Okenite, $Ca_{10}Si_{18}O_{46} \cdot 18H_2O$: the first example of a chain and sheet silicate

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Abstract

The crystal structure of okenite, $Ca_{10}Si_{18}O_{46} \cdot 18H_2O$, was solved with triclinic space group $P\bar{1}$ $a = 9.69$, $b = 7.28$, $c = 22.02$Å, $\alpha = 92.7°$, $\beta = 100.1°$, $\gamma = 110.9°$. The structure is composed of the following structural units: (a) tetrahedral sheets S, with composition $(Si_6O_{15})^{-6}$, characterized by five- and eight-membered rings of silicate tetrahedra, with five tetrahedra pointing in one direction and one tetrahedron pointing in the other direction; (b) three-repeat double chains C, with composition $(Si_6O_{16})^{-8}$ and characterized by four- and six-membered rings, made up by pairing two wollastonite chains, which point in opposite directions; (c) octahedral double chains O, formed by two strands of octahedra. These structural units are connected by corner sharing to give the complex layer SOCOS, with composition $[Ca_8(Si_6O_{16})(Si_6O_{15})_2(H_2O)_6]^{-4}$. Such complex layers alternate in the structure with sheets $[Ca_2(H_2O)_9 \cdot 3H_2O]^{+4}$. Weak supercell reflections revealed a larger unit cell with doubled a and b parameters in the unconventional space group $C\bar{1}$.

Introduction

Okenite, a hydrated calcium silicate, has long been of interest to a large number of mineralogists and crystal chemists: its consistent association with gyrolite and zeolites in basalts seemed indicative of some structural relations among them. Of particular interest is the role of water molecules in the structure of okenite, the definition of which could lead to an understanding of the dehydration mechanism which, according to Heller's X-ray studies (Gard and Taylor, 1956), leads topotactically to the formation of wollastonite.

Okenite was first described from Disko Island (Greenland) and was subsequently found in various other localities, such as Crestmore (California), Scawt Hill (Northern Ireland), Bordö (Faröer Islands), Bombay (India), usually in basalts. The most comprehensive account of its crystallographic properties was given by Gard and Taylor (1956) who studied a specimen from Bombay, India, consisting of fibrous aggregates. These authors studied okenite by electron diffraction, as single crystals of sufficient size for X-ray diffraction were not available. The results indicated that the crystals were triclinic with $a = 9.84$, $b = 7.20$, $c = 21.33$Å, $\alpha = 90.0°$, $\beta = 103.9°$, $\gamma = 111.5°$. The fiber direction was [010], with repeated lamellar twinning across the cleavage plane {001}. On the basis of the cell volume and a chemical analysis by Christie (1925), Gard and Taylor (1956) proposed that the cell contents are $Ca_9Si_{18}O_{63}H_{36}$, or $Ca_9(Si_6O_{15})_3 \cdot 18H_2O$.

Gard and Taylor (1956) also studied a mineral from Crestmore, California, which was previously character-ized as okenite on the basis of its chemical composition and optical properties, and demonstrated that it was in fact a new species for which they proposed the name nekoite. Crystal structures for both minerals were hypothesized by Mamedov and Belov (1958) on the basis of the chemical composition and unit cell dimensions. The crystal structure of nekoite was recently solved by Alberti and Galli (1980) who showed that it was in many respects different from the structural model of Mamedov and Belov (1958).

The present work was undertaken to determine the crystal structure of okenite in order to further our understanding of the crystal chemistry of the hydrated calcium silicates.

Experimental

A specimen of okenite from Kolhapur District, Maharastra State, India, donated by Prof. E. Passaglia, was used in this study. Careful examination of a large number of crystals from this specimen and testing by preliminary Weissenberg photographs resulted in the selection of crystals of sufficient quality for intensity measurement. By means of Weissenberg and precession photographs the lattice parameters were determined on a small fragment cut from a long lath-shaped crystal. The same crystal fragment was used to collect intensity data with a Philips PW 1100 single crystal diffractometer, after obtaining refined lattice parameters by least squares fitting of 20 medium range θ values: $a = 9.69(1)$, $b = 7.28(1)$, $c = 22.02(4)$Å, $\alpha = 92.7(2)°$, $\beta = 100.1(3)°$, $\gamma = 110.9(1)°$.

Diffraction intensities were measured with the ω-2θ scan technique using graphite-monochromatized Mo$K\alpha$ radiation. The scan rate was 0.04°/sec and the scan width 1.4°. A total of 780 independent reflections with $I \geq 2\sigma(I)$ were measured in the range $3° \leq \theta \leq 20°$. The number and range of reflections is limited relative to normal conditions because of the poor quality of the crystals. However all of the important features of the structure and the main crystal-chemical features of okenite could be defined.

The data were corrected for Lorentz and polarization factors. No absorption correction was applied, due to the small dimensions of the crystal and the relatively low value of the absorption coefficient (14.1 cm^{-1}).

Structure determination

Various attempts to solve the structure by direct methods were unsuccessful. The solution was obtained by interpretation of the Patterson function, which indicated the positions of four independent calcium cations in a centrosymmetric cell. The model was then built up step by step, by careful scrutiny of successive electron density syntheses in the light of crystal chemical reasoning: first, oxygen atoms were introduced to build a double octahedral chain; a double tetrahedral chain connecting two symmetrically related octahedral chains was then identified in a Fourier map; finally, two symmetrically related tetrahedral layers were recognized in the maps. Four calcium, nine silicon and twenty-six oxygen atoms were located by this stage.

One calcium cation and several water molecules were still missing, relative to the unit cell content suggested by Gard and Taylor (1956). A difference Fourier synthesis showed two prominent maxima which appeared to correspond, on the basis of their heights, to two sites (Ca5 and Ca6) with half occupancies. Successive difference Fourier syntheses showed ten further maxima which, on the basis of their heights and positions around Ca5 and Ca6 sites, were taken as water molecules, W1 to W10, with full or half occupancies.

