

The crystal structure of a “disordered” cancrinite

PAOLO BALLIRANO* and ADRIANA MARAS

Dipartimento di Scienze della Terra, Università di Roma “La Sapienza”, P.le A. Moro 5, I-00185 Roma, Italy

*Corresponding author, e-mail: paolo.ballirano@uniroma1.it

Abstract: An X-ray single-crystal structural investigation on a sample of cancrinite of formula $\text{Na}_{7.13}\text{Ca}_{0.87}(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{SO}_4)_{0.07}(\text{CO}_3)_{1.43} \cdot 2\text{H}_2\text{O}$ has been carried out. The cancrinite cage content has been found to be similar to that reported in previous structure refinements on natural and synthetic samples. However, differently from reference data, cations located inside the uninterrupted channel are distributed between two independent sites M1 and M2. Moreover carbonate groups are distributed, with partial occupancy, between two different z elevations (C1-OC1 and C2-OC2). The tetrahedral co-ordination of the sulphate group is obtained by partial substitution of carbon atoms at C1 and C2 by sulphur and oxygen. Two possible orientation with the apical oxygen pointing “down” or “up” are possible.

Key-words: cancrinite, cancrinite-group, feldspathoids, crystal structure.

Introduction

Cancrinite $(\text{Na,Ca})_{7-8}(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{CO}_3)_{1.2-1.7} \cdot 2\text{H}_2\text{O}$ (Bonaccorsi *et al.*, 1990) is the parent of the homonymous group of minerals. Its structure, determined by Nithollon & Vernotte (1955) and subsequently refined by Jarchow (1965), Smolin *et al.* (1981), Emiraliev & Yamzin (1982), and Grundy & Hassan (1982) among the others, is built up of layers of six-membered rings of $(\text{Si,Al})\text{O}_4$ tetrahedra piled along the z direction. The resulting framework consists of alternating columns of base-sharing undecahedral cages (cancrinite cages) and uninterrupted channels. These building units contain the extraframework cations (Na,Ca), anions and anionic groups (mainly CO_3 plus minor SO_4) and water molecules. Each unit cell contains two undecahedral cages and one uninterrupted channel. Following the most reliable structural data (Grundy & Hassan, 1982) two Na atoms are placed at the centre of the two bases of the cancrinite cage whereas the water molecule is disordered, in the middle of the cage, over three off-centre symmetry-related positions.

The carbonate groups are located at four different elevations inside the channel being distributed between two group of sites C1-OC1 and C2-OC2, respectively, each one characterised by a partial occupancy, whereas the remaining cations are located, at two different elevations, in a single site with partial occupancy. The complete occupation of the four carbonate levels is prevented by the occurrence of short C-C contacts of *ca.* 1.2–1.3 Å, leading to the non-stoichiometric compositions commonly found in cancrinites.

One interesting feature of cancrinite, strictly connected to the non-stoichiometry, is that it presents superstructures as many other members of the family. The satellite reflections define distinct supercells with various values of the c param-

eter. Such feature was firstly reported by Jarchow (1965) and subsequently by Foit jr. *et al.* (1973), Brown & Cesbron (1973) and Grundy & Hassan (1982). These superstructures have been interpreted as arising from the ordering of the Na,Ca cations, CO_3 groups, and vacancies inside the channels (Hassan & Buseck, 1992). However, despite the very deep investigation carried out by combined HRTEM and X-ray single-crystal structure analysis, some points are not fully disclosed. In particular there are differences between the CO_3 content determined by wet analysis (1.57 atoms per formula unit *pfu*) and single-crystal structure refinement (1.52 atoms *pfu*), and that derived from their model of ordering (1.63 atoms *pfu*). In fact both the cation and carbonate-groups occupancies were not refined, probably because the data were collected up to $65^\circ 2\theta$ ($\text{MoK}\alpha$) only. Moreover each one of the two ordering models proposed by the authors lead to different C1:C2 ratios that are not corresponding to the value of 1 used in the single-crystal structure analysis (Grundy & Hassan, 1982). Such discrepancy was explained as due to the presence of both models ... *in different channels or in different parts of the same channel....* According to this statement, it is not perfectly clear how this occurrence may be fitted within the superstructure period without the destruction of the superperiodicity.

