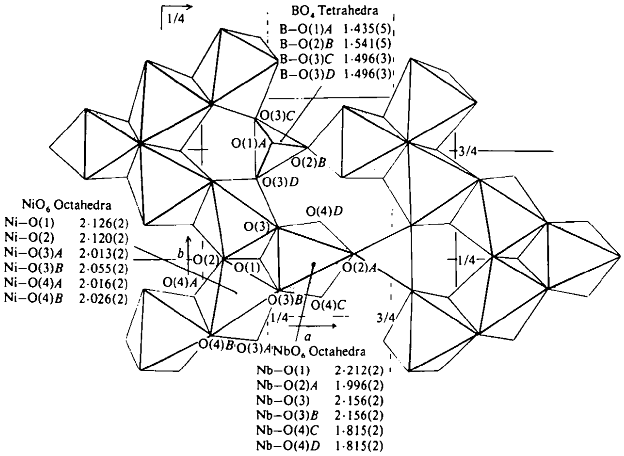

Fig. 1. One layer of the structure as viewed down the *c* axis.

Discussion. The structure contains layers that consist of zig-zag chains of edge-shared distorted NiO_6 and NbO_6 octahedra, and these metal-oxide chains are cross-linked within the layer through corner-shared BO_4 tetrahedra. As can been seen in the one-layer projection (Fig. 1), these chains fold at each NbO_6 octahedron and the intervening spaces between the metal-oxide chains constitute a set of analogous zig-zag chains of vacant octahedra, with BO_4 tetrahedra occupying selected sites. Each corner-shared BO_4 tetrahedron links one NbO_6 octahedron to two NiO_6 octahedra in another chain within the layer; the fourth BO_4 oxygen is then corner-shared with the unique oxygen of a triangular array (see below) of NbO_6 and NiO_6 octahedra in the next layer. The stacking direction of the layers coincides with the *c* axis of the lattice and each unit cell contains two layers that are related by an *a* glide. The position of the metal-oxide chains in one layer is directly over the vacant octahedra chains in the layer below it in the **c** direction.

This structure also may be described as possessing distorted hexagonal close-packed O atoms with the metal and B atoms occupying certain octahedral and tetrahedral interstices respectively. This ionic packing restricts the Ni^{2+} and Nb^{5+} ions to within $\pm 0{\cdot}28$ Å of the planes $z = 0{\cdot}0, 0{\cdot}5$ of the unit cell and the O atoms to within $\pm 0{\cdot}30$ Å of the planes $z = 0{\cdot}25, 0{\cdot}75$, with the B atoms sandwiched between these at $z = \pm 0{\cdot}09163$. The average Ni–O (2·059) and Nb–O (2·024 Å) bond lengths are in excellent agreement with those calculated (2·06, 2·01 Å) using the ionic radii for Ni^{2+}, Nb^{5+} and O^{2-} suggested by Shannon (1976). B–O distances range from 1·435 to 1·541 Å and are similar to those found in the isostructural compound Fe_3BO_6 (1·439 to 1·504 Å) described by Diehl & Brandt (1975) and by White, Miller & Neilsen (1965). The compound is also isostructural with the mineral norbergite $[Mg_2SiO_4Mg(OH,F)_2]$ (Taylor & West, 1929).

References

Diehl, R. & Brandt, G. (1975). *Acta Cryst.* **B31**, 1662–1665.

Enraf–Nonius. (1980). *Structure Determination Package.* Enraf–Nonius, Delft.

Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.

Stout, G. H. & Jensen, L. H. (1968). In *X-ray Structure Analysis.* New York: Macmillan.

Taylor, W. H. & West, J. (1929). *Z. Kristallogr.* **70**, 461–474.

Wanklyn, B. M., Wondre, F. R. & Davison, W. (1976). *J. Mater. Sci.* **11**(9), 1607–1614.

White, J. G., Miller, A. & Neilsen, R. E. (1965). *Acta Cryst.* **19**, 1060–1061.