In the stage just described cycles of least squares refinement were alternated with electron density and difference syntheses. When the solution of the structure was completed, a few final cycles were carried out. Individual isotropic temperature factors were included in the refined parameters. Unit weights and atomic scattering factors (Cromer and Mann, 1968) for neutral atoms were used throughout. The conventional R-value was 0.12.

Ordering and supercell reflections

The following observations were made upon completion of the process described in the preceding paragraph: (a) the occupancies of the calcium sites Ca5 and Ca6, nearly 1.1Å apart, are mutually exclusive; (b) full occupancy was found for W1, which presents reasonable bond distances to both calcium sites, and W8, which is not linked to calcium cations; half occupancies were found for the other water molecules; (c) these water molecules may be divided into two groups, one with reasonable bond distances to Ca5 and very long or impossibly short distances to Ca6; another with reasonable bond distances to Ca6 and long or impossibly short distances to Ca5; (d) water molecules in the first group present impossible distances to water molecules in the second group: the relative occupancies are thus mutually exclusive.

The fact that the two Ca–H_2O polyhedra occur with equal frequencies implies that there may be an ordering mechanism controlling their distribution. Therefore evidence of possible ordering was carefully searched for.

A doubling of the b parameter was found on long exposure b axis rotation photographs. Careful examination of Weissenberg photographs then indicated that the true cell is triclinic with parameters $a = 9.81$, $b = 14.56$, $c = 22.02$Å, $\alpha = 87.3°$, $\beta = 106.0°$ and $\gamma = 112.8°$, which can be derived from those of the subcell by means of the transformation matrix [110/0$\bar{2}$0/001]. In order to maintain the same orientation of the subcell, an equivalent C centered cell may be chosen, with doubled a and b parameters relative to the subcell parameters. The unit cell data for okenite are given in Table 1, where they are compared with those of the related mineral nekoite.

The supercell reflections, namely those with h, $k = 2n + 1$ relative to the C centered cell (henceforth odd reflections), are extremely weak and somewhat diffuse in the c direction. In order to measure the intensities of a sufficient number of odd reflections a larger crystal was chosen, a lath shaped crystal 0.55 mm long (b direction) and 0.25 mm wide, approximately 0.005 mm thick. The second data set was measured with the same techniques used for the preceding measurements and using the same θ range 3–20°; however up to three scans were made for reflections in the range $3° \leq \theta \leq 12°$, to improve accuracies of weak reflections. After correcting for Lorentz and polarization factors, the reflections with h, $k = 2n$, namely the subcell reflections (henceforth even reflections), were merged with those collected in the preceding data set. Two more refinement cycles of the "average" structure were carried out: the final R value for a total of 1808 even reflections with $F_{0bs} \geq 6 \sigma(F_{obs})$ was 0.138.

Table 1. Unit cell data of okenite and nekoite

OKENITE subcell	P $\bar{1}$	a = 9.69(1)	b = 7.28(1)	c = 22.02(4) Å
		α = 92.7(2)°	β = 100.1(3)°	γ = 110.9(1)°
true cell	C $\bar{1}$	a = 19.38(2)	b = 14.56(2)	c = 22.02(4) Å
		α = 97.7(2)°	β = 100.1(3)°	γ = 110.9(1)°
	P $\bar{1}$	a = 9.81(1)	b = 14.56(2)	c = 22.02(4) Å
		α = 87.3(2)°	β = 106.0(3)°	γ = 112.8(1)°
NEKOITE	P 1	b = 9.793(5)	c = 7.339(5)	a = 7.558(3)Å
		β =103.50(5)°	γ = 86.53(3)°	α = 111.77(7)°

Table 2. Final atomic parameters in the subcell

Atom in the octahedral chain, tetrahedral chain and tetrahedral sheet.

Atom	x	y	z	$B(\mathring{A}^2)$
Ca1	-0.028(1)	0.509(2)	0.1553(5)	0.9(2)
Ca2	-0.375(1)	0.577(2)	0.1238(5)	0.7(2)
Ca3	-0.383(1)	1.074(2)	0.1248(5)	0.8(2)
Ca4	-0.019(1)	1.014(2)	0.1719(5)	0.7(2)
Si1	-0.147(2)	0.142(2)	0.0241(7)	1.0(3)
Si2	-0.147(2)	0.715(2)	0.0232(8)	1.3(4)
Si3	-0.400(2)	0.299(2)	-0.0088(7)	1.1(3)
Si4	-0.266(2)	0.422(2)	0.2617(7)	1.9(3)
Si5	-0.276(2)	0.836(2)	0.2663(7)	1.0(3)
Si6	0.176(5)	0.846(2)	0.2926(7)	0.8(3)
Si7	0.053(3)	0.412(2)	0.2990(7)	0.5(3)
Si8	0.024(2)	1.067(2)	0.3654(7)	0.7(3)
Si9	0.481(2)	1.016(2)	0.2560(7)	0.7(3)
O1	-0.264(4)	0.393(5)	0.190(2)	0.5(6)
O2	-0.134(4)	0.714(5)	0.098(27)	0.9(7)
O3	0.206(4)	0.632(5)	0.128(2)	1.6(7)
O4	0.065(4)	0.800(5)	0.228(2)	2.2(9)
O5	-0.131(5)	0.186(6)	0.096(2)	2.0(9)
O6	0.037(4)	0.323(6)	0.231(2)	2.2(9)
O7	-0.265(4)	0.886(5)	0.197(2)	0.5(7)
O8	0.194(4)	1.100(5)	0.132(2)	1.7(8)
O9	-0.439(4)	0.291(5)	0.061(1)	0.4(7)
O10	0.459(4)	0.226(5)	-0.065(2)	0.5(7)
O11	0.418(5)	0.479(6)	0.178(2)	2.6(9)
O12	0.429(5)	0.976(6)	0.183(2)	1.9(9)
O13	0.002(3)	0.285(5)	0.000(2)	2.2(8)
O14	-0.168(3)	0.917(4)	-0.001(1)	0.1(6)
O15	0.289(3)	0.821(5)	0.014(2)	2.5(8)
O16	0.301(4)	0.459(5)	0.017(2)	0.4(6)
O17	-0.293(4)	0.626(5)	0.280(2)	1.4(7)
O18	-0.104(3)	0.435(5)	0.305(1)	1.2(7)
O19	0.608(4)	0.235(5)	0.284(2)	0.7(7)
O20	0.567(4)	0.866(5)	0.279(2)	1.3(7)
O21	-0.144(4)	0.992(5)	0.318(2)	0.9(7)
O22	0.002(4)	1.042(5)	0.437(2)	1.9(8)
O23	0.101(4)	0.297(5)	0.354(2)	0.6(6)
O24	0.123(4)	0.949(5)	0.348(2)	0.7(6)
O25	0.182(4)	0.644(5)	0.318(2)	0.6(6)
O26	0.347(4)	0.983(5)	0.291(2)	0.8(7)

