

Crystal structure of tiptopite, a framework berylllophosphate isotypic with basic cancrinite*

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ABSTRACT

The crystal structure of tiptopite, $K_2(Li_{2.9}Na_{1.7}Ca_{0.7}\square_{0.7})Be_6P_6O_{24}(OH)_2 \cdot 1.3H_2O$, has been solved and refined to residuals of 0.079 (unweighted) and 0.048 (weighted) for all 448 reflections. It is hexagonal, $P6_3$, with $a = 11.655(5)$, $c = 4.692(2)$ Å, and $Z = 1$. Tiptopite is isotypic with the members of the cancrinite group, being the berylllophosphate analogue of basic (hydroxyl) cancrinite, and could therefore be considered a zeolite. The tetrahedral framework is geometrically identical to that of cancrinite but is composed of BeO_4 and PO_4 groups, with Be and P completely ordered. In the channels, the large cation and the two nonframework oxygens occupy the same sites in the two structures. The major differences are (1) the replacement of two channel C atoms in cancrinite by one OH group in tiptopite and (2) the occupancy of the Na and water molecule sites in the cages in cancrinite by a vacancy and a K atom, respectively, in tiptopite.

INTRODUCTION

Tiptopite was described as a new mineral species of composition $(Li,K,Na,Ca,\square)_8Be_6(PO_4)_6(OH)_4$ by Grice et al. (1985). Their interpretation of the chemical analysis was based, in part, on the fact that the crystal-chemical data for tiptopite implied a species isotypic with the tectosilicate mineral cancrinite, ideally $Ca_2Na_6Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$. The data supporting that hypothesis included similarities in unit-cell dimensions, space group, and unit-cell contents and a general similarity in the intensity distribution observed upon comparison of single-crystal X-ray diffraction photographs of the two minerals. Nevertheless, there were some minor inconsistencies between the empirical formula of tiptopite and that of cancrinite, a fact that cast some doubt on the proposed silicate-berylllophosphate relationship. We have therefore determined the crystal structure of tiptopite to resolve these doubts and to provide additional data on silicate-phosphate isotypism. Moreover, because the formula proposed by Grice et al. indicated tiptopite to be a berylllophosphate analogue of the basic (hydroxyl) cancrinites, which are often classed as members of the zeolite family, the tiptopite structure would be of interest to zeolite science, in particular to the study of the synthetic phosphate zeolites (Flanigen and Grose, 1971; Barrer, 1982).

EXPERIMENTAL DETAILS

The unit-cell parameters, $a = 11.655(5)$ and $c = 4.692(2)$ Å, and space group, $P6_3$ or $P6_3/m$, determined by Grice et al. (1985) were verified for a crystal from the type

specimen using Weissenberg and precession photographs. Intensity data were then measured with a computer-controlled Supper-Pace diffractometer, using equi-inclination Weissenberg geometry and $MoK\alpha$ radiation monochromatized with a graphite flat-crystal monochromator. The intensities of 1382 reflections having $\sin \theta \leq 0.46$ and constituting three asymmetric units ($h \geq 0; k, l \geq 0$) were measured using high- and low-side background counts of 35 s and a scan rate of $2^\circ/\text{min}$. The crystal was a hexagonal prism, 0.07 mm in diameter and 0.25 mm long, and was mounted along the c axis. Reflection intensities were corrected for Lorentz-polarization and absorption effects ($\mu_1 = 11 \text{ cm}^{-1}$), and symmetry equivalents were averaged with the program SHELX-76 (Sheldrick, 1976), the internal consistency index being 0.030. The final data set contained 448 reflections, of which 28 having $|F| < 3\sigma|F|$ were considered to be unobserved.