The aim of this work is to obtain more accurate structure results for the substructure of cancrinite to be used for the rationalisation of the superstructures of cancrinites.

Experimental

A fragment (approximately 0.5 x 0.5 x 0.4 mm) of the crystal from Cava Satom (Cameroon), previously analysed by

Table 1. Chemical data of cancrinite. For comparison purposes reference data of Ballirano *et al.* (1995) are reported. Empirical formula calculated on 12 (Si + Al) basis. O_{rec} refers to the number of oxygen atoms recalculated after the inclusion of CO_3 to the formula.

	present work wt. %	reference data wt. %		present work atoms	reference data atoms
SiO ₂	35.09	37.08	Si	6.13	6.11
Al ₂ O ₃	28.47	30.03	Al	5.87	5.89
CaO	4.77	4.72	Ca	0.89	0.83
K ₂ O	< 0.01	-	K	-	-
Na ₂ O	20.37	19.82	Na	6.91	6.34
SO ₃	0.52	0.55	SO ₄	0.07	0.07
Cl	0.01	-	Cl	-	-
F	-	0.50	F	-	0.26
	89.23	92.97	O	25.34	24.86
O=F, Cl	-0.00	-0.21			
	89.23	92.76			
CO ₂ *	5.60	3.50	CO ₃	1.34	0.79
H ₂ O**	3.43	3.50	H ₂ O	2.00	1.92
total	98.26	99.76	O _{rec}	24.00	24.07

* Calculated following the procedure described in Ballirano *et al.* (1995).

** Corresponding to two molecules *pfu*.

Ballirano *et al.* (1995), was selected for single-crystal work. New electron microprobe analyses (Table 1) conducted on a Cameca SX50 point out to the following formula $Na_{6.91}Ca_{0.89}(Si_{6.13}Al_{5.87}O_{24})(SO_4)_{0.07}(CO_3)_{1.34} \cdot 2H_2O$. The CO_3 content was calculated to saturate the excess O charges using the procedure described in Ballirano *et al.* (1995). The following experimental setup was used: accelerating voltage 15 kV, beam current 5 nA, beam diameter 20 μ m to minimise alcaies' loss. Standards used were: corundum (Al), orthoclase (K), albite (Na), wollastonite (Ca, Si), barite (SO₄), sylvite (Cl), fluorophlogopite (F). Main differences with respect to reference data are the higher Na content and (consequently) the higher recalculated CO_3 content. Differently from Ballirano *et al.* (1995) no F was detected in the present work.

A few TEM photographs were collected on a further fragment of the crystal in order to observe the presence of superstructure reflections that were, however, not detected. This sample therefore corresponds to a "disordered cancrinite". 4232 reflections were collected in ω -scan mode up to a $2\theta_{max}$ of 90° on a Siemens P4 automated diffractometer. Miscellaneous data of the refinement are reported in Table 2. Starting structural parameters were those of Grundy and Hassan (1982). After a few cycles of refinement, difference Fourier maps clearly indicated that the M1 site was split as commonly found in other cancrinite-like minerals (davynite: Hassan & Grundy, 1990; Bonaccorsi *et al.*, 1990, 1992 and 1995; microsommite: Bonaccorsi *et al.*, 2001; pitiglianoite: Merlino *et al.*, 1991; quadridavynite: Bonaccorsi *et al.*, 1994; high-potassium vishnevite: Pushcharovskii *et al.*, 1989) but not reported so far for cancrinite *sensu stricto* (s.s.). The scattering power we used to refine the occupancy of the two cationic sites was that of Ca. Anisotropic displacement parameters were refined for all atoms. The refinement smooth-

Table 2. Miscellaneous data of the refinement of the structure of cancrinite.