Atoms in the calcium-water layer

Atom	x	y	z	occupancy	$B(\mathring{A}^2)$
Ca5	0.133(3)	0.896(4)	0.499(1)	0.5	1.8(5)
Ca6	-0.199(3)	0.949(4)	0.479(1)	0.5	2.9(6)
W1	0.265(6)	0.802(8)	0.588(3)	1.0	6.4(14)
W2	-0.067(18)	0.574(22)	0.442(7)	0.5	5.4(42)
W3	0.288(13)	0.768(17)	0.448(5)	0.5	5.2(26)
W4	-0.362(12)	0.806(15)	0.495(5)	0.5	8.0(25)
W5	-0.289(19)	0.613(24)	0.506(7)	0.5	14.8(45)
W6	0.378(16)	0.927(22)	0.474(7)	0.5	13.4(39)
W7	-0.098(20)	0.345(25)	0.550(8)	0.5	14.9(51)
W8	-0.535(10)	0.285(13)	0.399(4)	1.0	13.3(27)
W9	0.420(21)	0.755(27)	0.409(9)	0.5	4.2(55)
W10	0.471(10)	0.618(12)	0.373(4)	0.5	6.2(35)

Table 2 gives the final atomic parameters relative to the subcell and the isotropic thermal parameters, as well as the occupancy factors for the atoms in the calcium–water layer. Observed and calculated structure factors for the subcell reflections are listed in Table 3.[1]

[1] To obtain a copy of Table 3, order Document AM-83-219 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

The odd reflections were subsequently used to select and test the correct ordering scheme (see section on "water–calcium layer"). In the following sections the structure of okenite is described and discussed relative to the translations a and b of the subcell, which are valid for the whole structure, apart from the calcium–water layer which will be discussed later relative to the true periodicities of the C centered cell.

Description and discussion of the structure

The structure of okenite displays some novel components, which deserve separate discussion after a brief description of the whole structure, which is composed of the following structural units: (a) a double three-repeat chain C, with composition $(Si_6O_{18})^{-8}$ and characterized by four- and six-membered rings (Fig. 1); (b) tetrahedral sheets S, with composition $(Si_6O_{15})^{-6}$, characterized by five- and eight-membered rings (Fig. 2); (c) octahedral double chains O, formed by two strands of octahedra.

These structural units are connected by corner sharing, as illustrated in Figures 1 and 2, resulting in a complex layer. It can be described by the symbol SOCOS in terms of the symbols used for the separate components, and has composition $[Ca_8(Si_6O_{16})(Si_6O_{15})_2(H_2O)_6]^{-4}$. Such complex layers alternate in the structure with sheets occupied by calcium cations and water molecules $[Ca_2(H_2O)_{12}]^{+4}$.

Octahedral chain

The octahedral ribbon can be described as formed by two strands of edge-sharing octahedra. Such an arrangement of octahedra is very different from that hypothesized by Mamedov and Belov (1958), who proposed a continuous sheet of octahedra with a vacant site every fourth octahedron. It also differs from that found by Alberti and Galli (1980) in the crystal structure of nekoite; in fact, in their ribbon one strand is characterized by alternate full and empty octahedral positions. In okenite the octahedral ribbon is sandwiched between the tetrahedral sheet, through the sharing of five oxygen atoms, and the tetrahedral chains. One chain shares three apical oxygen atoms, whereas another shares a lateral oxygen atom, namely O10 (Fig. 1); thus three, out of the twelve independent oxygen atoms which coordinate the four calcium cations in the ribbon, are not shared with silicon and correspond to water molecules. One of them (O11) is located on the side of the tetrahedral sheet, two (O3 and O8) are located on the side of the tetrahedral chains.

The bond distances in the octahedra are given in Table 4: they are quite regular, varying within the ranges 2.32–2.41Å, 2.24–2.48Å, 2.30–2.52Å, 2.27–2.46Å for the Ca1, Ca2, Ca3 and Ca4 octahedra respectively.