STRUCTURE SOLUTION AND REFINEMENT

The solution of the structure was begun using direct methods [the MULTAN 78 package of Main (1978)] and the structure of cancrinite (Grundy and Hassan, 1982) as a guide. Statistics produced by MULTAN indicated the structure to be noncentrosymmetric, thus fixing the space group as $P6_3$, which is also the symmetry of cancrinite and basic cancrinite (Bresciani Pahor et al., 1982). Six peaks in the first E map corresponded closely to the framework T2, O1, O2, and O3 sites and the nonframework Na2 and O6 (=H₂O) sites in cancrinite. Structure-factor calculations were therefore initiated using as starting coordinates those given by Grundy and Hassan (1982) for all cancrinite framework atoms plus O6, assuming T2 corresponded to P, T1 to Be, and O6 to K [=M(1)]. However, in the last-named case, M(1) was placed on the three-fold

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TABLE 1. Positional coordinates and thermal parameters (\AA^2) in tiptopite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
P	0.0851(2)	0.4167(2)	3/4	0.009(1)	0.011(1)	0.007(1)	0.006(1)	0.007(1)	0.006(1)	0.009
Be	0.338(1)	0.418(1)	0.746(5)	0.007(5)	0.012(5)	0.009(4)	-0.017(7)	-0.003(7)	0.003(4)	0.009
O(1)	0.1902(6)	0.3843(6)	0.6518(15)	0.016(3)	0.012(3)	0.017(4)	0.001(3)	0.003(3)	0.006(3)	0.015
O(2)	0.1378(6)	0.5647(5)	0.7027(17)	0.015(3)	0.011(3)	0.009(4)	-0.008(3)	-0.004(3)	0.005(2)	0.012
O(3)	0.0547(6)	0.3801(5)	0.0688(15)	0.018(3)	0.022(4)	0.008(3)	0.000(3)	0.006(3)	0.009(3)	0.016
O(4)	0.3302(6)	0.3741(6)	0.0862(17)	0.013(3)	0.016(3)	0.009(4)	-0.004(3)	-0.002(3)	0.010(3)	0.013
M(1)	1/3	2/3	0.253(2)	0.044(2)	0.044(2)	0.019(2)	0	0	0.022(1)	0.036
M(2)	0.2207(8)	0.1137(7)	0.7486(30)	0.051(5)	0.036(4)	0.036(5)	-0.010(6)	0.003(7)	0.026(4)	0.041
O(5)	0	0	0.253(6)	0.009(3)	0.009(3)	0.090(10)	0	0	0.005(1)	0.036
O(6)	0.064(3)	0.130(4)	0.378(9)	0.02(1)						
O(7)	0.066(4)	0.130(4)	0.097(10)	0.02(1)						
O(8)	0.168(4)	0.322(4)	0.236(20)	0.02(1)						

Note: Anisotropic temperature factors are of the form $\exp -2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + \dots + U_{13}hla^*c^*\cos\beta^* + 2U_{23}kib^*c^*\cos\alpha^*)$.

axis in equipoint 2a rather than slightly off-axis in 6c as is the case for O6 in cancrinite. This produced a value of the residual (R) of 0.20, the calculations being carried out with the program SHELX-76. Calculations used neutral-atom scattering factors and anomalous dispersion factors, both from the *International Tables for X-Ray Crystallography* (1974), the reciprocal variances as weights, and isotropic temperature factors.

An electron-density and a difference electron-density synthesis showed that the Na1 and Na2 sites of cancrinite correspond, respectively, to a vacancy and a cation site in tiptopite, and, in addition, revealed a modest peak at (0, 0, 0.25), which is not an atomic site in cancrinite. Inclusion of these two atoms in the refinement, with the symbols M(2) [= (Li, Na, Ca)] and O(5), respectively, reduced the residual to 0.13. At this point, a second difference synthesis revealed three small peaks, two of which corresponded to O52 and O51 in cancrinite. These peaks, labeled O(6) and O(7), plus O(8), which does not correspond to any atom in the cancrinite structure, were refined as partially occupied oxygen positions. Their occupancy factors were arbitrarily fixed at 0.25, 0.25, and 0.17, respectively, to give reasonable refined temperature factors. Despite the small amount of scattering power represented by O(6), O(7), and O(8), their inclusion in the refinement reduced the residual to 0.09.

