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THE CRYSTAL STRUCTURE OF BASIC CANCRINITE, IDEALLY $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}3H_2O$

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ABSTRACT

The crystal structure of basic (hydroxyl) cancrinite, $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}2.8H_2O$, has been refined to a R value of 0.047 for 870 unique observed reflections in space group $P6_3$ using single-crystal X-ray-diffraction data. The Al and Si atoms of the aluminosilicate framework are fully ordered, as in other cancrinite-group minerals. Each cage contains one $[Na{\cdot}H_2O]^+$ cluster. The Na2 sites in the channels are fully occupied by Na atoms. The OH group and remaining H_2O also occur in the channels. The framework atoms, the $[Na{\cdot}H_2O]^+$ clusters, and the Na2 sites do not directly contribute to the superstructure in basic cancrinite. The superstructure arises from long-range order of OH^- ions and H_2O molecules and vacancies associated with these in the channels. The ideal formula for basic cancrinite is $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}3H_2O$.

Keywords: cancrinite-group minerals, basic cancrinite, crystal structure, superstructure.

SOMMAIRE

Nous avons affiné la structure cristalline d'une cancrinite hydroxylée, et donc basique, $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}2.8H_2O$, jusqu'à un résidu R de 0.047 dans le groupe spatial $P6_3$, en utilisant 870 réflexions uniques observées sur cristal unique (données de diffraction X). Les atomes Al et Si de la trame aluminosilicatée sont parfaitement ordonnés, tout comme dans les autres membres de la famille de la cancrinite. Chaque cage contient un agencement $[Na{\cdot}H_2O]^+$. Les sites Na2, dans les canaux, sont pleinement occupés par le sodium. Le groupe OH et les autres molécules d'eau se trouvent aussi dans les canaux. Les atomes de la trame, les groupements $[Na{\cdot}H_2O]^+$ et les sites Na2 ne contribuent pas directement à la surstructure de la cancrinite basique. Celle-ci serait à un agencement ordonné à longue échelle des ions OH^-, des molécules d'eau, et des lacunes le long des canaux. La formule chimique idéale de la cancrinite basique serait $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}3H_2O$.

(Traduit par la Rédaction)

Mots-clés: minéraux de la famille de la cancrinite, cancrinite basique, structure cristalline, surstructure.

INTRODUCTION

Synthetic basic (hydroxyl) cancrinite is isotypic with cancrinite-group minerals (Jarchow 1965, Barrer *et al.* 1970, Bresciani Pahor *et al.* 1982) and polymorphic with basic (hydroxyl) sodalite $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}2H_2O$ (Hassan & Grundy 1983). The latter compound is the high-temperature polymorph (Anderson 1968). Basic cancrinite also is isotypic with the mineral tiptopite, $K_2(Li_{2.9}Na_{1.7}Ca_{0.7})[Be_6P_6O_{24}](OH)_2{\cdot}1.3H_2O$, which is the beryllophosphate analog of basic cancrinite (Peacor *et al.* 1987).

The structure of cancrinite is composed of AlO_4 and SiO_4 tetrahedra, and the Al and Si atoms are completely ordered. The tetrahedra are corner-linked to form a framework consisting of chains of cages parallel to the z axis. These cages are bounded at the top and bottom by parallel six-membered rings consisting of alternating AlO_4 and SiO_4 tetrahedra. The 3-fold axis (parallel to the z axis) runs through the center of these rings. The cages are further linked to form channels bounded by puckered twelve-membered rings of $(Al,Si)O_4$ tetrahedra around the 6_3 axes (Fig. 1).

In cancrinite, one interstitial cation site, Na1, is located in the cage on the 3-fold axis and is slightly displaced from the plane of the six-membered rings. Each cage contains a water molecule (on site O6), which is disordered about the 3-fold axis because of hydrogen bonding, and a Na atom, which is located on the Na1 site, thus forming $[Na{\cdot}H_2O]^+$ clusters. In davyne, the cage contains $[Ca{\cdot}Cl]^+$ clusters instead of $[Na{\cdot}H_2O]^+$ clusters (Hassan & Grundy 1990). Another interstitial cation site, Na2, is located near the walls of the channels, in close proximity to the center of six-membered rings. The channels also contain the large anionic groups, *e.g.*, CO_3, SO_4, and OH, and the remaining cations (*e.g.*, Na, Ca, and K) occur on the Na2 site (Grundy & Hassan 1982).