Three-repeat double chain

Silicate chains were classified by Liebau (1972) according to their multiplicity (the number of shared chains) and their periodicity (the number of tetrahedra in the identity
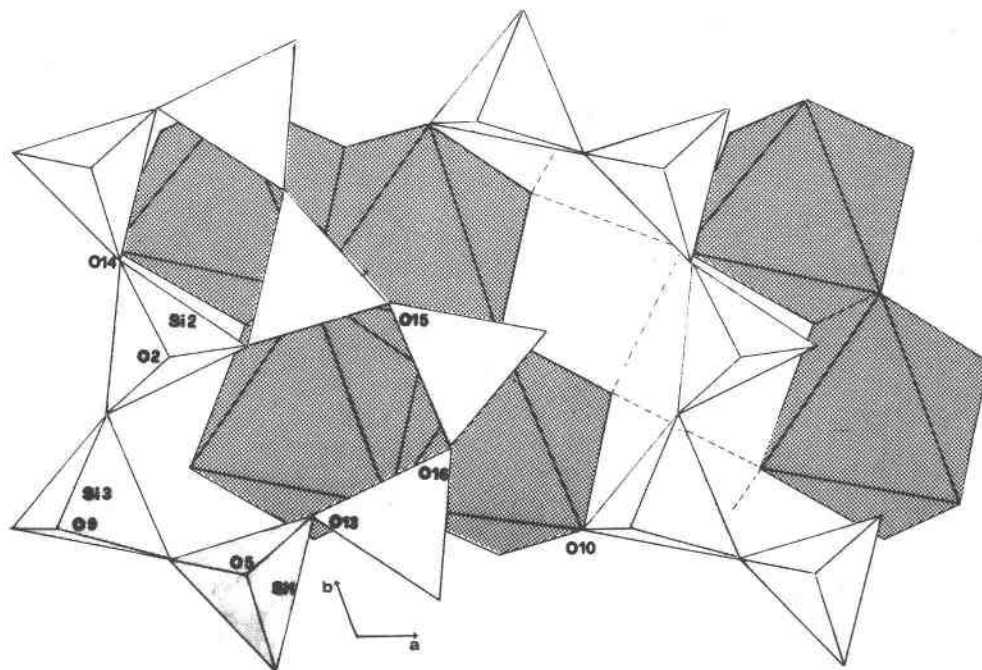
Fig. 1. Projection along c^* of the crystal structure of okenite included in a slab between $z \sim -0.20$ and $z \sim 0.10$. The figure shows the connections between tetrahedral chains and octahedral ribbons; on the right side one half of the tetrahedral double chain and one half of the octahedral ribbon are drawn to show their connection to adjacent chains. Hydrogen bonds are indicated by the dashed lines.
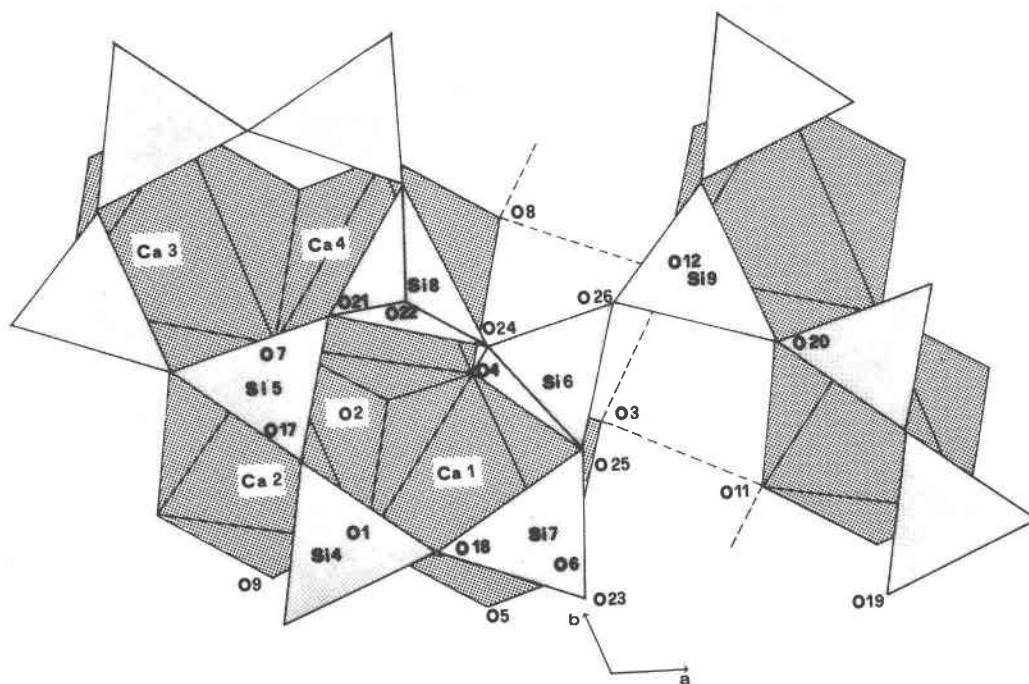

Fig. 2. Projection along c^* of the crystal structure of okenite included in a slab between $z \sim 0.10$ and $z \sim 0.44$. The figure shows the connection between the tetrahedral sheet and the octahedral ribbons. O2, O5 and O9 indicate the positions of the common corners of the octahedral ribbon and the underlying double chain (Fig. 1). Hydrogen bonds are indicated by the dashed lines.

period of the chain). In his classification the silicate chain of okenite may be defined as a three-repeat double chain (Dreier–Doppelkette): it is made up by pairing two wollastonite-like chains which have tetrahedral vertices that point in opposite directions. There are different ways of pairing two wollastonite chains. In one case a wollastonite-like chain is doubled by a symmetry plane passing through the apical oxygen atoms: thus each tetrahedron in a chain shares an oxygen atom with a tetrahedron in the other chain, giving rise to the ribbon with four-membered rings which is found in the structure of epididymite (Robinson and Fang, 1970). In another case two wollastonite-like chains may be paired by sharing one oxygen every third tetrahedron, giving rise to the ribbon, characterized by eight-membered rings, which was found in the structure of xonotlite (Mamedov and Belov, 1956). Finally, two wollastonite–like chains may be paired by sharing two out of three tetrahedra in each chain: the three-repeat

double chain of okenite is thus created; it is characterized by alternating four- and six-membered rings. The two shared single chains are related by centers of symmetry and their apical oxygen atoms are pointed in opposite directions, bonding them to two symmetry related octahedral ribbons.