Introduction of anisotropic temperature factors for all atoms except O(6), O(7), and O(8), for which isotropic temperature factors were used throughout, reduced the residual to its final values of 0.079 (unweighted) and 0.048 (weighted) for all 448 reflections and 0.074 (unweighted) and 0.047 (weighted) for the 420 observed reflections. Table 1 contains the final set of refined atomic parameters; Table 2,¹ the observed and calculated structure factors; and Table 3, the selected interatomic distances and angles. The final formula adopted for tiptopite is $K_2(Li_{2.9}Na_{1.7}Ca_{0.7}\square_{0.7})Be_6P_6O_{24}(OH)_2 \cdot 1.3H_2O$. This represents an approximation derived from the combined

TABLE 3. Selected interatomic distances (\AA) and angles ($^\circ$) in tiptopite

Phosphate tetrahedron			
P-O(1)	1.522(9)	O(3)-P-O(4)	106.8(4)
P-O(2)	1.530(6)	O(1)-P-O(2)	108.4(4)
P-O(4)	1.534(8)	O(1)-P-O(3)	109.0(4)
P-O(3)	1.547(7)	O(1)-P-O(4)	109.3(3)
Mean	1.533	O(2)-P-O(3)	110.0(4)
		O(2)-P-O(4)	112.2(4)
		Mean	109.5
O(3)-O(4)	2.47(1)	O(1)-O(3)	2.50(1)
O(1)-O(2)	2.48(1)	O(2)-O(3)	2.54(1)
O(1)-O(4)	2.49(1)	O(2)-O(4)	2.54(1)
Beryllate tetrahedron			
Be-O(2)	1.60(1)	O(3)-Be-O(4)	106(1)
Be-O(1)	1.62(1)	O(1)-Be-O(4)	108(1)
Be-O(3)	1.62(1)	O(1)-Be-O(2)	108(1)
Be-O(4)	1.67(2)	O(1)-Be-O(3)	110(1)
Mean	1.63	O(2)-Be-O(4)	111(1)
		O(2)-Be-O(3)	114(1)
		Mean	109
O(1)-O(2)	2.60(1)	O(1)-O(3)	2.65(1)
O(3)-O(4)	2.62(1)	O(2)-O(4)	2.70(1)
O(1)-O(4)	2.65(1)	O(2)-O(3)	2.70(1)
Nonframework cations			
M(1)-O(2)	2.889(9) \times 3	M(2)-O(5)	2.23(1)
M(1)-O(2)	3.251(9) \times 3	M(2)-O(3)	2.38(1)
Mean	3.070	M(2)-O(4)	2.43(1)
		M(2)-O(1)	2.51(1)
M(1)-O(3)	3.406(5) \times 3	M(2)-O(7)	2.51(5)
M(1)-O(1)	3.409(8) \times 3	M(2)-O(7)	2.56(5)
		M(2)-O(6)	2.59(4)
		M(2)-O(6)	2.62(4)
		Mean	2.48
Nonframework anions (<2.5 \AA)			
O(5)-O(6)	1.43(4) \times 3	O(6)-M(2)	1.10(4)
O(5)-O(7)	1.50(5) \times 3	O(6)-O(7)	1.32(6)
O(5)-O(7)	2.08(5) \times 3	O(6)-O(7)	1.66(6)
O(5)-O(6)	2.20(5) \times 3	O(6)-O(7)	1.68(6)
O(5)-M(2)	2.23(8) \times 3	O(6)-O(8)	2.05(6)
O(5)-O(5)	2.346(1) \times 2	O(6)-O(6)	2.27(7) \times 2
O(7)-M(2)	1.16(5)	O(8)-M(2)	1.03(4)
O(7)-O(8)	2.04(7)	O(8)-O(4)	1.82(6)
O(7)-O(7)	2.27(7) \times 2	O(8)-O(3)	1.93(7)
		O(8)-O(1)	2.05(9)
Cation-cation (<3.8 \AA)			
P-Be	2.86(2)	P-M(1)	3.723(5)
P-Be	2.89(1)	P-M(2)	3.17(1)
P-Be	2.90(2)	Be-M(1)	3.73(2)
P-Be	2.94(1)	Be-M(2)	3.10(1)
Mean	2.90	M(2)-M(2)	3.235(6)

Note: esd's are in parentheses.

