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THE CRYSTAL STRUCTURE OF CARLETONITE, $KNa_4Ca_4Si_8O_{18}(CO_3)_4(F, OH) \cdot H_2O$, A DOUBLE-SHEET SILICATE

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ABSTRACT

Carletonite, a new mineral from Mont St. Hilaire, Quebec, is tetragonal *P4/mbm*, with a = 13.178 Å, c = 16.695 Å, and z = 4. The structure was solved by three-dimensional Patterson synthesis and refined by full-matrix least-squares method using anisotropic temperature parameters. The final R index for 1085 "observed" reflections is 0.0368.

Carletonite has a layer structure. Within one period of c, it contains a silicate layer of composition $NaKSi_8O_{18} \cdot H_2O$, a carbonate layer of composition $NaCO_3 \cdot \frac{1}{2}H_2O$ and two carbonate layers of composition $NaCa_2CO_3(F, OH)_{0.5}$. In the silicate layer two apophyllite-like Si_4O_{10} single-sheets based on four- and eight-membered rings share half their non-bridging oxygen atoms to form an Si_8O_{18} double-sheet.

Least-squares refinement of occupancy factors confirmed deficiencies of Na, K, Ca, and CO_3 in carletonite, as were indicated by chemical analyses. The water content from chemical analyses is considerably higher than that derived from structure analysis. The excess water may be accommodated in large interstices of the structure and in vacant sites of the CO_3 groups, and it may have the function of stabilizing the defect structure.

INTRODUCTION

Carletonite is a recently described new mineral from Mont St. Hilaire, Quebec (Chao, 1971a). Its chemical formula, based on two chemical analyses, is $K_{0.74}Na_{3.56}Ca_{3.74}Mg_{0.03}Si_{7.89}Al_{0.11}O_{18}(CO_3)_{3.65}F_{0.41} \cdot 2.05H_2O$. It is tetragonal and belongs to the space group *P4/mbm*. Cell parameters derived from Weissenberg and precession photographs were refined by the least-squares method using X-ray powder diffraction data obtained at room temperature with CuK_α radiation (λ = 1.5418 Å), a 114.59 mm camera, and metallic Si as an internal standard. The refined values are a = 13.178(3) Å and c = 16.695(4) Å. With Z = 4, the density calculated from the chemical analyses is 2.426 g/cm^3, in reasonable agreement with the measured value, 2.45(1) g/cm^3.

Carletonite has perfect basal cleavage similar to apophyllite. In addition, the a parameter of carletonite (13.178 Å) is comparable to $\sqrt{2}$ times the a parameter of apophyllite (8.965 Å, Chao, 1971b), suggesting structural similarity between the two minerals. However, the Si to O ratio of 8:18 in carletonite indicates a new type of layer structure, probably formed by two apophyllite-like Si_4O_{10} sheets sharing half of their unshared oxygen atoms. To test this hypothesis, a structure determination of carletonite was carried out.

EXPERIMENTAL PROCEDURES

Because attempts to prepare spheres from cleavage fragments of carletonite consistently yielded saucer-shaped grains due to the perfect basal cleavage, a small equidimensional fragment approximately 0.06 × 0.06 × 0.06 mm was used in this study. A manual Supper equi-inclination single-crystal diffractometer with a scintillation counter was employed to collect the X-ray diffraction intensities, using MoK_α radiation ($\lambda = 0.7107$ Å). All reflections with positive *hkl* up to $\sin\theta = 0.40$ were measured by the fixed-2θ ω-scan method, using scanning speed of 2°/min. Intensities of the symmetry-related *hkl* and *khl* pairs were averaged. The agreement between $I(hkl)$ and $I(khl)$ is within 5 percent, except for some very weak reflections for which the discrepancies are as large as 50 percent. A total of 1220 independent reflections were obtained. Of these, 135 reflections have net intensities less than three times the square root of the background intensities and were designated "unobserved." These were arbitrarily assigned half the background intensities. Lorentz and polarization corrections were made in the usual manner. No attempt was made to correct for absorption because the small size of the crystal used ($\mu r = 0.04$).