It seems useful to recall that two series were recognized by Takéuchi (1976) in pyroxenoid minerals. The two pyroxenoid series, $w–p$ and $p–p$ according to Takéuchi (1976), present quite different tetrahedral–octahedral stacking: the tetrahedral triplets, namely the C–shaped clusters of three tetrahedra, occur on the same octahedron in the $w–p$ series, whereas they occur on a tetrahedral void in the $p–p$ series; as a consequence the tetrahedral–octahedral linkage at the basal oxygens of tetrahedra is opposite in the two series, antiparallel in $p–p$ series if the relationship in the $w–p$ series is defined as parallel. The connection between tetrahedral and octahedral ribbons in okenite is quite similar to that found in the $p–p$ series of pyroxenoids. By repeated application of such a stacking mechanism, a double-chain silicate structure with composition $Ca_4Si_6O_{15} \cdot 4H_2O$ could be obtained.

Tetrahedral sheet

The tetrahedral sheet is formed by two independent three-repeat chains (dreierketten) which link together to form ribbons of five-membered rings. The ribbons are jointed laterally with translationally-equivalent ribbons to make up eight-membered rings (Fig. 2). The model proposed by Mamedov and Belov (1958) for the tetrahedral sheet in okenite and nekoite, as well as the actual sheet of nekoite (Alberti and Galli, 1980) are similarly characterized by five- and eight-membered rings. However the three sheets are topologically distinct: in the hypothetical sheet of Mamedov and Belov (1958), with point symmetry $2/m$, the tetrahedra point in opposite directions in equal numbers; in nekoite the sheet, with point symmetry m, has four tetrahedra with vertices pointing in one direction and two in the opposite direction; in okenite the sheet, with point symmetry 1, has five tetrahedra with vertices pointing down and one with vertex pointing up.

The three sheets may be described as composed of three-repeat chains, but whereas that hypothesized by Mamedov and Belov (1958) is made of one kind of chain, two different kinds of chain are present in those actually found in nekoite and okenite.

The bond distances for the tetrahedra are given in Table 4; the relatively high standard deviations prevent any meaningful discussion of bond distances and angles.

Complex layer SOCOS

The tetrahedral sheets S, the octahedral ribbons O and the tetrahedral double chains C are linked by corner sharing to give the complex layer SOCOS, with composition $[Ca_8(Si_6O_{16})(Si_6O_{15})_2(H_2O)_6]^{-4}$. The crystal structure of okenite thus not only possesses unique tetrahedral

Table 4. Si-O and Ca-O bond lengths, in Å, in the complex layer

Si1 tetrahedron		Si2 tetrahedron		Si3 tetrahedron	
Si1-O5	1.58(5)	Si2-O2	1.63(4)	Si3-O9	1.65(4)
-O13	1.64(3)	-O13[II]	1.58(3)	-O10[III]	1.59(4)
-O14[I]	1.63(3)	-O14	1.65(3)	-O15[II]	1.62(3)
-O15[II]	1.60(3)	-O16[II]	1.64(4)	-O16[II]	1.71(4)
mean	1.61	mean	1.63	mean	1.64
Si4 tetrahedron		**Si5 tetrahedron**		**Si6 tetrahedron**	
Si4-O1	1.59(4)	Si5-O7	1.60(4)	Si6-O4	1.56(4)
-O17	1.64(4)	-O17	1.54(4)	-O24	1.65(4)
-O18	1.66(4)	-O20[III]	1.67(4)	-O25	1.62(4)
-O19[III]	1.63(4)	-O21	1.60(4)	-O26	1.62(4)
mean	1.63	mean	1.60	mean	1.61
Si7 tetrahedron		**Si8 tetrahedron**		**Si9 tetrahedron**	
Si7-O6	1.57(4)	Si8-O21	1.65(4)	Si9-O12	1.58(5)
-O18	1.62(4)	-O22	1.64(4)	-O19[IV]	1.64(4)
-O23	1.60(4)	-O23	1.63(3)	-O20	1.64(4)
-O25	1.68(3)	-O24	1.57(4)	-O26	1.57(4)
mean	1.62	mean	1.62	mean	1.61
Ca1 octahedron		**Ca2 octahedron**		**Ca3 octahedron**	
Ca1-O1	2.41(4)	Ca2-O1	2.39(4)	Ca3-O1[IV]	2.44(4)
-O2	2.39(4)	-O2	2.38(3)	-O5[IV]	2.49(4)
-O3	2.32(3)	-O7	2.48(4)	-O7	2.52(4)
-O4	2.38(4)	-O9	2.27(3)	-O9[IV]	2.30(3)
-O5	2.41(4)	-O10[II]	2.24(4)	-O10[II]	2.30(4)
-O6	2.33(4)	-O11[III]	2.41(5)	-O12[III]	2.34(4)
mean	2.37	mean	2.36	mean	2.40

Ca4 octahedron	
Ca4-O2	2.44(3)
-O4	2.32(4)
-O5	2.46(5)
-O6	2.38(4)
-O7	2.40(4)
-O8	2.27(4)
mean	2.38

Symmetry code				
I	atom at	x	$-1+y$	z
II	atom at	$-x$	$1-y$	$-z$
III	atom at	$-1+x$	y	z
IV	atom at	x	$1+y$	z

Table 5. Valence bond sums for the oxygen atoms in the complex layer; values corrected for the hydrogen bond contributions are given in parentheses

Anion	Cations bonded to the anion	Bond valence sum
O1	Ca1 Ca2 Ca3 Si4	2.04
O2	Ca1 Ca2 Ca4 Si2	1.97
O3	Ca1	0.35 (0.10)
O4	Ca1 Ca4 Si6	1.79
O5	Ca1 Ca3 Ca4 Si1	1.98
O6	Ca1 Ca4 Si7	1.78
O7	Ca2 Ca3 Ca4 Si5	1.91
O8	Ca4	0.38 (0.19)
O9	Ca2 Ca3 Si3	1.73
O10	Ca2 Ca3 Si3	1.87
O11	Ca2	0.31 (-0.07)
O12	Ca3 Si9	1.42 (1.87)
O13	Si1 Si2	2.04
O14	Si1 Si2	1.92 (2.10)
O15	Si1 Si3	2.06 (2.18)
O16	Si2 Si3	1.84 (1.92)
O17	Si4 Si5	2.10
O18	Si4 Si7	1.94
O19	Si4 Si9	1.94
O20	Si5 Si9	1.81
O21	Si5 Si8	1.94
O22	Ca5 Ca6 Si8	1.72
O23	Si7 Si8	2.02
O24	Si6 Si8	2.10
O25	Si6 Si7	1.86
O26	Si6 Si9	2.06

chains and sheets but also has a remarkably new association of chains and sheets.

