupancy refers to the scattering curve of Ca

^c The occupancy refers to the scattering curve of K

tetrahedral cations T(1) and T(2) and of the O(3) oxygen linking them together. The split tetrahedral cations TA and TB are 0.3 Å apart and the OA and OB oxygens nearly 0.7 Å apart. Because the split atoms maintain nearly the same *y* value, the A and B configurations can be interpreted as due to a rotation on the *xz* plane of the T(1) and T(2) tetrahedra around the O(1)–O(6) and O(2)–O(5) edges respectively. Therefore one may put forward the hypothesis that unit cells aligned along *c* have the same A (or B) configuration, whereas a change of configuration would be possible in the *a* and *b* directions, being the O(1), O(2), O(5), and O(6) oxygens in the same site for both configurations (the last ones are on the mirror plane) (see Fig. 1).

An analogous rotation of tetrahedra, giving rise to two framework configurations, has already been observed in the heat-induced phase of natrolite (Alberti and Vezzalini, 1983). However, in natrolite this rotation

Table 3. Bond distances (Å) and angles (°) for the tetrahedra

T(1)A	-O(3)A = 1.671(12) Å	T(1)B	-O(1) = 1.665(8)
	-O(6) = 1.612(8)		-O(3)B = 1.543(15)
	-O(1) = 1.586(9)		-O(6) = 1.608(8)
	-O(7) = 1.626(15)		-O(7) = 1.593(14)
	Mean 1.624		Mean 1.602
T(2)A	-O(2) = 1.617(7)	T(2)B	-O(2) = 1.639(7)
	-O(3)A = 1.580(12)		-O(3)B = 1.635(14)
	-O(5) = 1.647(6)		-O(5) = 1.582(6)
	-O(8) = 1.645(12)		-O(8) = 1.569(13)
	Mean 1.622		Mean 1.606
T(3)	-O(4) = 1.611(8)	T(4)	-O(2) = 1.642(5) × [2]
	-O(8) = 1.633(7)		-O(4) = 1.632(8)
	-O(1) = 1.624(5) × [2]		-O(9) = 1.674(5)
	Mean 1.623		Mean 1.648
T(1)A - T(1)B	= 0.23(1)	T(2)A - T(2)B	= 0.35(1)
O(3)A - O(3)B	= 0.63(2)	O(7) - O(7)	= 0.75(2)
O(8) - O(8)	= 0.77(2)		
T(1)A - O(1) - T(3)	= 150(2)°	T(2)B - O(5) - T(2)B	= 148(1)
T(1)B - O(1) - T(3)	= 145(1)	T(1)A - O(6) - T(1)A	= 153(2)
T(2)A - O(2) - T(4)	= 146(1)	T(1)B - O(6) - T(1)B	= 147(2)
T(2)B - O(2) - T(4)	= 139(1)	T(1)A - O(7) - T(1)A	= 153(3)
T(1)A - O(3)A - T(2)A	= 146(1)	T(1)B - O(7) - T(1)B	= 156(3)
T(1)B - O(3)B - T(2)B	= 172(1)	T(2)A - O(8) - T(2)A	= 145(2)
T(4) - O(4) - T(3)	= 166(4)	T(2)B - O(8) - T(2)B	= 161(4)
T(2)A - O(5) - T(2)A	= 147(1)	T(3) - O(9) - T(4)	= 147(1)

was caused by heating and the extraframework sites were strongly affected by this phenomenon, in dachiardite the only cause seems to be the avoidance of the T-O-T angles of 180°, which is very far from the value of ~140° normally found in silicates. The T-O-T angles around O(3)A, O(3)B, O(7) and O(8) are rather high (~170°) only in one case, as shown in Table 3. The T-O distances (see Table 3) are rather irregular for T(1)A, T(1)B, T(2)A and T(2)B tetrahedra, but clearly better for T(3) and T(4). The T-O mean distance is 1.621 Å and corresponds to an Al content of 11 % (Jones, 1968), a value lower than that derived from the chemical analysis (nearly 20 %); this discrepancy however is not unusual in zeolites (Galli et al., 1982 and related literature).

The T(4) tetrahedron is richest in Al (~28 %), so that a partial order is present.