For subsequent calculations of structure factors, scattering factors of Si^{4+}, Al^{3+}, C^{3+}, Ca^{2+}, Na^+, K^+, C°, O^-, and F^- from the *International Tables for X-ray Crystallography* (1962) were used.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

A three-dimensional Patterson synthesis was used in the solution of the structure. Over ninety percent of the maxima in the Patterson map could be accounted for by three atoms in the general positions and one atom in a special position 4*f* in the space group *P*4/*mbm*. These were assigned to Ca, Si(1), Si(2), and K on the basis of relative peak heights. Three cycles of least-squares refinement of these four atoms reduced the *R* index from the initial value 0.51 to 0.46. Successive three-dimensional Fourier syntheses were then calculated from the contributions of all atoms already located, each revealing a few more lighter atoms, until all atoms, except H_2O(12), were located and identified. The identification of atoms was primarily based on relative peak heights on the Fourier maps and consideration of the interatomic distances and coordination. Six cycles of full-matrix least-squares refinement of all these atoms with individual isotropic temperature factors and full site-occupancy resulted in a *R* index 0.070.

A difference synthesis was computed, revealing a maximum of approximately $5e/\text{Å}^3$ at $x = 0.45$; $y = 0.05$; $z = 0$, at the intersection of two mirror planes. Because the charge balance was already satisfied by the rest of the atoms, it was assumed to be a water oxygen, H_2O(12). Its site is only 2.04 Å away from its symmetry-equivalent site about the two-fold axis, and therefore this H_2O molecule must be assumed to be disordered, occupying only one of the two sites in any one cell.

Site-occupancy factors were then introduced as least-squares variables, still with isotropic temperature factors for all twenty-two atoms including $H_2O(12)$. The scattering factor for F was adjusted to the weighted mean scattering factors of 0.41 F^- and 0.59 O^-. All Al was assigned to Si(2) because all four oxygen atoms are shared in the Si(1) tetrahedron whereas only three are shared in the Si(2) tetrahedron and the mean Si–O distance in the Si(2) tetrahedron is 0.01 Å larger than that in the Si(1) tetrahedron. The small amount of Mg, presumably present in substitution for Ca, was ignored. After two cycles of refinement, the *R* index fell to 0.056. The introduction of site-occupancy factors in the least-squares refinement did not affect the positional parameters, but significantly changed the temperature factors.

The refinement was continued using site-occupancy factors and anistropic temperature factors. Due to limitations of the computer available to the author, only eleven atoms were refined at one time; the rest were held unchanged. Eight cycles of refinement reduced *R* to 0.050. At this stage of the structure determination bond valences were calculated (Donnay and Allmann, 1970), revealing that the assignment of $H_2O(11)$ and (F, OH) had to be reversed. After this was corrected another six cycles of least-squares refinement were executed and the *R* index rapidly decreased to a final value 0.0368 for 1085 observed reflections and 0.0427 for all 1220 reflections. The final shifts of the parameters were all less than 10^{-6}. The coefficients of correlation between the occupancy factor and the principal temperature parameters for all atoms range from 0.397 to 0.772. The final atomic positions, thermal parameters, and occupancy factors are listed in Table 1. The observed and calculated structure factors are given in Table 2[1]. A compilation of some important distances and angles is given in Table 3.

The final occupancy factors for the carbon atoms are considerably larger than 0.9, the expected value calculated from the chemical analysis. This was obviously due to the inexact approximation of the carbon scattering curve by C^{3+}. It was therefore decided to test the refinement of the structure using the C° scattering curve. After eight more cycles of least-squares refinement the *R* index increased slightly from the previous value 0.0427 to 0.0432 for all reflections. The positional parameters for the carbon atoms and all parameters for the

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[1] Table 2 may be ordered as NAPS Document 01771 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, N.Y. 10022; remitting in advance $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.

TABLE 1

Final atomic fractional coordinates, thermal parameters (x 10^5) and occupancy factors.

Thermal parameters are in the form: $esp[-(h^2B_{11}+k^2B_{22}+\ell^2B_{33}+2hkB_{12}+2h\ell B_{13}+2k\ell B_{23})]$.

e.s.d.'s in parentheses.