Tetrahedral structures were classified by Zoltai (1960) into four major types, depending on the extension of the tetrahedral structures to infinity in zero-, one-, two- and three-dimensions: isolated groups, chains and rings, sheets, frameworks. To allow for the theoretical possibility of a crystal to be composed of two or more different types of tetrahedral components, a fifth type was established by Zoltai (1960), mixed-types of tetrahedral structures. Okenite is so far the only known member in that structural class.

Valence balance and hydrogen bonding in the complex layer

The balance of the bond valences was computed for all the oxygen atoms in the complex layer. The calculations were made according to the method proposed by Donnay and Allmann (1970): O22 was assumed to be bonded to two distinct inversion pairs of Ca5 and Ca6 cations, each having half occupancy. The results are reported in Table 5. They confirm that O3, O8 and O11 are water molecules and show that, among the oxygen atoms of the tetrahedral sheet, only O12 receives a sum of bond strengths which

differs greatly from 2.0, namely 1.42. A list of all the short distances between oxygen atoms not bonded to the same cation strongly indicated that the three water molecules are engaged in a system of hydrogen bonding, which also involves O12 and links together adjacent octahedral ribbons. From that list the system of hydrogen bonding which gives the best bond valence sums was deduced (Fig. 3): in calculating hydrogen bond strengths, use was made of the correlation between strength and length established by Zachariasen (1963). The values given in parentheses in Table 5 are the bond valence sums corrected for the hydrogen bond contributions, which remove the valence imbalances for oxygen anion O12 and water molecules O3, O8 and O11.

Water-calcium layer

The complex layers SOCOS alternate in the structure with interlayer sheets occupied by calcium cations and water molecules. Whereas the complex layer was described above relative to the *a* and *b* translations of the subcell, the whole structure must be referred to a triclinic *C* centered cell with doubled *a* and *b* parameters (Table 1): such doubling is dependent on the ordering of calcium cations and water molecules in the interlayer sheet, as was previously suggested on the basis of the refinement with subcell reflections. Two distinct ordering schemes may be postulated: (1) pairs of edge-sharing Ca5 polyhedra alternate on symmetry centers with pairs of edge sharing Ca6 polyhedra; (2) edge sharing Ca5 and Ca6 polyhedra alternate with symmetry-related edge-sharing Ca6 and Ca5 polyhedra. Both ordering schemes were tested using the reflections with $h, k = 2n + 1$, namely the superstructure reflections, with $F_{obs} \geq 6 \sigma (F_{obs})$ (only 57 reflections). The test was made by comparing the ob-
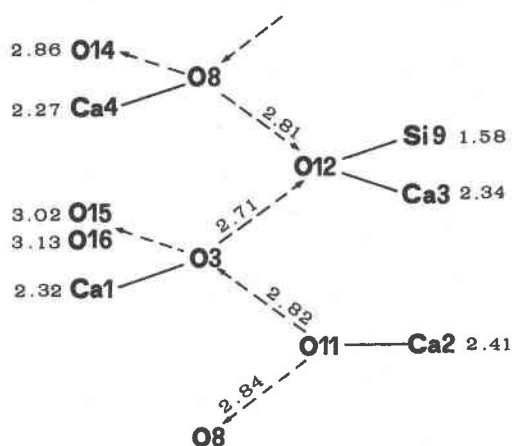

Fig. 3. The hydrogen bond system within the complex layer. Hydrogen bonds are indicated by arrows which go from the donor to the acceptor atom. O3 is engaged in a bifurcated hydrogen bond with O15 and O16. Bond lengths, in Å, are indicated near the cations; hydrogen bond distances, in Å, are indicated near the acceptor atoms or over the arrows.

Table 7. Final positional coordinates in the C cell and thermal parameters of the atoms in the interlayer sheet

Atom	x	y	z	B(Å²)
Ca5	0.066(1)	0.448(2)	0.499(1)	1.7(4)
Ca6	0.401(1)	0.475(2)	0.480(1)	2.9(5)
W1	0.129(7)	0.402(9)	0.576(6)	8.7(39)
W2	-0.032(5)	0.285(7)	0.455(5)	10.7(25)
W3	0.140(5)	0.378(7)	0.447(4)	6.3(25)
W4	0.188(4)	0.558(5)	0.506(4)	12.1(17)
W5	0.358(5)	0.313(6)	0.506(4)	12.1(23)
W6	0.319(5)	0.551(6)	0.533(4)	11.9(21)
W7	0.455(5)	0.661(7)	0.556(5)	13.4(25)
W8	0.226(7)	0.631(9)	0.401(7)	10.2(42)
W9	0.284(5)	0.373(7)	0.406(5)	11.4(25)
W10	0.270(5)	0.691(7)	0.627(5)	2.0(25)
W1t	0.363(7)	0.599(9)	0.402(6)	3.8(39)
W8t	0.269(7)	0.365(9)	0.590(7)	12.8(42)

served structure factors with those calculated using only the atoms of the interlayer sheet for the two distinct ordering schemes. The comparison indicated that scheme (1) is the correct one.