Barrer *et al.* (1970) determined the structure of a basic cancrinite with chemical formula $Na_{7.14}[Al_6Si_{7.08}O_{26.16}]{\cdot}4.05H_2O$ using X-ray data obtained from powdered material. They divided the Na2 site into two positions. Oxygen atoms occur in the channels, and the presence of some kind of silicate anion also was detected in the channels. Approximately one H_2O occurs in each cage.

Bresciani Pahor *et al.* (1982) refined the structure of a basic cancrinite of chemical formula $Na_{7.44}[Al_6Si_{6.03}O_{24.04}]{\cdot}5.61H_2O$ to an R value of 0.034 for 648 observed reflections that have I ≥

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CANCRINITE

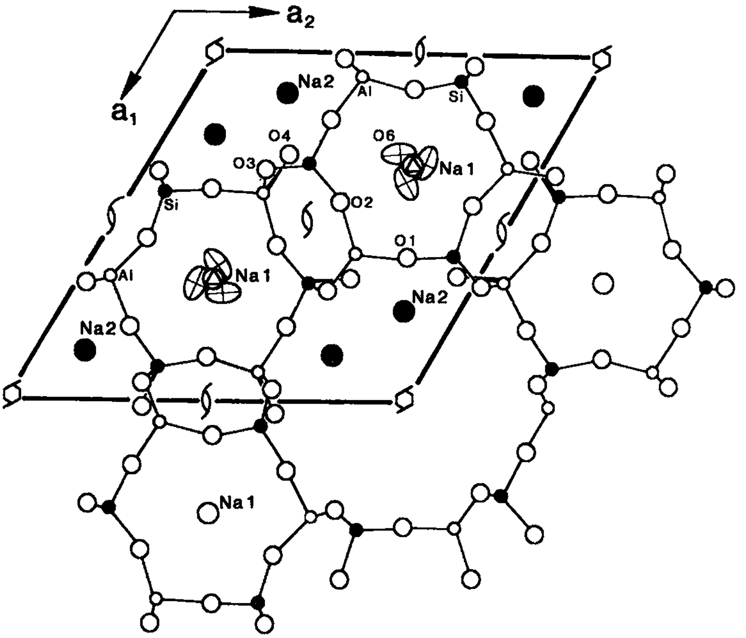

FIG. 1. Projection of the structure of cancrinite down [001], showing the site nomenclature, symmetry elements for space group $P6_3$, large channels along the 6_3 axes, and cages along the 3-fold axes (Grundy & Hassan 1982, modified by Papike 1988).

$3\sigma(I)$. The framework-atom positions and the interstitial cation sites were found to be similar to those in the cancrinite structure determined by Jarchow (1965). The cage contains 0.59 H_2O on the 3-fold axis. Three peaks in a channel correspond to O atoms, which are in similar positions to those reported by Barrer *et al.* (1970). One position is on the 6_3 axis, and the other two positions are off the 6_3 axis and have occupancy factors of 0.35 and 0.33, respectively. These positions are possible locations for O atoms of OH^- and H_2O. These results lead to an ideal formula of $Na_{7.5}[Al_6Si_6O_{24}](OH)_{1.5}•5H_2O$ for basic cancrinite. A comparison of the unit-cell contents with the results of Barrer *et al.* (1970) indicates that agreement between sets of crystallographic results is better than that between chemical analyses (Bresciani Pahor *et al.* 1982). The structures of basic cancrinite and tiptopite also were discussed and compared by Peacor *et al.* (1987).

TABLE 1. BASIC CANCRINITE: CHEMICAL COMPOSITION*

Oxide	wt. %	No of ions** per unit cell	
SiO_2	36.27	Si	6.19
Al_2O_3	28.93	Al	5.81
Na_2O	24.06	Na	7.95
H_2O	6.24	H_2O	2.77
		OH	2.00
Total	95.50		

Chemical formula from analysis:

$Na_{8.0}[Al_{5.8}Si_{6.2}O_{24}](OH)_{2.0}·2.77\ H_2O$

Chemical formula from refinement:

$Na_8[Al_6Si_6O_{24}](OH)_{2.04}·2.68H_2O$

*wet analysis, J. Muysson, McMaster University
(H_2O by Penfield gravimetric method)
**based on Al+Si = 12.