Acta Cryst. (1982). **B38**, 893–895

Structure of a Basic Cancrinite

By N. Bresciani Pahor, M. Calligaris, G. Nardin and L. Randaccio

Istituto di Chimica, Università di Trieste, 34127 *Trieste, Italy*

(*Received* 18 *April* 1981; *accepted* 21 *September* 1981)

Abstract. Basic cancrinite, $(Na_2O)_{1{\cdot}24}Al_2O_3$-$(SiO_2)_{2{\cdot}01}.1{\cdot}87H_2O$, from electron microprobe analysis, hexagonal, $P6_3$, $a = 12{\cdot}678$ (8), $c = 5{\cdot}179$ (6) Å, $V = 720{\cdot}9$ Å^3, $Z = 3$; Mo $K\alpha$ radiation; final $R = 0{\cdot}034$ for 648 independent reflections. According to the framework interatomic distances [mean Al–O 1·742 (5), Si–O 1·615 (5) Å] the ordered distribution of Si and Al atoms is maintained as in the natural $(Ca,Na)CO_3$ cancrinite, as well as the oxygen framework and cation sites. However, significant differences with respect to the structure analysis of another synthetic basic cancrinite are found.

0567-7408/82/030893-03$01.00

Introduction. The structure of the natural aluminosilicate (Na,Ca)CO$_3$ cancrinite, determined by Jarchow (1965), has an ordered Si,Al framework built up by undecahedral cages linked in such a way as to form main channels bounded by puckered twelve-membered rings around the 6_3 axes, and channels bounded by six-membered rings around the threefold axes. One cation site, Na(2), was located near the wall of the main channel in front of the six-membered ring, the other, Na(1), being on the C_3 axis slightly displaced from the mean plane of the six-membered ring bounding the minor channel. The CO_3^{2-} anion was located on the 6_3 axis just in the middle of the main channel. Each undecahedral cage contains one water molecule.

Table 1. *Atomic parameters with e.s.d.'s in parentheses*

	f*	x	y	z	B/B_{eq} (Å)
Al	1·0	0·0751 (1)	0·4132 (1)	0·7510	0·68 (4)
Si	1·0	0·3286 (1)	0·4115 (1)	0·7500 (5)	0·65 (4)
O(1)	1·0	0·2027 (3)	0·4037 (4)	0·6650 (8)	1·39 (14)
O(2)	1·0	0·1168 (3)	0·5650 (3)	0·7264 (12)	1·87 (18)
O(3)	1·0	0·3519 (3)	0·3239 (3)	0·5589 (8)	1·47 (16)
O(4)	1·0	−0·0431 (3)	0·3174 (3)	0·5409 (8)	1·25 (13)
O(5)	0·34 (1)	0	0	0·9193 (94)	5·4 (7)†
O(6)	0·35 (1)	0·1100 (27)	0·0567 (27)	0·3408 (64)	7·8 (7)†
O(7)	0·33 (2)	0·1062 (26)	0·575 (26)	0·0999 (67)	5·8 (7)†
O(8)	0·59 (1)	$\frac{1}{3}$	$\frac{2}{3}$	0·1963 (83)	8·8 (14)†
Na(1)	0·95 (1)	$\frac{1}{3}$	$\frac{2}{3}$	0·6273 (12)	2·40 (13)
Na(2)	0·99 (1)	0·1307 (2)	0·2652 (3)	0·2883 (7)	2·93 (12)

* Fractional occupancy.
† Refined isotropically.

Table 2. *Distances of interest* (Å)