	Occupancy factor	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si(1)	.965(6)	.0731(1)	.2644(1)	.4077(1)	102(8)	124(8)	80(4)	-28(10)	-12(6)	-22(8)
Si(2)*	.972(6)	.2162(1)	.1189(1)	.3077(1)	114(8)	105(8)	85(5)	21(10)	-4(8)	11(8)
Ca	.940(4)	.0604(1)	.1773(1)	.1416(0)	98(5)	96(5)	73(3)	-2(8)	-2(6)	0(6)
K	.882(8)	½	0	.2962(1)	291(23)	B_{11}	227(10)	---	---	---
Na(1)	.923(14)	0	0	.2754(2)	138(34)	B_{11}	153(15)	---	---	---
Na(2)	.905(11)	.1399(3)	.6399(3)	.1424(2)	247(29)	B_{11}	179(12)	-256(27)	-130(35)	$-B_{13}$
Na(3)	.925(14)	.2227(4)	.2773(4)	0	221(38)	B_{11}	81(14)	-131(37)	---	---
C(1) (C^{3+})	1.098(34)	.2127(5)	.0572(5)	0	153(39)	171(46)	116(25)	38(59)	---	---
(C^o)	.756(14)	.2127(4)	.0572(4)	0	-89(36)	-51(39)	-25(23)	51(57)	---	---
C(2) (C^{3+})	1.184(37)	.1197(7)	.3803(7)	.1674(4)	257(71)	B_{11}	180(26)	-15(67)	17(68)	$-B_{13}$
(C^o)	.785(20)	.1196(7)	.3804(7)	.1674(4)	-5(56)	B_{11}	14(24)	-20(60)	27(64)	$-B_{13}$
O(1)	1.014(10)	.1475(2)	.1807(2)	.3722(2)	322(23)	298(22)	183(13)	32(33)	28(26)	-86(27)
O(2)	1.004(10)	.2718(2)	.0308(2)	.3599(2)	246(21)	207(20)	156(12)	2(29)	-49(26)	13(23)
O(3)	.991(10)	.1517(2)	.0783(2)	.2357(2)	158(20)	170(20)	138(12)	-8(27)	-12(23)	-8(24)
O(4)	1.019(15)	.3072(4)	.1928(4)	.2776(2)	216(41)	B_{11}	122(16)	-9(41)	-60(47)	$-B_{13}$
O(5)	1.005(15)	.1251(5)	.3749(5)	.4020(3)	234(42)	B_{11}	177(18)	-63(44)	2(52)	$-B_{13}$
O(6)	1.025(15)	.0509(3)	.2358(3)	½	275(30)	236(31)	162(18)	-69(42)	---	---
O(7)	.970(10)	.2110(2)	.1046(2)	.0674(2)	216(21)	166(21)	98(11)	40(29)	1(23)	-7(22)
O(8)	.984(15)	.1834(5)	.3166(5)	.1360(3)	175(43)	B_{11}	172(18)	-91(43)	70(55)	$-B_{13}$
O(9)	.969(16)	.0389(3)	.2146(4)	0	154(33)	449(38)	86(17)	45(48)	---	---
O(10)	.913(10)	.0306(2)	.3497(2)	.1825(2)	146(24)	136(30)	201(14)	-20(29)	52(26)	-71(27)
$H_2O(11)$	.791(23)	0	0	.4157(6)	596(114)	B_{11}	298(44)	---	---	---
$H_2O(12)$	.554(29)	.4452(30)	.0548(30)	0	1242(329)	B_{11}	949(161)	-953(355)	---	---
F*	1.001(18)	0	0	.1179(3)	164(50)	B_{11}	149(22)	---	---	---

* Si(2) = ($Si_{.972}$, $Al_{.028}$), F = ($F_{0.41}$, $OH_{0.59}$).

TABLE 3

Selected interatomic distances (Å) and angles (°)
(e.s.d. in parentheses)

Si(1) tetrahedron

Si(1)-O(1)	1.590(3)
Si(1)-O(2)	1.588(3)
Si(1)-O(5)	1.612(4)
Si(1)-O(6)	1.613(3)
O(1)-O(2)	2.646(4)
O(1)-O(5)	2.623(5)
O(1)-O(6)	2.589(4)
O(2)-O(5)	2.561(5)
O(2)-O(6)	2.619(4)
O(5)-O(6)	2.645(5)
O(1)-Si(1)-O(2)	112.8(2)
O(1)-Si(1)-O(5)	110.0(2)
O(1)-Si(1)-O(6)	107.9(2)
O(2)-Si(1)-O(5)	106.3(2)
O(2)-Si(1)-O(6)	109.8(2)
O(5)-Si(1)-O(6)	110.2(2)

Si(2) tetrahedron

Si(2)-O(1)	1.625(3)
Si(2)-O(2)	1.627(3)
Si(2)-O(3)	1.567(3)
Si(2)-O(4)	1.623(4)
O(1)-O(2)	2.575(4)
O(1)-O(3)	2.649(4)
O(1)-O(4)	2.636(5)
O(2)-O(3)	2.683(4)
O(2)-O(4)	2.581(5)
O(3)-O(4)	2.640(5)
O(1)-Si(2)-O(2)	104.7(2)
O(1)-Si(2)-O(3)	112.2(2)
O(1)-Si(2)-O(4)	108.4(2)
O(2)-Si(2)-O(3)	114.2(2)
O(2)-Si(2)-O(4)	105.1(2)
O(3)-Si(2)-O(4)	111.7(2)