Superstructure reflections are commonly observed in cancrinite-group minerals (Jarchow 1965, Brown & Cesbron 1973, Foit *et al.* 1973, Grundy & Hassan 1982, Hassan & Grundy 1984). Grundy & Hassan (1982) studied an example of cancrinite with a well-developed superstructure using high-resolution transmission electron microscopy (HRTEM) and X-ray-diffraction analysis. These authors excluded the possibility that the superstructure arises from periodic variation in the stacking sequence of the six-membered rings. The X-ray refinement of the structure shows that the carbonate groups occur on the 6_3 axis, with their carbon atoms in two positions, C1 and C2, 1.2 Å apart and with an occupancy factor of 0.38 for each of the site. The cage contains one $[Na{\bullet}H_2O]^+$ cluster, and the Na2 site contains 0.67 Na, 0.25 Ca, and 0.08 vacancies. This corresponds to the omission of 3 to 4 CO_3 groups within the 40.94 Å period of the supercell. The cancrinite superstructure arises from ordering of carbonate-group vacancies and the resulting ordering of the cations and vacancies on the Na2 sites. A model of the long-range order was established and gives a good match between calculated and observed reflections attributed to the superstructure, both in X-ray and electron diffraction patterns (Grundy & Hassan 1982). Recently, HRTEM imaging was used to show the order among the CO_3-group vacancies in cancrinite (Hassan & Buseck 1992).

Neither Barrer *et al.* (1970) nor Bresciani Pahor *et al.* (1982) reported the presence of superstructure reflections in basic cancrinite. These reflections are present in our sample. An accurate refinement of the crystal structure thus was carried out to determine the origin of the superstructure in basic cancrinite and to check some of the subtle structural features previously reported for basic cancrinite.

EXPERIMENTAL DETAILS

Crystals of basic cancrinite were prepared hydrothermally at 1 kbar total pressure and at 723 K (Anderson 1968). The crystals are water clear, hexagonal prisms, elongated along the z axis. The chemical analysis gives a ratio of Al and Si atoms of 0.94, which is close to the expected value of 1.0 (Table 1). The number of Na atoms is at the maximum value of 8.0. Six Na atom valence units (v.u.) satisfy the charge deficiency on the aluminosilicate framework $[Al_6Si_6O_{24}]^{6-}$, and the remaining 2 v.u. on the two Na atoms are expected to be satisfied by two OH^- ions. There is a deficiency of 4.5 wt.% in the analytical total, so that the amount of H_2O is inferred to be greater than that indicated (Table 1).

Single-crystal X-ray precession photographs contain diffraction symmetry and lattice extinctions compatible with space group $P6_3$ (Fig. 2). All the substructure reflections are sharp. Crystals of basic cancrinite show superstructure reflections that are different. No superstructure reflections occur in some crystals; the "extra" reflections seen are not superstructure reflections because they are not commensurate with the substructure reflections (Fig. 2a). These "extra" reflections arise from a minor phase. A weak one-dimensional superstructure affecting the c^* axis occurs in some crystals and gives a supercell repeat of about $3c_{\mathrm{canc}}$ (Fig. 2b). The superstructure reflections are streaked parallel to c^*. The crystal structure of both crystals used to record the precession photographs shown (Fig.1) was refined. The final structures are identical within the estimated errors, so that the results for only one crystal are reported here.

Unit-cell parameters were obtained by least-squares refinement of 26 substructure reflections having $10° \leq 2\theta \leq 35°$ automatically aligned on a four-circle single-crystal X-ray diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. The cell