Si–O(1)	1·610 (5)	Al–O(1)	1·738 (5)
Si–O(2$^{\rm i}$)	1·620 (5)	Al–O(2)	1·728 (4)
Si–O(3)	1·612 (2)	Al–O(3$^{\rm iii}$)	1·756 (4)
Si–O(5$^{\rm ii}$)	1·619 (5)	Al–O(4)	1·744 (5)
Na(1)–O(8$^{\rm ix}$)	2·96 (4)	Na(2)–O(1)	2·474 (5)
–O(8)	2·23 (4)	Na(2)–O(3)	2·879 (5)
Na(1)–O(1)	2·895 (4)	Na(2)–O(3$^{\rm vii}$)	2·398 (5)
O(1$^{\rm i}$)		Na(2)–O(4)	2·909 (6)
O(1$^{\rm iv}$)		Na(2)–O(4$^{\rm viii}$)	2·417 (5)
Na(1)–O(2)	2·433 (4)	Na(2)–O(5$^{\rm v}$)	2·99 (1)
O(2$^{\rm i}$)		Na(2)–O(6)	2·54 (4)
O(2$^{\rm iv}$)		Na(2)–O(6$^{\rm vi}$)	2·56 (1)
		Na(2)–O(6$^{\rm vii}$)	2·88 (3)
		Na(2)–O(7)	2·68 (4)
		Na(2)–O(7$^{\rm vi}$)	2·76 (2)
		Na(2)–O(7$^{\rm iii}$)	2·38 (3)
O(5)···O(5$^{\rm v}$)	2·59 (7)	O(6)···O(6$^{\rm vi}$)	2·09 (5)
···O(6$^{\rm ix}$)	2·50 (5)	···O(6$^{\rm ii}$)	2·86 (4)
···O(6$^{\rm x}$)	1·27 (3)	···O(7)	1·25 (5)
···O(7$^{\rm ix}$)	1·50 (4)	···O(7$^{\rm vi}$)	2·42 (5)
···O(7$^{\rm x}$)	2·03 (5)	···O(7$^{\rm xi}$)	2·39 (4)
O(7)···O(7$^{\rm vi}$)	2·02 (5)	···O(7$^{\rm x}$)	2·73 (4)
···O(7$^{\rm ii}$)	2·84 (5)	···O(7$^{\rm ii}$)	1·77 (4)
		···O(7$^{\rm ii}$)	1·81 (5)

Symmetry code

(i) $-y, x-y, z+1$
(ii) $y, y-x, z+\frac{1}{2}$
(iii) $x-y, x, z+\frac{1}{2}$
(iv) $y-x, 1-x, z$
(v) $-x, -y, z-\frac{1}{2}$
(vi) $-y, x-y, z$
(vii) $x-y, x, z-\frac{1}{2}$
(viii) $y, y-x, z-\frac{1}{2}$
(ix) $x, y, z+1$
(x) $-x, -y, z+\frac{1}{2}$
(xi) $y-x, -x, z$

Later the synthesis and the structure determined from an X-ray powder analysis were reported (Barrer, Cole & Villinger, 1970) for the basic cancrinite of formula $(Na_2O)_{1\cdot19}Al_2O_3(SiO_2)_{2\cdot36}\cdot1\cdot35H_2O$ (II).

The Si,Al framework was found to be the same as in (Ca,Na)CO$_3$ cancrinite, the positions of the framework oxygens being different. This was attributed to the influence of the guest species. Furthermore, three cation sites were detected, one in the same position as the Na(1) site, the others deriving from the splitting of Na(2) into two positions. Finally, nearly one water molecule was found in the undecahedral cage, as in the natural cancrinite, but three more peaks, assigned to O atoms, were detected in the main channel, where some kind of silicate anion was suggested to be also present.

When single crystals of a synthetic basic cancrinite (I) became available, we decided to perform an accurate crystal structure determination to check some of the above subtle structural features. The single crystals were analysed by means of wavelength dispersive microprobe analysis using a fully automated ARLSEMQ instrument: SiO$_2$ 36·32, Al$_2$O$_3$ 30·46, CaO 0·13, Na$_2$O 22·99, H$_2$O (by difference) 10·10%.

Reflections were collected in the range $3\cdot5 \le \theta \le 28°$ on an automated Siemens AED diffractometer using Mo $K\alpha$ radiation. A total of 648 averaged independent reflections, having $I \ge 3\sigma(I)$, were corrected for Lorentz–polarization factors. In accordance with previous work the space group $P6_3$ was selected. The structure was refined by full-matrix least-squares techniques with anisotropic temperature factors for the cations and framework atoms. The occupancy and temperature factors for atomic species with fractional ocupancy were refined separately, being alternately held constant. The final R value was 0·034. The atomic scattering factors were those of Moore (1963) and the XRAY system (Stewart, Kundell & Baldwin, 1970) was used. Atomic coordinates are listed in Table 1, and bond lengths of interest are given in Table 2.*

Discussion. The present results show that the framework-atom positions and the cation sites are very similar to those reported for the carbonate cancrinite. In fact the positions of the framework atoms are the same within the experimental error, whereas the cation sites, with occupancy factors implying 7·82 Na$^+$ per

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36413 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

unit cell, were found to be slightly displaced from those reported by Jarchow (1970). Thus the influence of the guest species on the positions of framework oxygens, suggested by Barrer, Cole & Villinger (1970), is not observed in the basic cancrinite (I). Analogously no evidence for a splitting of the Na(2) site, suggested for the basic cancrinite (II), has been detected. The peak O(8), with fractional occupancy 0·59, is located in the undecahedral cage along the C_3 axis, 2·23 (4) Å from Na(1), and corresponds to the water molecule with occupancy factors 1 and 0·91 found in the natural and the basic cancrinite (II) respectively.