Si(1)-O(1)-Si(2)	159.7(2)
Si(2)-O(2)-Si(1)'	149.0(2)
Si(2)-O(4)-Si(2)''	142.2(2)
Si(1)-O(5)-Si(1)''	139.9(2)
Si(1)-O(6)-Si(1)'''	145.6(2)

Ca-polyhedron

Ca-O(3)	2.371(3)
Ca-O(3)'	2.434(3)
Ca-O(7)	2.527(3)
Ca-O(7)'	2.541(3)
Ca-O(8)	2.450(5)
Ca-O(9)	2.430(5)
Ca-O(10)	2.405(3)
Ca-F	2.500(4)

K-polyhedron

K-O(2)	3.215(3)	(4x)
K-O(5)	2.925(4)	(2x)
K-O(10)	2.773(3)	(4x)

Na(1)-polyhedron

Na(1)-O(3)	2.345(4)	(4x)
Na(1)-F	2.630(4)	
Na(1)-H_2O(11)	2.342(8)	

Na(2)-polyhedron

Na(2)-O(4)	2.464(7)	
Na(2)-O(7)	2.376(5)	(2x)
Na(2)-O(10)	2.349(5)	(2x)
Na(2)-H_2O(12)	2.857(48)	

Na(3)-polyhedron

Na(3)-O(7)	2.544(6)	(4x)
Na(3)-O(8)	2.386(7)	(2x)
Na(3)-O(9)	2.558(6)	(2x)

C(1)-triangle

C(1)-O(7)	1.288(7)	(2x)
C(1)-O(9)	1.268(7)	
O(7)-O(7)'	2.252(4)	
O(7)-O(9)	2.202(5)	(2x)
O(7)-C(1)-O(7)'	122.0(2)	
O(7)-C(1)-O(9)	119.0(2)	(2x)

C(2)-triangle

C(2)-O(8)	1.298(9)	
C(2)-O(10)	1.266(7)	(2x)
O(8)-O(10)	2.201(6)	(2x)
O(10)-O(10)'	2.230(4)	
O(8)-C(2)-O(10)	118.3(2)	(2x)
O(10)-C(2)-O(10)'	123.4(2)	

H_2O-O approaches

H_2O(11)-H_2O(11)'	2.815	
H_2O(11)-O(1)	3.158	(4x)
H_2O(12)-O(9)	3.280	(4x)

F-O approaches

F-O(3)	2.988	(4x)
F-O(7)	3.215	(4x)

other twenty atoms remain essentially unchanged with differences less than a fraction of the corresponding estimated standard deviations. However, the thermal perameters and the occupancy factors for the carbon atoms were drastically changed (Table 1); the new occupancy factors were much smaller than the expected value 0.9; and the principal thermal parameters became negative. These results suggest that the scattering curves of C^{+} or C^{2+} are probably more realistic for carbon atoms in carbonates, but no attempt was made to refine the structure using the C^{+} or C^{2+} curves.

Description and Discussion of the Structure

Carletonite is a phyllosilicate (Figs. 1 and 2). Within one period along *c*, it contains a silicate layer of the composition $Na(1)KSi_8O_{18}\cdot H_2O(11)$ (Fig. 2), a carbonate layer or C(1)-layer of the composition $Na(3)C(1)O_3\cdot \frac{1}{2}H_2O(12)$ and two carbonate layers or C(2)-layers of the composition $Na(2)Ca_2C(2)O_3(F, OH)_{0.5}$ (Figs. 1 and 3).