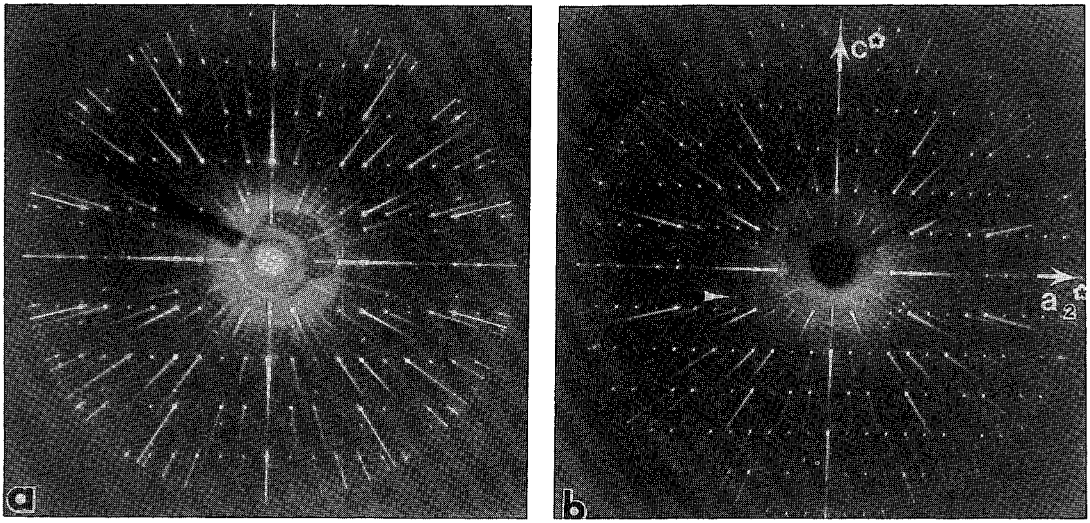

FIG. 2. [100] zone X-ray precession photographs of basic cancrinite. (a) No well-defined superstructure reflections are present. Some of the "extra" reflections arise from a minor phase because they are not commensurate with the substructure reflections. (b) Weak superstructure reflections (*e.g.*, arrow) give rise to a supercell with $3c_{\mathrm{canc}}$. Such reflections are streaked parallel to c^* (seen on negative but not on print). Mo$K\alpha$ radiation, Zr filter; (a) $\mu = 20°$, (b) $\mu = 25°$. Note that (a) and (b) are printed at different magnifications.

TABLE 2. CRYSTAL DATA AND DATA-COLLECTION INFORMATION

a (Å)	12.664(2)
c (Å)	5.159 (1)
V ($Å^3$)	716.54
Space Group	$P6_3$
Z	1
Density Calc. (g/cm^3)	2.27
Crystal size (mm)	0.20 x 0.20 x 0.23
μ (cm^{-1})	7.63
μR	0.16
Radiation/Monochromator	Mo/C
MoKα (Å)	0.71069
Total no. of I	2029
No. of unique reflections	959
No. of non-equiv. $\lvert F_o \rvert > 3\sigma \lvert F \rvert$	870
Final $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.047
Final $R_{w=1} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.057

parameters and other information pertinent to X-ray data collection and refinement are given in Table 2. All reflection intensities were measured from two asymmetric units (*h,k*>0; ±*l*>0) out to a maximum 2θ of 65° using a Syntex P2$_1$ diffractometer. The diffractometer was operating in the θ - 2θ scan mode, with 2θ scan range of (Mo$K\alpha_1$ - 0.85°) to (Mo$K\alpha_2$ + 0.85°) and variable scan rates of 3 to 29.3° min^{-1}, depending on the intensity of a preliminary scan. The two standard reflections measured after every 50 reflections did not change. The data were corrected for Lorentz, polarization, background effects, and spherical absorption (Table 2). Equivalent reflections were averaged to produce a unique data-set. Refinements were carried out using the resulting structure-factors for which $|F_o| > 3\sigma|F|$. All crystallographic calculations were made using the XRAY76 Crystallographic System (Stewart 1976).

STRUCTURE REFINEMENT

The initial positional parameters and isotropic temperature-factors used were those of cancrinite (Grundy & Hassan 1982). Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). Initially, no oxygen atoms corresponding to OH and H_2O were placed in the channels. Refinement of this structural model using the full-matrix least-squares method, unit weights, and a variable overall scale-factor progressed rapidly. Isotropic temperature-factors were converted to anisotropic forms, and the structural model converged to an *R* index of 0.061. The resulting structural geometry is comparable to that in cancrinite (Grundy & Hassan 1982). Difference-Fourier sections for a channel show electron-density peaks in positions similar to the oxygen atoms of the carbonate group in cancrinite, as well as a position on the 6_3 axis. Oxygen atoms were placed on these sites, and their occupancy factors were adjusted to match the results of the chemical analysis. The refinement converged to an *R* index of 0.047. Difference-Fourier sections at this stage showed no significant features except for a small amount of residual density (1.3 e/$Å^3$) on the 6_3 axis at (0, 0, 0.97). Site occupancies and temperature factors for all the interstitial ions were refined, while the framework atom parameters were held invariant (Table 3). The resulting occupancy-factors give a chemical formula that agrees well with that obtained from the chemical analysis (Table 1). The final structural parameters are presented in Tables 3, 4, and 5. A table of structure factors is available at a nominal charge from the Depository of Unpub-