Space group	P6 ₃
a (Å)	12.6216(8)
c (Å)	5.1293(4)
Diffractometer	Siemens P4
Radiation	MoK α
Crystal size (mm)	0.5 x 0.5 x 0.4
Scan mode	ω
Scan speed	3-30°/min*
$2\theta_{max}$	90°
Number of measured reflections	4232
Number of independent reflections	3883
Number of observed reflections	3630
($I_0 > 2\sigma(I_0)$)	
R _{int} (%)	2.60
Refined params	116
R(%) for all reflections	3.65
R(%) for $I_0 > 2\sigma(I_0)$	3.34
wR ² (%)	8.62
Refinement program	SHELXL-97 (Sheldrick, 1997)

* According to reflection intensity estimated by a prescan.

Table 3. Positional and isotropic displacement parameters and site scattering (s.s.) (electrons *pfu*) of cancrinite.

	x	y	z	U _{iso}	Site scattering
Si	0.91733(2)	0.58917(2)	0.25081(6)	0.00850(4)	
Al	0.66291(2)	0.58775(2)	0.25000(7)	0.00865(5)	
O1	0.79802(6)	0.59493(7)	0.3432(1)	0.0151(1)	
O2	0.88515(8)	0.44900(7)	0.2757(2)	0.0196(1)	
O3	0.95548(6)	0.64105(7)	0.9557(1)	0.0158(1)	
O4	0.67937(7)	0.64914(7)	0.9394(1)	0.0157(1)	
H ₂ O	0.6872(7)	0.3869(6)	0.814(1)	0.058(1)	
Na	2/3	1/3	0.3664(4)	0.0309(2)	
M1	0.8762(2)	0.7555(2)	0.6885(8)	0.0207(5)	37.8(3)
M2	0.8719(3)	0.7469(3)	0.733(1)	0.0294(8)	36.0(4)
C1	0	0	0.830(3)	0.052(5)	5.6(1)
OC1	0.8812(2)	0.9422(2)	0.825(1)	0.054(2)	24.0(2)
C2	0	0	0.591(3)	0.046(5)	4.6(1)
OC2	0.8802(3)	0.9403(4)	0.598(2)	0.049(2)	14.9(2)

Table 4. Anisotropic displacement U_{ij} parameters of cancrinite (x10⁴).

	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Si	81.6(7)	94.3(7)	82.9(7)	46.9(5)	1.8(8)	4.3(7)
Al	83.8(8)	93.6(8)	85.9(8)	47.3(6)	2.4(8)	2.8(9)
O1	119(2)	227(3)	144(2)	114(2)	17(2)	23(2)
O2	221(3)	125(2)	271(4)	108(2)	26(3)	12(2)
O3	141(2)	247(3)	97(2)	105(2)	29(2)	40(2)
O4	169(2)	236(3)	113(2)	136(2)	13(2)	49(2)
H ₂ O	745(40)	740(39)	309(18)	414(42)	16(23)	-26(22)
M1	181(4)	188(6)	248(9)	90(4)	5(3)	-8(4)
M2	224(7)	442(16)	282(13)	216(9)	85(7)	169(10)
Na	233(3)	233(3)	462(8)	117(1)	0	0
C1	148(12)	148(12)	1254(142)	74(6)	0	0
OC1	198(9)	194(9)	1202(47)	85(7)	68(13)	33(13)
C2	154(15)	154(15)	1083(138)	77(8)	0	0
OC2	154(13)	254(18)	1029(66)	87(12)	-58(19)	56(22)

Table 5. Relevant bond distances (Å) and angles (°) of cancrinite.