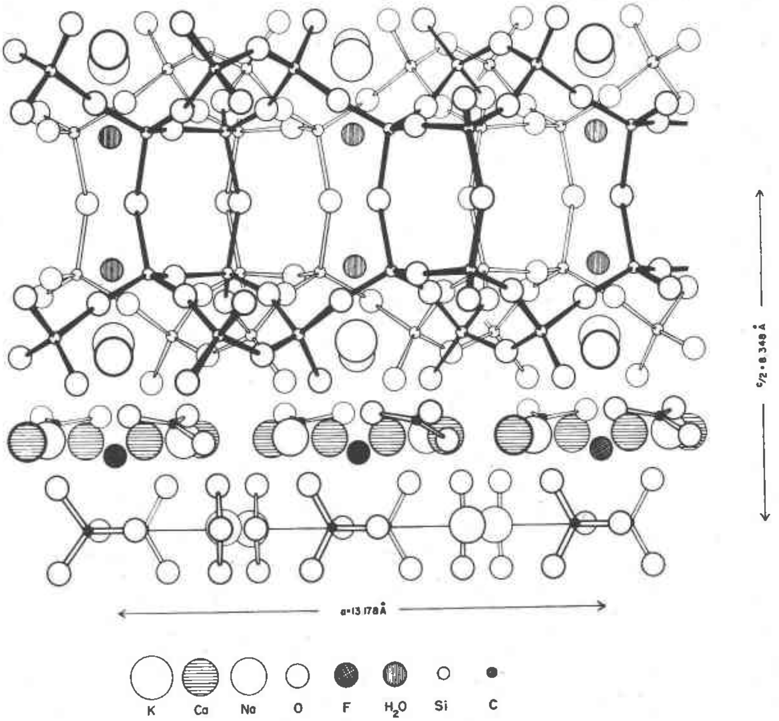

FIG. 1. The crystal structure of carletonite projected on (100) showing, from top to bottom, the double-sheet silicate layer, the C(2)-layer and the C(1)-layer.

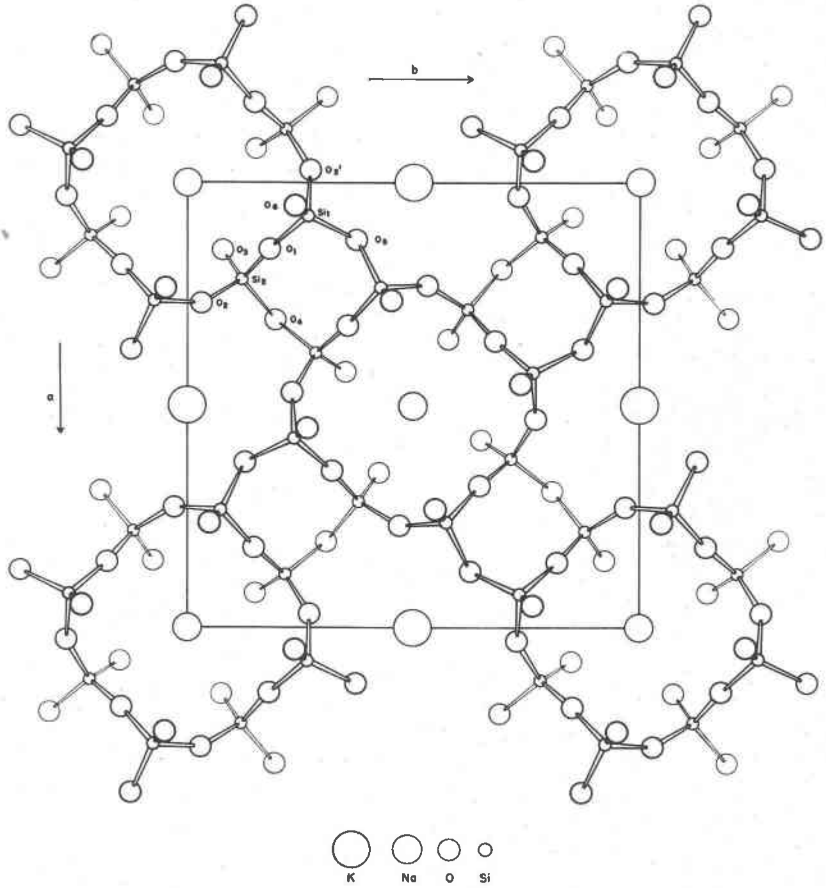

FIG. 2. The lower half of the Si_8O_{18} double-sheet of carletonite projected on (001). It is linked to the upper half, its mirror equivalent, by O_6.

In the silicate layer there are two independent Si tetrahedra sharing O(1) and O(2) to form eight-membered rings about the four-fold axes of symmetry. Within one eight-membered ring, the apical oxygen atoms (O(3) and O(6)) in alternate tetrahedra point in opposite directions. Each eight-membered ring is linked laterally by four-membered rings to four adjacent eight-membered rings across the diagonal mirror planes, resulting in a continuous single sheet. Each single-sheet is cross-linked, by sharing O(6) atoms, to another sheet across the horizontal mirror plane at $z = \frac{1}{2}$ to form a double-sheet of the composition Si_8O_{18}. Both Si tetrahedra are slightly distorted. In the Si(1) tetrahedron there are two short Si–O distances, 1.588 Å and 1.590 Å, within the eight-membered ring, and two longer distances, 1.612 and 1.613 Å, outside the eight-membered ring. Si(2) is approximately equi-distant to three shared oxygen atoms at 1.625 Å, but is considerably closer, 1.567 Å, to the fourth, O(3) atom, which is not shared. The short Si(2)–O(3) distance and the relatively large O(3)–Si(2)–O angles (111.7° to 114.2°) suggest the presence of $p - d\ \pi$-bonding (Cruickshank, 1961, and Brown and Gibbs, 1969). The mean Si(2)–O distance of 1.611 Å is 0.010 Å longer than the mean Si(1)–O distance of 1.601 Å, mainly due to partial substitution of Si by Al in the Si(2) tetrahedron.