TABLE 3. ATOMIC COORDINATES, ISOTROPIC, AND ANISOTROPIC* THERMAL PARAMETERS ($Å^2$x10^4)

Atom	Site	Site content		x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
						Framework atoms							
O1	6c	1.0	O	.2022(4)	.4034(4)	.6653(10)	176	104(16)	252(20)	173(18)	116(16)	-2(15)	5(16)
O2	6c	1.0	O	.1184(4)	.5647(4)	.7269(15)	235	204(17)	141(16)	359(29)	106(14)	54(26)	40(25)
O3	6c	1.0	O	.0287(4)	.3531(4)	.0579(9)	170	172(18)	264(21)	74(20)	120(17)	37(16)	44(17)
O4	6c	1.0	O	.3190(4)	.3611(5)	.0421(9)	207	254(21)	267(21)	101(20)	197(19)	11(17)	26(18)
Si	6c	1.0	Si	.3298(1)	.4125(1)	.75	88	89(5)	96(5)	79(5)	55(4)	-11(8)	3(7)
Al	6c	1.0	Al	.0764(1)	.4133(1)	.7515(6)	80	71(5)	86(5)	84(6)	35(5)	-5(8)	11(9)
						Interstitial atoms							
O51	6c	0.17	O	.0514(27)	.1087(26)	.6714(59)	214(55)						
O52	6c	0.17	O	.0541(32)	.1096(30)	.9377(74)	236(58)						
O5	2a	0.34	O	0	0	.6931(61)	361(59)						
O6	6c	0.33	O	.6152(21)	.3097(42)	.6835(50)	587	637(152)	653(206)	471(120)	232(220)	56(101)	90(157)
Na1	2b	1.0	Na	2/3	1/3	.1250(15)	334	218	218	567(40)	109(7)	0	0
Na2	6c	1.0	Na	.1320(3)	.2669(3)	.2867(9)	410	286(14)	563(20)	383(24)	288(14)	-32(16)	-62(19)

*anisotropic temperature-factor = $\exp[-2\pi^2\Sigma^3{}_{i=1}\Sigma^3{}_{j=1}(U_{ij}a_ia_jh_ih_j)]$

lished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

STRUCTURE DESCRIPTION AND DISCUSSION

Framework

The geometry of the aluminosilicate framework (Table 4) is similar to that in cancrinite (Grundy & Hassan 1982) and to that obtained for basic cancrinite by Bresciani Pahor *et al.* (1982). The average Al–O and Si–O distances and the valence sums for the framework cations indicate complete ordering of the Al and Si atoms. The valence sums for the framework O atoms also are satisfactory (Table 4; Brown & Shannon 1973).

Cage

The cages in basic cancrinite, cancrinite, and vishnevite contain one $[Na\cdot H_2O]^+$ cluster. The Na1 site on the 3-fold axis is fully occupied by a Na atom. The bond-valence sum about Na1 is 1.0 v.u., as expected (Table 5). The O6 site is fully occupied by an oxygen atom of the water molecule, but this site is disordered about the 3-fold axis because of hydrogen bonding, as in other cancrinite-group minerals (Grundy & Hassan 1982, Hassan & Grundy 1984). However, Bresciani Pahor *et al.* (1982) placed the O6 site on the 3-fold axis, with an occupancy factor of 0.59.

Channel

The Na2 sites in the channels are fully occupied by Na atoms, and these sites are similar to those given by Bresciani Pahor *et al.* (1982), but the O atom sites O51 and O52 located in the channels are slightly different and have occupancy-factors that are one-half those given by Bresciani Pahor *et al.* (1982, Table 3). The O5 site on the 6_3 axis has an occupancy-factor identical to that given by Bresciani Pahor *et al.* (1982), but the O5 position is different, although related. The two O5 positions are related by a displacement along the z axis from the plane of the triangular array of Na2 sites, whereas a similar displacement in the opposite direction occurs in the specimen of Bresciani Pahor *et al.* (1982); thus the Na2–O5 distances are similar in both specimens (Table 5). The Na atom on the Na2 site could be in either a trigonal bipyramidal coordination by bonding to oxygen atoms on the O51 positions, or an octahedral coordination by bonding to the O atoms on the O52 positions (Table 5). Similar coordinations occur in cancrinite (see Fig. 7 in Grundy & Hassan 1982). In both coordinations, the bond-valence sum about Na2 is close to the expected value of 1 v.u. (Table 5).