As expected the peak distribution around the 6_3 axis inside the main channel is different from that reported for the carbonate cancrinite, where a CO_3^{2-} anion was located on the 6_3 axis. The locations of O(5), O(6) and O(7), with occupancy factors of 0·34 (1), 0·35 (1) and 0·33 (2) respectively, are not far from those reported for the basic cancrinite (II) (Barrer, Cole & Villinger, 1970), with occupancy factors 0·49 (5), 0·44 (3) and 0·36 (3) respectively. The above results suggest the ideal formula $Na_6Al_6Si_6O_{24}.1{\cdot}5NaOH.5H_2O$ for (I). The coordination around Na(1) and Na(2) is shown in Fig. 1, and Na—O and O···O distances less than 3 Å are given in Table 2.

The unit-cell contents derived from chemical and crystallographic analyses for both basic cancrinites (I) and (II) are compared in Table 3. It is noteworthy that the agreement between crystallographic analyses appears to be better than that between chemical analyses. Furthermore a similar peak distribution for the non-framework atoms was found in both structures, with the exception of the splitting of the Na(2) site. The above comparison indicates that (I) and (II) are essentially the same, the larger content of Si, determined from chemical analysis of (II), probably being due to impurities. Thus the presence of silicate anions in the main channel is doubtful.

Despite the accuracy of the crystal structure determination, it was not possible to locate the OH^- anions. However, since in the carbonate cancrinite the CO_3^{2-} anions are located on the 6_3 axis in the main channel, it appears that the O(5), O(6) and O(7) positions are all acceptable locations for the OH^- anions. Thus the presence of guest anions, such as OH^- or CO_3^{2-}, and associated cations which block the channels is sufficient to explain why basic cancrinites are not useful molecular sieve sorbents, even in the absence of stacking faults and without assuming the presence of silicate anions.

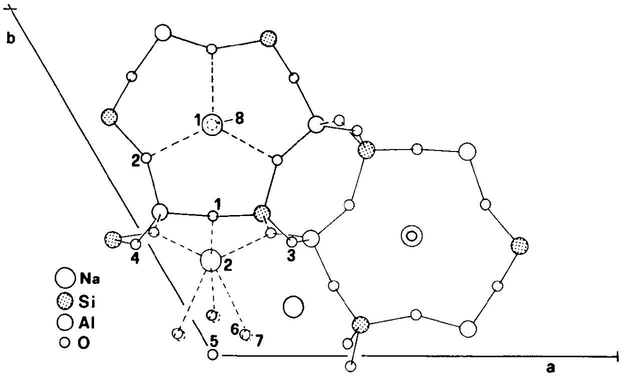

Fig. 1. A view of the structure along the *c* axis together with the numbering scheme for the crystallographically independent atoms.

Table 3. *Unit-cell content derived from chemical* (*c*) *and crystallographic* (*x*) *analyses for the two basic cancrinites* (I) *and* (II)

	(I)		(II)	
	c	*x*	*c*	*x*
Al	6·00	6	6·00	6
Si	6·04	6	7·08	6
Na	7·42	7·8	7·14	7·15
O	30·40	29·9	30·78	31·6

The work has been carried out with the financial support from the 'Progetto Finalizzato Chimica Fine e Secondaria' of CNR, Rome. The authors thank Dr L. V. C. Rees of Imperial College, London, for supplying the single crystals and Dr P. Comin-Chiaramonti for carrying out the microprobe analyses.

References

Barrer, R. M., Cole, J. F. & Villinger, H. (1970). *J. Chem. Soc. A*, pp. 1523–1531.

Jarchow, O. (1965). *Z. Kristallogr.* **122**, 407–422.

Moore, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY system, Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.