The excess negative charges in the silicate layer are partically balanced by Na(1) and K atoms. Na(1), on the four-fold axis near the centre of the eight-membered rings, is in six-fold coordination with four O(3) atoms from the silicate layer, one (F, OH) atom at 2.630 Å

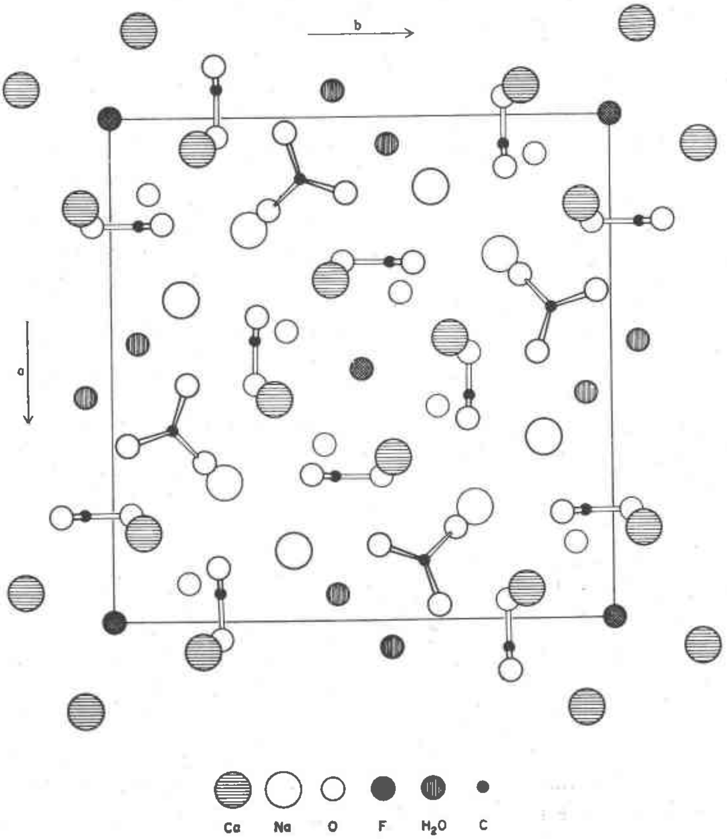

FIG. 3. The carbonate sheets of carletonite projected on (001).

directly below it and one $H_2O(11)$ at 2.342 Å directly above it. Na(1) is displaced from the O(3) plane by 0.66 Å toward the $H_2O(11)$ molecule. K is situated on the two-fold axis at the centre of the irregular hole or highly distorated eight-membered ring. It is coordinated irregularly with ten oxygen atoms at a mean distance of 2.980 Å, six in the silicate layer and four in the C(2)-layer.

In the C(1)-layer, the C(1) atom lies in the horizontal mirror plane at $z = 0$, at a mean distance of 1.281 Å from three oxygen atoms in a vertical plane. Carbon lies in the plane of the oxygen triangle as evidenced by the sum of O–C–O angles of 360.0°. Na(3) is irregularly surrounded by eight carbonate oxygen atoms at a mean distance of 2.51 Å, six from the C(1)-layer, and two from the C(2)-layers.

The C(2)-layer lies between the C(1)-layer and the silicate-layer, on both sides of the mirror plane at $z = 0$. It carries excess positive charges and serves the function of linking the C(1)-layer and the silicate-layer which have excess negative charges. The $C(2)O_3$ group is also planar with the sum of the O–C–O angles equal to 360.0°. The $C(2)O_3$ plane is inclined to (001) at an angle of 20°39′. Na(2) in this layer is bonded to one O(4) atom from the silicate-layer, two O(7) atoms from the C(1)-layer, two O(10) atoms from the C(2)-layer, and one $H_2O(12)$ molecule. Ca has eight nearest neighbours, one (F, OH) and two oxygen atoms from the C(2)-layer, three oxygen atoms from the C(1)-layer, and two oxygen atoms from the silicate-layer.