¹ To obtain a copy of Table 2, order Document AM-87-347 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 4. Comparison of atomic site in cancrinite and tiptopite

Cancrinite*				Tiptopite		
Equi-point	Site	Contents	Coordinates	Site	Contents	Coordinates
6c	T1	6 Si	0.33, 0.41, ⅓	Be	6 Be	0.34, 0.42, 0.75
6c	T2	6 Al	0.08, 0.41, 0.75	P	6 P	0.09, 0.42, ⅓
6c	O1	6 O	0.20, 0.40, 0.66	O(1)	6 O	0.19, 0.38, 0.65
6c	O2	6 O	0.11, 0.56, 0.73	O(2)	6 O	0.14, 0.56, 0.70
6c	O3	6 O	0.03, 0.35, 0.06	O(3)	6 O	0.06, 0.38, 0.07
6c	O4	6 O	0.31, 0.36, 0.04	O(4)	6 O	0.33, 0.37, 0.08
2b	Na1(cg)	2 Na	⅔, ⅓, 0.13	Vacant(cg)	—	—
6c	Na2(ch)	4Na + 1.5Ca + 0.50□	0.12, 0.25, 0.30	M(2)(ch)	2.9Li + 1.7Na + 0.7Ca + 0.7□	0.11, 0.22, 0.25
2a	C1(ch)	0.75C + 1.25□	0, 0, 0.67			
2a	—	—	—	O(5)(ch)	2(OH)	0, 0, 0.75**
2a	C2(ch)	0.75C + 1.25□	0, 0, 0.91			
6c	O51(ch)	2.25O + 3.75□	0.06, 0.12, 0.67	O(7)(ch)		0.13, 0.06, 0.60**
6c	O52(ch)	2.25O + 3.75□	0.06, 0.12, 0.91	O(6)(ch)		0.13, 0.07, 0.88**
6c	O6(cg)	2H ₂ O + 4□	0.62, 0.32, 0.69	M(1)(cg)	2K	⅔, ⅓, 0.75**
6c	Vacant(ch)	—	—	O(8)(ch)		0.17, 0.32, 0.24

* Atomic positions from Grundy and Hassan (1982); ch = channel, cg = cage.

** Coordinates transformed by $(y, y - x, \frac{1}{2} + z)$.

chemical and structural analyses, with the contents of the M(2) site adjusted slightly to maintain charge balance.

After the refinement had converged, another difference synthesis was calculated as a check on the "final" model of the structure. This revealed two very small but potentially significant features, namely a maximum of $1 \text{ e } \text{Å}^{-3}$ at $(0, 0, 0.478)$ on the 6_3 axis and a set of three equivalent maxima of $0.6 \text{ e } \text{Å}^{-3}$ clustered around the three-fold axis at $(0.32, 0.62, 0.30)$. The former is located approximately midway between adjacent O(5) atoms at $(0, 0, 0.253)$ and $(0, 0, 0.753)$, and the latter are only ca. 0.7 Å from the M(1) site at $(\frac{1}{3}, \frac{2}{3}, 0.253)$. The possible significance of these two features will be discussed presently.

STRUCTURE DESCRIPTION AND DISCUSSION

The structure of cancrinite, which is the prototype for that of tiptopite, was first determined in detail by Jarchow (1965), although the configuration of its tetrahedral framework had been deduced many years earlier by Pauling (1930). The structure was subsequently refined by Smolin et al. (1981) using X-ray diffraction data, by Grundy and Hassan (1982) using X-ray diffraction data and high-resolution transmission-electron microscopy, and by Emiraliev and Yamzin (1982) using neutron diffraction data. The structure of its hydroxyl analogue, basic cancrinite, has been determined by Barrer et al. (1970), Bresciani Pahor et al. (1982), and Hassan and Grundy (I. Hassan, pers. comm.). The latter three studies all used synthetic specimens, as basic cancrinite is not known to occur naturally.