Si	-O2	1.6101(7)	O1	-Si-	O2	107.32(4)
	-O1	1.6147(7)	O1	-Si-	O3	110.52(4)
	-O3	1.6240(7)	O1	-Si-	O4	107.74(4)
	-O4	1.6247(7)	O2	-Si-	O3	112.21(5)
	—		O2	-Si-	O4	111.95(5)
			O3	-Si-	O4	107.03(4)
< Si-O >		1.618(6)	< O-Si-O >			109(2)
Al	-O2	1.7237(7)	O1	-Al-	O2	106.04(4)
	-O1	1.7291(7)	O1	-Al-	O3	107.22(4)
	-O3	1.7383(7)	O1	-Al-	O4	109.58(4)
	-O4	1.7476(7)	O2	-Al-	O3	114.02(4)
	—		O2	-Al-	O4	114.45(5)
			O3	-Al-	O4	105.32(3)
< Al-O >		1.735(9)	< O-Al-O >			109(4)
			Si	-O1-	Al	146.52(5)
			Si	-O2-	Al	151.32(6)
			Si	-O3-	Al	133.23(4)
			Si	-O4-	Al	133.33(5)
			< Si-O-Al >			141.10
M1	-O1	2.494(2)	M2	-O4		2.356(4)
	-O4	2.509(3)		-O3		2.368(4)
	-O3	2.532(3)		-O1		2.600(4)
	-O4	2.865(2)		-O4		2.948(4)
	-O3	2.897(2)		-O3		2.976(4)
	-OC1	2.316(7)		-OC1		2.432(4)
	-OC1	2.407(3)		-OC1		2.455(4)
	-OC1	2.429(3)		-OC1		2.556(8)
	-OC2	2.353(5)		-OC2		2.374(8)
	-OC2	2.367(5)		-OC2		2.488(6)
	-OC2	2.505(8)		-OC2		2.501(6)
< with OC1 >		2.556	< with OC1 >			2.586
< with OC2 >		2.565	< with OC2 >			2.576
Na	-H ₂ O	2.373(6)	C1	-OC1	x3	1.299(3)
	-O2	x3	C2	-OC2	x3	1.310(4)
	-O1	x3	C1	-C2		1.23(2)
	-H ₂ O	2.892(6)	C1	-C2		1.34(2)

ly converged to $wR^2 = 8.62\%$ and $R = 3.65\%$ for all 3883 independent reflections and to $R = 3.34\%$ for 3650 observed reflections ($I_0 > 2\sigma(I_0)$). Positional and isotropic displacement parameters and site scattering are reported in Table 3, anisotropic displacement parameters in Table 4, relevant bond distances and angles in Table 5, bond valence analysis in Table 6.

An FT-IR spectrum was measured using the powder obtained from a fragment of the same crystal used for the single-crystal analysis. About 4 mg of the sample were hand mixed in an agate mortar with 200 mg of KBr to obtain a pellet after compression on a dye at *ca.* 9 tons. Data were collected on a Perkin-Elmer FT-IR 2000, averaging 48 scans with a nominal resolution of 4 cm^{-1} in the $5200\text{--}450\text{ cm}^{-1}$ range. In order to reduce the presence of adsorbed water we used the same procedure reported by Ballirano *et al.* (2000). The plots of the $4000\text{--}3000$ and $1600\text{--}1300\text{ cm}^{-1}$ range are reported in Fig. 1a and 1b.

Structure description

Framework and cancrinite cage

The structure has a perfectly ordered Si,Al distribution as indicated by the average $\langle \text{Si-O} \rangle / \langle \text{Al-O} \rangle$ value of 0.933 (Hassan & Grundy, 1990). The SiO_4 tetrahedron is more regular than the AlO_4 one as indicated by the smaller bond distances dispersion. This reduced dispersion is also observed in the O-T-O bond angles. The two T-O-T angles involving the O3 and O4 oxygen atoms are significantly smaller (*ca.* 133°) than those involving O1 (*ca.* 147°) and O2 (*ca.* 151°).

The refined position of the Na atom and the water molecule in the cancrinite cage is consistent with reference data (see for example Grundy & Hassan, 1982).