The coordinates of the various atoms in the C cell were obtained as follows: from each atom A of the complex layer SOCOS at (x, y, z) in the subcell (Table 2), two atoms, A at coordinates $(x/2, y2, z)$ and At at coordinates $(x/2 + 1/2, y/2, z)$ in the C cell, were generated; the coordinates of atoms in the interlayer sheet were introduced according to ordering scheme (1). Three refinement cycles were carried out, using 2108 even and 207 odd reflections with $F_{obs} \geq 2\ \sigma(F_{obs})$. In the course of the refinement only the positional and thermal parameters of the atoms in the interlayer sheet were allowed to vary, whereas the atoms of the complex layer were kept fixed with positions and B values corresponding to those obtained in the preceding refinement with subcell reflections. The final R value was 0.16. The relatively high value of R and the discrepancies between calculated and observed structure factors for some odd reflections are easily explained if we recall that the structure factors of odd reflections, while mainly dependent on atoms in the interlayer sheet, are also related to deviations from strict translational symmetry of the complex layer SOCOS. However, a full refinement, including the atoms of the complex layer, was prevented by the small number of reflections, the inaccuracies in intensity data due to the poor quality of the crystals, and the high correlations between translationally pseudosymmetric atoms. The observed and calculated structure factors for C cell reflections are listed in Table 6[2].

Table 7 gives the final positional and thermal parameters of the atoms in the interlayer sheet in the C centered cell: the pairs W1, W1t and W8, W8t are distinct atoms in the true cell but their positions correspond to nearly

[2] To obtain a copy of Table 6, order Document AM-83-220 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

coincident sites in the subcell. The main structural features of the interlayer sheet are illustrated in Figure 4 in terms of calcium polyhedra. Two edge-sharing Ca5 octahedra are located across a symmetry center, with two symmetry-related O22 anions at the common edge. O22 is the apical oxygen atom in the Si8 tetrahedron. The octahedral coordination around Ca5 is completed by four water molecules W1, W2, W3 and W4. Similarly, two edge-sharing Ca6 polyhedra are located across an adjacent symmetry center, with two inversion-related O22t anions defining the common edge. The polyhedron around Ca6 is completed by the five water molecules W1t, W5, W6, W7 and W9. Three other water molecules W8, W8t and W10, not directly linked to calcium cations, are engaged in a complex system of hydrogen bonds, which involve all the water molecules in the sheet and provide interconnection of the polyhedral pairs (Fig. 4). The whole sheet is anchored to the complex layer, not only through O22 and O22t anions, but also through hydrogen bonding to oxygen anions of the tetrahedral sheet.

Table 6 gives the bond lengths in the calcium polyhedra, W⋯W distances less than 3.1Å and W⋯O distances less than 3.0Å.

Thermal behavior and crystal chemical considerations

Okenite is the first example of a silicate having both tetrahedral chains and sheets. A general view of the structure, showing the interconnections of the various building blocks, is given in Figure 5. The crystal chemical formula which best summarizes the result of the structure analysis is

$$[Ca_8(Si_6O_{16})(Si_6O_{15})_2(H_2O)_6]^{-4}\ [Ca_2(H_2O)_9 \cdot 3H_2O]^{+4}$$

or, more compactly, $Ca_{10}Si_{18}O_{46} \cdot 18H_2O$.

In a recent paper Phadke and Kshirsagar (1980) presented three new analyses of okenite samples from three different localities in India, Bombay, Nasik and Poona, and compared them with the chemical analyses of Christie (1925) and by Sukheswala $et\ al.$ (1974) for okenite from Bombay and Poona. The cell content which was derived from these analyses, calculated on the basis of forty-six oxygen atoms, was $Ca_{10}Si_{18}O_{46} \cdot 19H_2O$ for four analyses, whereas twenty water molecules were calculated from the old analysis by Christie (1925) for okenite from Bombay and the analysis by Sukheswala $et\ al.$ (1974) for okenite from Nasik.

In the same paper Phadke and Kshirsagar (1980) described the dehydration and thermal decomposition of okenite from all the three localities. In all the analyzed samples the DTA and DTG patterns were similar and contained three peaks, at 100, 190, and 370°C. These can be correlated with the three kinds of structural water in okenite: the water molecules as W8, W8t and W10 not linked to cations, the water molecules around Ca5 and
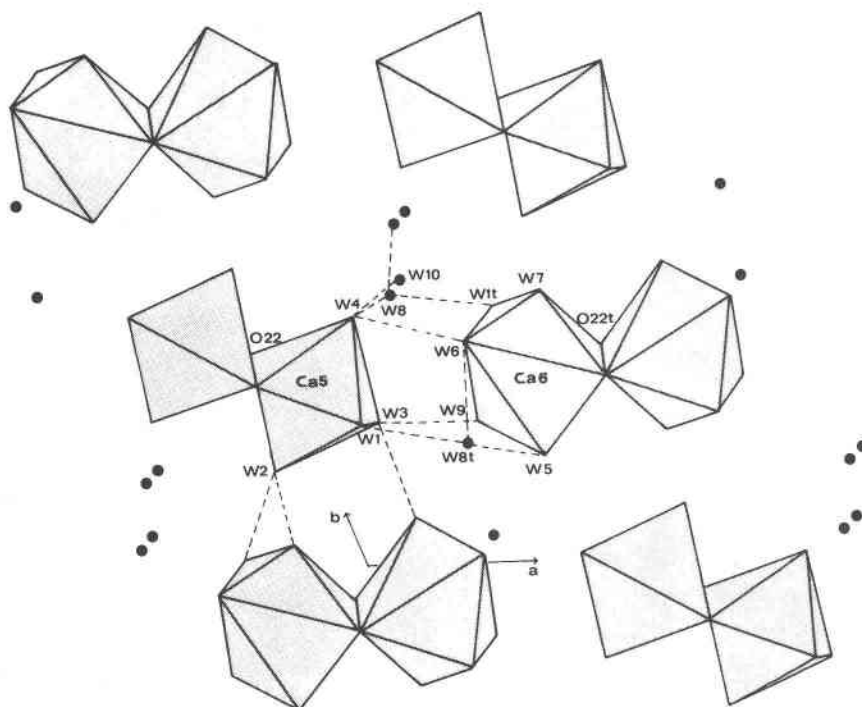
Fig. 4. Interlay sheet viewed along *c**. Coordination polyhedra around Ca5 and Ca6 cations are drawn. Filled circles indicate water molecules not linked to calcium cations. Dashed lines indicate W⋯W hydrogen bonds.