The least-squares refinement of the site occupancy factors confirmed the non-stoichiometry of carletonite indicated by the chemical analyses (Table 4). The low occupancy factors of the silicon atoms are probably due to the inaccuracy of the scattering factor for Si^{4+} used in the refinement and are not true indication of deficiency. This view is supported by the fact that the occupancy factors of all the silicate oxygen atoms (O(1)–(6) in Table 1) are very close to 1.0. Despite the large deviation of occupancy factors of the carbon atoms from the expected values the deficiency of carbon is suggested by the low site-occupancy factors of all the carbonate oxygen atoms (O(7)–(10), Table 1).

It is interesting to note that the total H_2O content derived from least-squares refinement is considerably lower than the analytical amount. The excess water indicated by the analysis is probably real and may be accommodated in the vacant sites of the carbonate groups. It may have the function of stabilizing the defect structure.

The H_2O molecule is not bonded to any atom in the structure. The nearest cation neighbour, Na(2), is 2.857 Å away, a distance significantly

TABLE 4

Formula of Carletonite

(Oxygen atoms excluded)

	Occupancy Factor	Number of Atoms per Formula	
	L.S. Refinement	L. S. Refinement	Chemical Analysis[1]
Si(1)	0.965 (4x)	7.748	8.00
Si(2)	0.972 (4x)		
Na(1)	0.923	3.658	3.56
Na(2)	0.905 (2x)		
Na(3)	0.925		
K	0.882	0.882	0.74
Ca	0.940 (4x)	3.760	3.77[2]
C(1)	1.098 (2x)	3.812[3]	3.65
C(2)	1.184 (2x)		
H_2O(11)	0.791	1.640	2.05
H_2O(12)	0.554		
OH=H_2O	1.001x0.59 (0.5x)		
F	1.001x0.41	0.410	0.41

1. Calculations based on 8 Si atom per formula.

2. Including 0.03 atom of Mg.

3. Calculated from occupancy factors of O(7-10), assuming 1.0 represents full site-occupancy.

outside the range 2.25–2.78 Å for Na–O distances given in the *International Tables* (Vol. 3). The shortest H_2O(12)–O approach is 3.280 Å, well outside the range 2.49–3.15 Å for O–O distances cited in the *International Tables* for hydrogen bonds of organic salts containing water. Thus the environment of H_2O(12) differs from that of water in zeolites in which H_2O molecules are either bonded to one divalent cation or to two monovalent cations (Taylor, 1934). H_2O(12) is probably not crystalline water but represents a concentration of the excess water trapped in the structure. The ideal chemical formula of carletonite should be written as $KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH, F) \cdot H_2O$, or $KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH, F) \cdot (H_2O)_{1+x}$, with $x = 0\text{–}1.0$, if the excess water is included.

The connection of the perfect {001} cleavage of carletonite with the double-sheet structure is obvious. The good {100} cleavage is presumably produced along the distorted eight-membered rings where the breaking of the Si–O bonds is kept at a minimum.

RELATED STRUCTURES

The Si_8O_{18} double-sheets in carletonite are structurally intermediate between the tetragonal Si_4O_{10} single-sheet structures, represented by apophyllite and gillespite ($BaFeSi_4O_{10}$), and the framework structures of the harmotome-phillipsite group of zeolites. Consequently, it bears similarities to all these structures.

In both apophyllite (Taylor and Náray-Szabó, 1931; Colville *et al.*, 1971; Chao, 1971b; and Prince, 1971) and gillespite (Pabst, 1943, and Wainwright, 1969) the SiO_4 tetrahedra share three oxygen atoms to form puckered single-sheets composed of four-membered rings at two different levels linked by distorted eight-membered rings. In both minerals the unshared oxygen atoms of the adjacent rings point in opposite directions, in contrast to the Si_4O_{10} sheets of micas which are composed of six-membered rings at the same level with all the unshared oxygen atoms pointing in the same direction. In apophyllite, however,

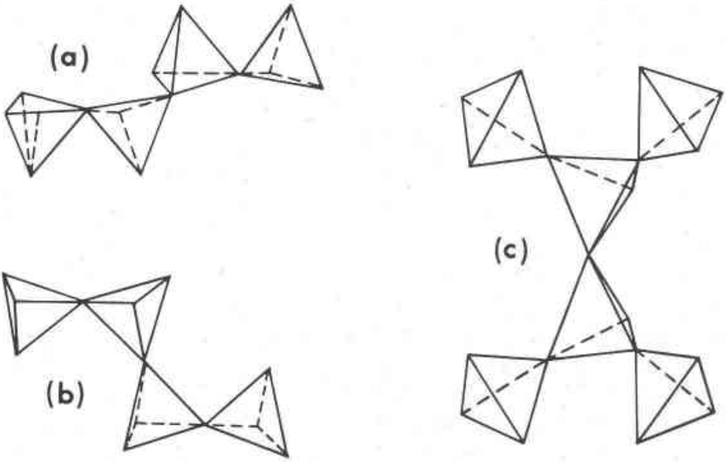

FIG. 4. Manner of linkage of adjacent rings of SiO_4 tetrahedra in:
(a) apophyllite, sharing a basal oxygen atom,
(b) gillespite, sharing an apical oxygen atom,
(c) carletonite, sharing both basal and apical oxygen atoms.