From a chemical standpoint, the relationship between the aluminosilicates of the cancrinite group and the beryllophosphate compound tiptopite is the coupled substitution $\text{Al}^{3+}\text{Si}^{4+} = \text{Be}^{2+}\text{P}^{5+}$ in the tetrahedral sites. Reference to Table 4 shows that the aluminosilicate framework of cancrinite is geometrically identical to the beryllophosphate framework of tiptopite, corresponding atoms

in the two structures having very nearly the same coordinates. Moreover, in both frameworks there is complete ordering of tetrahedral cations, i.e., (Al,Si) and (Be,P). Likewise, the channel atoms Na2, O51, and O52 in cancrinite correspond to M(2), O(7), and O(6), respectively, in the channels of tiptopite. The degree of occupancy of the channel-cation site is also about the same at 5.5 atoms.

The major differences between the two structures are in the contents of the cages and, in part, the channels (Table 4). Specifically, the two channel C sites, C1 and C2, in cancrinite are, in effect, replaced by one hydroxyl oxygen, O(5), located about midway between C1 and C2 on the three-fold axis. The analogy between O(5) and (C1 + C2) becomes more evident when it is noted that C1 and C2 are only 1.6 Å apart and are actually alternative positions for 1.5 C atoms split between a pair of two-fold equipoints (Grundy and Hassan, 1982). Their ideal position would be at $(0, 0, 0.79)$, which corresponds to the O(5) site in tiptopite. Likewise, the two cage atoms, Na1 and O6 (=H₂O), in cancrinite correspond, respectively, to a vacancy and the M(1) cation (=K) in tiptopite. In effect, there is a substitution of $(2\text{□} + 2\text{K}^+)$ for $(2\text{Na}^+ + 2\text{H}_2\text{O}^0)$ between the two minerals. Note, however, that O6 and M(1) do not quite occupy equivalent positions, as the latter is in 2b at $(\frac{2}{3}, \frac{1}{3}, 0.75)$, whereas the former is displaced off-axis to position 6c at $(0.62, 0.32, 0.69)$. Such disorder may also occur to a very minor degree in tiptopite because, as previously noted, the final difference synthesis showed three small, off-axis maxima clustered around the three-fold axis close to M(1). This anomaly may represent K atoms or perhaps water molecules, as in cancrinite. The channel atom O(8) has no counterpart in the cancrinite structure.

The structures of the basic cancrinites $(\text{Na}_2\text{O})_{1.24}(\text{Al}_2\text{O}_3)_{-}(\text{SiO}_2)_{2.01} \cdot 1.87\text{H}_2\text{O}$ (Bresciani Pahor et al., 1982) and $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2.8\text{H}_2\text{O}$ (I. Hassan, pers. comm.)

TABLE 5. Empirical bond valences (v. u.) in tiptopite

	M(1)	M(2)*	P	Be	O(1)	O(2)	O(3)	O(4)	O(5)
M(1)					0.04 ($\times 2$)	0.11 ($\times 2$)	0.04 ($\times 3$)		
M(2)					0.10	0.05 ($\times 2$)	0.14	0.13	0.20 ($\times 3$)
P					1.31	1.28	1.22	1.27	
Be					0.52	0.55	0.52	0.46	
O(1)	0.04 ($\times 3$)	0.10	1.31	0.52					
O(2)	0.11 ($\times 3$)		1.28	0.55					
	0.05 ($\times 3$)								
O(3)	0.04 ($\times 3$)	0.14	1.22	0.52					
O(4)		0.13	1.27	0.46					
O(5)		0.20							
Σv	0.72	0.57	5.08	2.05	2.01	2.15	2.00	1.86	0.60

* Valences were calculated from weighted averages of Li-O, Na-O, and Ca-O. The sum for M(2) is low because bonds to O(6) and O(7) were neglected owing to the unknown occupancy factors of these sites.