Table 4. Cation, oxygen and water molecules distances less than 3 Å

C(1) – O(1) = 2.85(1)	C(2) – C(2) = 1.64(6)
O(2) = 2.65(1)	W(1) = 2.32(4)
O(9) = 2.57(1)	W(1) = 2.64(4)
C(1) = 2.29(1)	
C(1) = 2.78(2)	
W(1) = 2.29(1)	
W(2) = 2.70(2)	W(1) – C(1) = 2.29(1) [× 2]
W(2) = 3.04(2)	C(2) = 2.32(4)
W(3) = 2.02(4)	C(2) = 2.64(4)
W(3) = 2.37(4)	W(4) = 2.98(4) [× 2]
W(4) = 1.95(3)	W(5) = 2.95(3)
W(4) = 2.34(4)	
W(5) = 2.57(2)	
W(5) = 2.92(3)	
W(3) – O(2) = 2.98(4)	W(2) – C(1) = 2.70(2) [× 2]
C(1) = 2.02(4)	W(3) = 0.85(4) [× 2]
C(1) = 2.37(4)	W(3) = 2.93(4) [× 2]
W(2) = 0.85(4)	W(4) = 2.97(3) [× 2]
W(2) = 2.93(4)	
W(3) = 1.56(7)	
W(3) = 2.93(7)	
W(4) = 2.18(5)	W(4) – O(3)A = 2.96(4)
W(5) = 2.99(4)	C(1) = 1.95(3)
	C(1) = 2.34(4)
	W(1) = 2.98(4)
W(5) – C(1) = 2.57(2) [× 2]	W(2) = 2.97(3)
C(1) = 2.92(3) [× 2]	W(3) = 2.18(5)
W(1) = 2.95(3)	W(4) = 1.61(6)
W(3) = 2.99(4) [× 2]	W(4) = 2.59(7)
W(4) = 0.84(3) [× 2]	W(5) = 0.84(3)
W(4) = 2.95(4) [× 2]	W(5) = 2.95(4)

Extraframework sites

The X-ray refinement indicates seven extraframework sites, four of which are very near the corresponding ones found by Gottardi and Meier (1963). The fourth extraframework site of Gottardi and Meier, which was attributed to cations on the basis of stereochemical considerations, is interpreted here as a water molecule and is placed exactly on the mirror plane.

Two of these seven sites were attributed to cations and five to water molecules on the basis of their distances from the framework oxygens, the other extraframework sites and the agreement between chemical analysis and occupancies at the end of the refinement.

Two systems of channels are present in the dachiardite structure, the main one parallel to *b*, is delimited by ten-membered rings, whereas the other runs

parallel to c and is delimited by eight-membered rings. C(1) is at the crossing of the two channel systems and is 8-fold coordinated to three oxygens of the framework and to five water molecules (see Table 4). C(2) is in the channel parallel to c and has short distances only with two water molecules W(1), which are at the centre of the 8-ring window; whereas the distances with the framework oxygens are large (3.3 Å or more). The agreement between chemical analysis and occupancies at the end of the refinement leads to the following cation distribution; all Ca in C(1) and all Cs in C(2). It is difficult to define the true distribution of the other cations, even if it is probable that the residual charge in C(2) pertains to a monovalent cation of large ionic radius like K. This cation distribution is not in disagreement with that determined by Merlino (personal communication) for the Na-exchanged dachiardite. In this form in fact all the Na is in a site practically coincident with C(1); in natural dachiardite the small cations, mainly Ca, are in C(1). Besides, being C(1) in the larger channel, the possibility of solvation for divalent cations in this position is better. The short distances C(1)–W(1) and C(2)–W(1) can be explained by the strong thermal motion of W(1) in the C(1)–C(2) direction and by the partial occupancies of these cations.

All water molecules, except W(1), are in the main channel. The W(5)–W(4) and W(4)–W(4) (sites equivalent by mirror plane) distances are very short (see Table 4); furthermore the refinement shows the same population for these sites. Consequently the occupancies of W(4) and W(5) (see Table 2) were fixed to 0.50 and 0.25 respectively. W(2) and W(3) show analogous behaviour; consequently the occupancies of these water molecules were fixed. In this way all the water molecules sites can be considered completely occupied whereas the cation sites have partial occupancies (34 % and 14 % for C(1) and C(2) respectively).

The extraframework sites do not seem to be affected by the splitting of the framework, in fact they are coordinated only to the fixed oxygens. In conclusion, with this attribution of extraframework sites, the agreement between the number of electrons found by the chemical analysis and by the X-ray refinement is very good, as shown in Table 1, for both the cations and the water molecules.

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