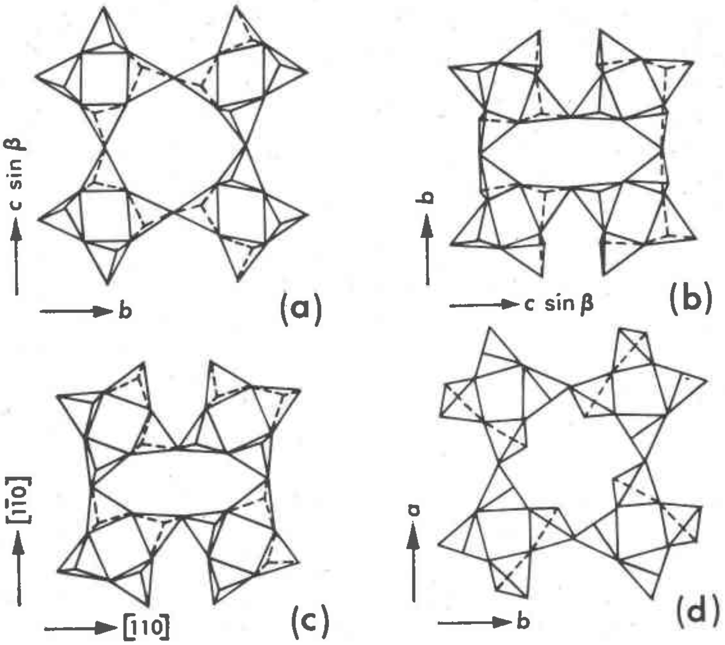

FIG. 5. Comparison of the alumino-silicate frameworks in: (a) harmotome, (b) sanidine, and (c) paracelsian, with (d) the double-sheet in carletonite. (Figs. (a), (b), and (c) after Sadanaga *et al.* (1961), Fig. 9).

two adjacent rings are linked by a basal oxygen atom (Fig. 4a), whereas in gillespite they are linked by an apical oxygen atom (Fig. 4b). The compounds, $CaCuSi_4O_{10}$, (Egyptian blue), $SrCuSi_4O_{10}$, and $BaCuSi_4O_{10}$, are isostructural with gillespite (Pabst, 1959). Leached gillespite, $H_{16}(Si_4O_{10})_4$, also tetragonal in symmetry, has a structure which may be derived from the gillespite structure by removal of Ba and Fe and the balancing of charges by hydrogen atoms (Pabst, 1958). The structure of carletonite is unique in that both apophyllite and gillespite types of linkages of the rings are present (Fig. 4c); the adjacent rings within the same single-sheets are linked by a basal oxygen atom and two rings in different single-sheets are linked by an apical oxygen atom.

Macdonaldite, $BaCa_4H_2Si_{16}O_{88}\cdot(8 + x)H_2O$ (Cannillo and others, 1968) and delhayelite, $Ca_4(Na_3Ca)K_7(Si_{14}Al_2)O_{38}Cl_2F_4$ (Cannillo and others, 1969) also have structures based on double-sheets of the carletonite type. However, in macdonaldite and delhayelite only one Si tetrahedron within each four-membered ring in a single-sheet is shared with the adjacent single-sheet to form a double-sheet of the composition (Si, Al)$_8$O$_{19}$.

The structures of harmotome (Sadanaga *et al.*, 1961), phillipsite (Steinfink, 1962), and gismondite (Fischer, 1963) are characterized by four-membered rings of (Si, Al)O$_4$ tetrahedra, each having two tetrahedra pointing upwards and two downwards. These rings are laterally linked by eight-membered rings (Fig. 5a), resembling those in carletonite (Fig. 5d). The difference lies in that the adjacent sheets in these zeolites are cross-linked to form framework structures whereas in carletonite they form double-sheets which are separated by carbonate-layers. The similarity between carletonite and harmotome-phillipsite zeolites may be extended to the feldspar structure except that in feldspars the eight-membered rings are distorted (Fig. 5b and 5c).

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