closely resemble the structure of cancrinite, the differences being in the contents of the channels. Taking $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2.8\text{H}_2\text{O}$ as an example, the only major differences are (1) the replacement of C1 and C2 in cancrinite by an oxygen atom, O(5), at (0, 0, 0.693) and (2) the presence of a small electron density residual of $1.3 \text{ e } \text{Å}^{-3}$ at (0, 0, 0.47) in the difference map. These same two features appear at essentially the same positions in the channels of tiptopite. This means that the only major differences between tiptopite and $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2.8\text{H}_2\text{O}$ are (1) the contents of the cages, i.e., ($2\text{□} + 2\text{K}^+$) for ($2\text{Na}^+ + 2\text{H}_2\text{O}^0$) as described above, and (2) the channel atom O(8), which has no counterpart in basic cancrinite.

Calculation of bond-valence sums (Brown, 1981) for tiptopite (Table 5) leads to the conclusion that O(5) is either a water or hydroxyl oxygen. If O(5) is part of a hydroxyl group, this suggests that (0, 0, 0.478) is the location of its associated H atom. However, this would lead to an $-\text{O}(5)-\text{H}-\text{O}(5)-$ configuration along the *c* axis, in which the H is shared approximately equally by adjacent oxygens; i.e., there is a nearly symmetrical H-bond chain along *c*. Now the O(5)–O(5) distance is fixed by symmetry at *c*/2 [i.e., a very short 2.346(1) Å], and it is known that H bonds tend to become more symmetrical with decreasing distance between donor and acceptor oxygens. Moreover, the O(5)–O(5) distance is within the range of 2.29 to 2.48 Å given by Kehr et al. (1980) for the shortest known H bonds, some of which have been determined to be symmetrical. It is significant that the electron-density residual at (0, 0, 0.478) in tiptopite also occurs in $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2.8\text{H}_2\text{O}$ at the same position and with the same magnitude. It is therefore likely that it represents a real atomic position rather than just a spurious peak in the difference synthesis. An attempt was made to refine this position as an H atom in the tiptopite structure, but this was not successful.

The alternative interpretation of O(5) is that it is part of a water molecule, as proposed for the analogous atom O(5) in basic cancrinite (I. Hassan, pers. comm.). It is not possible to choose between the two alternatives on the basis of the available data, although the hydroxyl inter-

pretation has the virtue of explaining the electron-density feature at (0, 0, 0.478).

The partially occupied channel sites, O(6), O(7), and O(8), also remain something of an enigma. All of them were refined as oxygen atoms, an assumption supported in the case of O(6) and O(7) by their correspondence to oxygen positions in the structure of cancrinite (Grundy and Hassan, 1982) and the basic cancrinites studied by Barrer et al. (1970) and Hassan and Grundy (I. Hassan, pers. comm.), but no reliable attribution can be made from the data at hand. As with O(5), they are most probably part of water molecules or hydroxyl groups. Table 3 shows that O(8) is not bonded to any of the cations. This may mean that O(8) is part of a water molecule that forms only H bonds to other anions or that O(8) is a spurious atomic position, derived from a false peak in the difference synthesis.

Reference to Table 3 shows what are apparently numerous, improbably short distances involving the non-framework anions O(5), O(6), O(7), and O(8). These can be rationalized as fictitious contacts between vacant positions on the equipoints fractionally occupied by M(2), O(6), O(7), and O(8). A second interpretation is that some of these distances are evidence of phosphate and/or sulfate groups located in the channels, as proposed by Grice et al. (1985). Ten of the O–O distances in question in Table 5 can be so accounted for, as they are within three standard deviations of the ranges for P–O and S–O distances (P–O = 1.44 to 1.64 Å, S–O = 1.42 to 1.61 Å) given by Baur (1970), but this is hardly definitive. Given the limitations of the existing data, the nature of the chemical species occupying the “channel anion” sites and their precise role in the structure remain problematical.

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