The position of the O-H asymmetric stretching absorption bands in the IR spectrum at 3607 and 3539 cm^{-1} (Fig. 1a) points out to $\text{O}\cdots\text{O}_w$ contacts of 3.16 and 2.93 Å respectively, as derived from the correlation function $d(\text{O}\cdots\text{O})\text{--}v$ of Libowitzky (1999) for silicates only. Comparison of these values with the shortest observed $\text{O}\cdots\text{O}_w$ contacts of 3.164 (O2), 3.245 (O2), 3.319 (O1), 3.381 (O3), 3.419 (O4), and 3.471 (O2) Å does not lead to an univocal hydrogen location (Fig. 2).

Channel

The channel hosts two independent cationic sites (M1 and M2) and two independent groups of sites for carbonate anions (C1-OC1 and C2-OC2) (Fig. 3). The M1 and M2 cations are located at different z coordinates $z(\text{M1}) = 0.6885(8)$ and $z(\text{M2}) = 0.733(1)$, midway between those of the carbonate groups that are distributed, with partial occupancy, between two different z elevations of $0.825(1)$ (OC1) and $0.598(2)$ (OC2). The complex nature of this coupled cation/ CO_3 distribution is confirmed by the presence in the FT-IR spectrum of an envelope of bands, assigned to the C-O asymmetric stretching of the carbonate group, located in the $1600\text{--}1300\text{ cm}^{-1}$ range (Fig. 1b). Both M1 and M2 are coordinated by 3 oxygen atoms of the framework (O1, O3, and O4) and 3 oxygen atoms of carbonate groups (either OC1, OC2 or OC3) plus two longer ($> 2.86\text{ Å}$) contacts with O3 and O4. The average values of both M1-O and M2-O bonds differ only 0.01 Å in the case of the presence of either C1 or C2 and differ less than 0.03 Å between them. According to these small differences it is not possible to invoke a site splitting induced by a chemical-driven cationic ordering (*i.e.* all Ca in a preferred site) as observed in K-bearing cancrinite-group minerals (Pushcharovskii *et al.*, 1989; Hassan & Grundy, 1990; Bonaccorsi *et al.*, 1990; Merlino *et al.*, 1991; Bonaccorsi *et al.*, 1992, 1994, 1995 and 2001). The sum of the site scattering (*s.s.*) value of M1 and M2 is equal to 73.8 electrons *pfu*. This value is greater than the 71.8 electrons *pfu* from EMPA. Bond valence analysis indicates for both M1 and M2 a formal charge of 1.06.

The C1 site has a *s.s.* greater than C2 ($5.6(1)$ and $4.6(1)$ respectively). If we consider those sites as occupied by carbon atoms, this would correspond to a total of $1.70(3)$ car-

Table 6. Bond valence analysis following Brese & O'Keeffe (1991). M sites are considered as filled by Na atoms, C1 and C2 by C atoms.