Ca6 in the interlayer sheet, and finally the water molecules in the octahedral ribbons.

Phadke and Kshirsagar (1980), on the basis of the sharp exothermic peak in the DTA curves, maintained that the conversion of anhydrous okenite to wollastonite and cristobalite ($Ca_{10}Si_{18}O_{46} \rightarrow 10\ CaSiO_3 + 8\ SiO_2$) "begins at 855°C, with a maximum at 890°C and completion at about 915°C". Gard and Taylor (1956) conclusively demonstrated, by means of electron diffraction studies, that the conversion is a topotactic reaction, "in which the okenite *b*-direction becomes the wollastonite *b*-direction and the okenite (001) plane becomes, at least approximately, the wollastonite (001)", assuming for wollastonite the conventional setting with $a = 7.94$, $b = 7.32$, $c = 7.07$Å, $\alpha = 90°2'$, $\beta = 95°22'$, $\gamma = 103°20'$. The topotactic character of the transformation is quite in keeping with the present structural results; not only are octahedral ribbons and three-repeat chains present in both okenite and wollastonite, but their relative orientation is similar in both structures. The transformation therefore does not require a full rearrangement of the structure but could proceed through a separation of the three-repeat chains and a readjustment of large, nearly intact structural blocks.

It seems worthwhile to recall that while okenite and nekoite, as well as xonotlite and foshagite, transform to wollastonite on heating, truscottite and gyrolite transform to pseudowollastonite. The presence of octahedral ribbons in the first group and of continuous layers of calcium octahedra in truscottite (Merlino, 1972) and gyrolite (Merlino, in preparation) appears to be the determining factor.
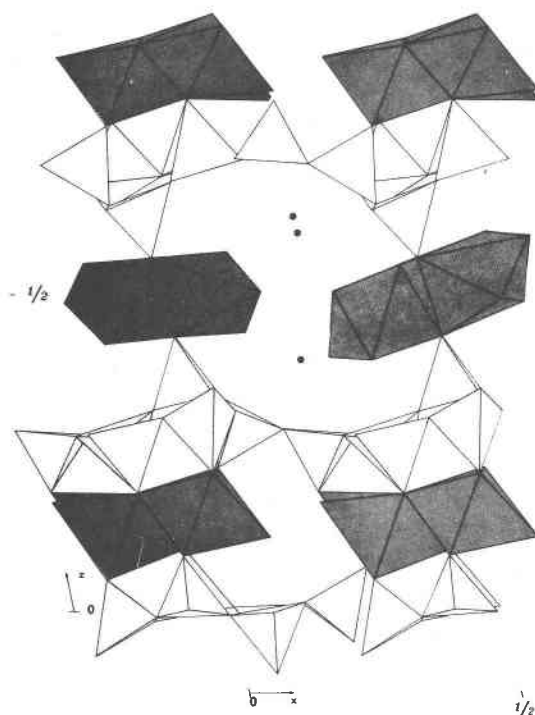
The detailed mechanisms of thermal transformation of

Fig. 5. Crystal structure of okenite as viewed along *b*.

Table 8. Bond lengths and hydrogen bond distances, in Å, in the interlayer sheet. W···W and W···O distances, less than 3.1 Å and 3.0 Å respectively, are reported

Ca5 polyhedron		Ca6 polyhedron		Water-water distances<3.10 Å	
Ca5-O22	2.26	Ca6-O22t	2.21	W1···W8t	2.91
-O22^I	2.21	-O22t^{II}	2.37	W2···W7	2.92
-W1	2.18	-W5	2.34	W2···W1t	2.79
-W2	2.47	-W6	2.63	W3···W5^{III}	3.01
-W3	2.44	-W7	2.87	W4···W6	2.55
-W4	2.31	-W9	2.46	W4···W8	2.70
mean	2.31	-W1t	2.74	W4···W10	3.03
		mean	2.52	W5···W8t	2.99
				W6···W8t	2.96
				W8···W10^{IV}	2.68

Symmetry code					Water-oxygen distances < 3.0 Å	
I	atom at	-x	1-y	1-z		
II	atom at	1-x	1-y	1-z	W3···O25	2.83
III	atom at	0.5-x	0.5-y	1-z	W7···O24t^{II}	2.94
IV	atom at	0.5-x	1.5-y	1-Z	W8···O26	2.88
V	atom at	-0.5+x	0.5+y		W9···O20	2.96
					W10···O20t^{II}	2.89
					W10···O25t^{II}	2.84
					W1t···O19t^V	2.73

okenite deserve further study; X-ray diffraction and electron microscopy studies are necessary on the tranformation products at all stages of dehydration. For these phases reasonable structural models could be postulated on the basis of the structure of okenite. In this context it is proper to observe that various crystals of okenite from Bombay showed the presence of a second phase, which has the same a and b parameters of okenite, but a shorter c parameter ($\simeq 20.5$Å). It gives elongated reflections, besides the sharp reflections of okenite, in Weissenberg photographs obtained with b as rotation axis. This phase is at present under investigation in order to determine its precise relation to okenite and its dehydration products.

Another interesting field of study is related to the pseudosymmetry and possible polytypism in okenite. Various kinds of stacking faults could occur in okenite: inversion in the ordering sequence of calcium polyhedral pairs could occur in the interlayer sheet; alternatively, the tetrahedral sheets and chains could be displaced because of the strong pseudotranslation, 3.64Å, of the octahedral ribbon. Electron microscopy studies are necessary in order to determine the existence of possible stacking faults in the mineral and to define possible polytypic varieties.

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