TABLE 4. FRAMEWORK INTERATOMIC DISTANCES, ANGLES, AND BOND VALENCES

SiO_4 tetrahedron			AlO_4 tetrahedron		
T1-O1	1.622(5)Å	1.000v.u.	T2-O1	1.717(6)Å	0.783v.u.
-O2	1.615(7)	1.019	-O2	1.718(5)	0.781
-O3	1.626(9)	0.989	-O3	1.727(5)	0.764
-O4	1.620(5)	1.005	-O4	1.747(7)	0.727
Mean	1.621	4.014	Mean	1.727	3.056
		Edges of tetrahedra (Å)			
O1-O2	2.612(5)		O1-O2	2.749(8)	
-O3	2.623(11)		-O3	2.817(7)	
-O4	2.656(8)		-O4	2.794(11)	
O2-O3	2.693(9)		O2-O3	2.888(7)	
-O4	2.678(11)		-O4	2.897(6)	
O3-O4	2.616(7)		O3-O4	2.772(7)	
Mean	2.646		Mean	2.820	
		Angles in tetrahedra (°)			
O1-T1-O2	107.6(3)		O1-T2-O2	106.3(2)	
-O3	107.7(3)		-O3	109.7(3)	
-O4	110.0(3)		-O4	107.5(4)	
O2-T1-O3	112.4(3)		O2-T2-O3	113.9(3)	
-O4	111.8(3)		-O4	113.4(4)	
O3-T1-O4	107.4(4)		O3-T2-O4	105.8(2)	
Mean	109.5		Mean	109.4	
Bridging Angles(°)			Bond-valence sums for framework O atoms		
T1-O1-T2	148.5(4)		O1 = 0.783+1.000+0.065+0.161	= 2.009 v.u.	
T1-O2-T2	149.2(3)		O2 = 0.781+1.019+0.179	= 1.979	
T1-O3-T2	135.9(4)		O3 = 0.764+0.989+0.189	= 1.942	
T1-O4-T2	135.9(3)		O4 = 0.727+1.005+0.182	= 1.914	
Mean	142.4				

TABLE 5. CATION-ANION DISTANCES AND BOND VALENCES FOR INTERSTITIAL ATOMS

	Trigonal bipyramid			Octahedral	
Na2-O1	2.462(7)Å	0.161(2)v.u.	Na2-O1	2.462(7)Å	0.161(2)v.u.
-O3	2.394(8)	0.189(3)	-O3	2.394(8)	0.189(3)
-O4	2.408(6)	0.182(2)	-O4	2.408(6)	0.182(2)
-O51[a]	2.636(30)	0.110(7)	-O52[a]	2.659(70)	0.105(15)
-O51[b]	2.589(67)	0.122(13)	-O52[a]	2.670(35)	0.102(7)
-O51[b]	2.646(34)	0.108(7)	-O52[b]	2.523(33)	0.141(10)
-O3	2.879(7)	0.067(0)	-O3	2.879(7)	0.067(0)
-O4	2.913(11)	0.063(0)	-O4	2.913(11)	0.063(0)
-O5	2.966(6)	0.057(0)	-O5	2.966(6)	0.057(0)
Mean	2.655	Σ1.058	Mean	2.653	Σ1.066
Na1-O1 x 3	2.894(5)	0.195(0)	Bond-valence sums for oxygens		
-O2 x 3	2.417(5)	0.537(2)	O5 = 3 x 0.057	= 0.171 v.u.	
-O6[a]	2.899(26)	0.065(3)	O51 = 0.122+0.108+0.110	= 0.340	
-O6[b]	2.369(26)	0.200(12)	O52 = 0.105+0.102+0.141	= 0.348	
Mean	2.650	Σ0.996			

a = above; b = below.

CRYSTAL CHEMICAL AND END-MEMBER FORMULA

The present structural model does not allow an unambiguous distinction to be made between OH^- and H_2O in the channels. However, O51, O52, and O5 are all possible sites for the O atoms of these groups. The OH group should occur at a shorter distance to the Na2 site than that of H_2O. Therefore, the longer Na2–O5 distance indicates that O5 corresponds to H_2O, and O51 and O52 to OH (Table 5). The occupancy of these sites by OH and H_2O also is supported by the bond-valence sums about these sites, because both O51 and O52 are more valence-enhanced than O5 (Table 5). These results give a chemical formula, $Na_8[Al_6Si_6O_{24}](OH)_{2.04}{\bullet}2.68H_2O$, that agrees well with the results of the chemical analysis, thus indicating that the site assignments are essentially correct. In comparison, the chemical formula given by Bresciani Pahor *et al.* (1982) is $Na_{7.84}[Al_6Si_6O_{24}]{\bullet}5.98(H_2O,OH)$.