	Si	Al	O1	O2	O3	O4	H ₂ O	Na	M1 x 0.573 (0.821 Na 0.179 Ca)	M2 x 0.545 (0.890 Na 0.110 Ca)	C1	C2	OC1	OC2	total
Si	–	–	1.026	1.038	1.000	0.998	–	–	–	–	–	–	–	–	4.062
Al	–	–	0.810	0.822	0.800	0.770	–	–	–	–	–	–	–	–	3.202
O1	1.026	0.810	–	–	–	–	–	0.057 ↓ x 3	0.153 x 0.573	0.115 x 0.545	–	–	–	–	2.043
O2	1.038	0.822	–	–	–	–	–	0.180 ↓ x 3	–	–	–	–	–	–	2.040
O3	1.000	0.800	–	–	–	–	–	–	0.138 x 0.573	0.215 x 0.545	–	–	–	–	2.048
O4	0.998	0.770	–	–	–	–	–	–	0.052 x 0.573	0.041 x 0.545	–	–	–	–	2.030
H ₂ O	–	–	–	–	–	–	–	0.213 0.052	0.056 x 0.573	0.045 x 0.545	–	–	–	–	0.265
Na	–	–	0.057 x 3	0.180 x 3	–	–	0.213 0.052	–	–	–	–	–	–	–	0.976
M1	–	–	0.153 ↓ x 0.573	–	0.138 ↓ x 0.573	0.149 ↓ x 0.573	–	–	–	–	–	–	0.248 x 0.469 ↓ x 0.573	0.224 x 0.383 ↓ x 0.573	1.065
M2	–	–	0.114 ↓ x 0.545	–	0.215 ↓ x 0.545	0.223 ↓ x 0.545	–	–	–	–	–	–	0.194 x 0.469 ↓ x 0.573	0.216 x 0.383 ↓ x 0.573	1.063
C1	–	–	–	–	–	–	–	–	–	–	–	–	0.183 x 0.469 ↓ x 0.573	0.149 x 0.383 ↓ x 0.573	3.837
C2	–	–	–	–	–	–	–	–	–	–	–	–	0.181 x 0.469 ↓ x 0.545	0.212 x 0.383 ↓ x 0.545	3.723
OC1	–	–	–	–	–	–	–	–	–	–	–	–	0.170 x 0.469 ↓ x 0.545	0.156 x 0.383 ↓ x 0.545	1.899
OC2	–	–	–	–	–	–	–	–	–	–	–	–	0.130 x 0.469 ↓ x 0.545	0.150 x 0.383 ↓ x 0.545	1.861
	4.062	3.202	2.043	2.040	2.048	2.030	0.265	0.976	1.065	1.063	3.837	3.723	1.899	1.861	

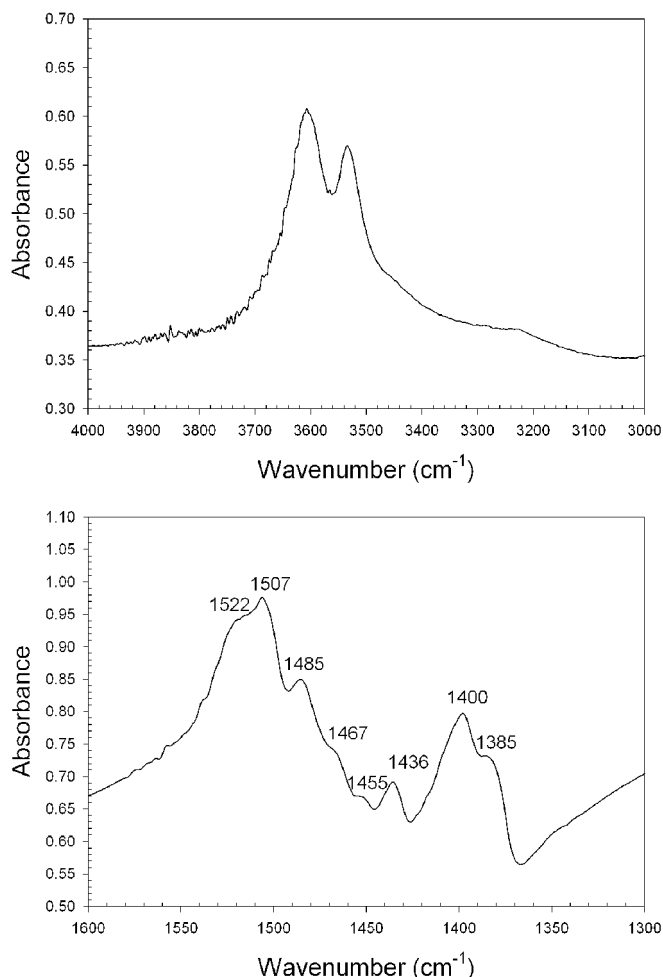


Fig. 1. FT-IR spectrum of cancrinite: a) 4000-3000 cm^{-1} range; b) 1600-1300 cm^{-1} range.