Deducing an ideal end-member formula from the structural model for basic cancrinite requires an evaluation of O–O distances for the O atoms of OH and H_2O in the channel. There are six equivalent positions for O51 or O52 per cell, and each set of positions is arranged in two trigonal planes. Two equivalent positions occur for O5. For any half of a unit cell, occupancy of a O51 position allows simultaneous occupancy of a O52 position in that half of the cell, but excludes occupancy of the O5 position and *vice versa.* This result permits, by exclusion of the O5 position, full occupancy of (a) four positions [2 O51 and 2 O52] per cell, or (b) with only the O5 sites, two positions per cell, or (c) three positions per cell [one O51 and one O52 in one-half a cell and O5 in the other half of the cell].

Full occupancy of four positions as in (a) requires $2OH^-$ for charge balance and also $2H_2O$, which seems an unlikely model because H_2O is not expected to be in such close coordination with the Na2 cation position. On average, only two O5*x* (where *x* equals 1 or 2) positions per cell are expected to be filled with OH. Because of the remoteness of the O5 position from the Na2 position, O5 contains H_2O rather than OH. Therefore, O5 does not contribute in any major way to charge balance in the channel (Table 5). For a full complement of 6 Na per channel, there must be 2 OH on the O5*x* positions, and the extra O observed must be H_2O on the O5 position [case(c)], which is confirmed by the refinement. Therefore, an ideal end-member formula for basic cancrinite is $Na_8[Al_6Si_6O_{24}](OH)_2{\bullet}3H_2O$, whereas Bresciani Pahor *et al.* (1982) suggested an ideal end-member formula $Na_{7.5}[Al_6Si_6O_{24}](OH)_{1.5}{\bullet}5H_2O$ for their specimen.

SUPERSTRUCTURE IN BASIC CANCRINITE

The origin of the superstructure reflections in basic cancrinite can be deduced by the elimination of parts of the structure that do not directly contribute to the supercell formation. Both cancrinite and basic cancrinite have a similar framework geometry, in which the Al and Si atoms are fully ordered, so that their structures do not contain stacking faults (see Hassan & Grundy 1990). Each cage in both structures contain one $Na[{\bullet}H_2O]^+$ cluster. Neither the frameworks nor the cage clusters contribute to the superstructure. The Na2 site does not show positional disorder in either structure. Because the Na2 site is fully occupied by Na atoms in basic cancrinite, it does not contribute to the formation of a supercell. The weak superstructure reflections in basic cancrinite arise from ordering of OH and H_2O and vacancies associated with these in the channels.

From the precession photograph, the spacing of the superstructure reflections gives a supercell repeat of approximately $3c_{canc}$ (Fig. 2b). In the cell with water molecules only, the charge on the Na2 site must be balanced through the O3 and O4 positions (Table 5), which causes some correlation between the degree of order of OH and H_2O in adjacent channels; this order produces the weak superstructure in some crystals of basic cancrinite (Fig. 2b). The X-ray scattering factors for OH and H_2O are small, and thus the superstructure reflections in basic cancrinite are weak compared to those in cancrinite and vishnevite. The variable development of the superstructure reflections indicates the presence of subtle changes in the H_2O content and degree of order of OH and H_2O in the channels of basic cancrinite. Nonrandom distribution of these species also cause streaking in the superstructure reflections along the c^* direction (Fig. 2b).

CONCLUSIONS

Basic cancrinite has an aluminosilicate framework in which the Al and Si atoms are fully ordered. The framework atoms, the cage clusters, $[Na{\bullet}H_2O]^+$, and the Na2 site, which is fully occupied by Na atoms, do not directly contribute to the satellite reflections in basic cancrinite. These reflections arise from ordering of OH, H_2O, and vacancies in the channels. The ideal end-member formula for basic cancrinite is $Na_8[Al_6Si_6O_{24}](OH)_2{\bullet}3H_2O$.

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