bonate group *pfu*. There are four possible levels per unit cell where the carbonate groups can be hosted, as well as for the cations, but, due to short contacts, the maximum allowed number of carbonate groups *pfu* should not exceed *ca.* 1.78 (Ballirano *et al.*, 1998). The carbon atoms are not exactly co-planar with the three oxygen atoms of the corresponding anionic groups showing an off-set of +0.027 Å (C1) and -0.037 Å (C2). The carbon off-set is similar in magnitude to that reported for some carbonates (Zemann, 1981). Because of this off-set, distances between planes of oxygen atoms of the carbonate groups are 1.163(9) and 1.402(9) Å (the latter not corresponding to OC1-OC2 contacts because of the 60° relative rotation of the two planes) whereas those between C1 and C2 are of 1.23(2) and 1.34(2) Å. Bond distances C1-OC1 (1.299(3) Å) and C2-OC2 (1.310(4) Å) are both slightly larger than the $\langle d_{102} \rangle$ of 1.284(18) Å of Zemann (1981).

The anisotropic displacement parameters of OC1 and OC2 are similar in magnitude as well as those of C1 and C2. Differently by Grundy & Hassan (1982), the U_{33} of C1 (0.13(1) Å²) has a value similar to that of C2 (0.11(1) Å²).

An alternative way to describe the mutual carbonates/cations distribution is possible. In fact the carbon atoms are coordinated by six cations forming three short (*ca.* 2.8 Å) and

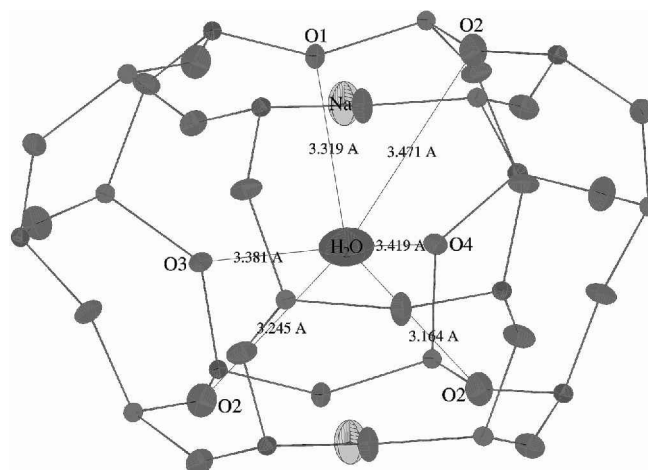


Fig. 2. Water molecule coordination. For the sake of clarity, only one of the three symmetry related H_2O position is plotted. Within 3.5 Å six contacts are observed: 3.164 (O2), 3.245 (O2), 3.319 (O1), 3.381 (O3), 3.419 (O4), and 3.471 (O2) Å.

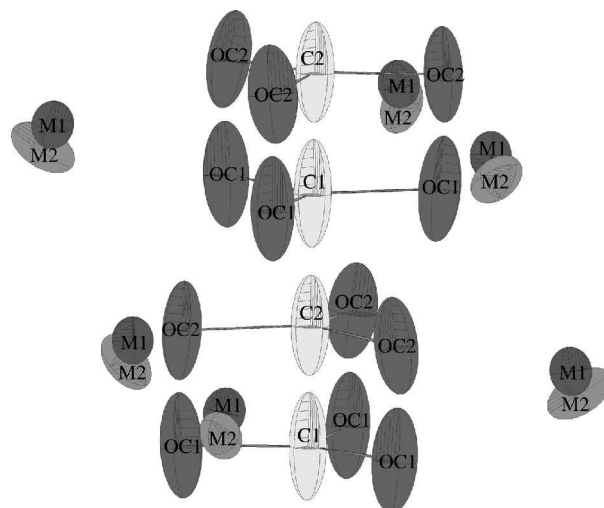


Fig. 3. Distribution of cations and carbonate groups as seen along [010].

three long (*ca.* 3.3 Å) contacts, in a way reminiscent that of aragonite (De Villiers, 1971; Dal Negro & Ungaretti, 1971). The six-fold M_6C coordination may be achieved by means of different combinations of two triple of cations (either M1 or M2) and a carbon atom (either C1 or C2) (Table 7). The M_6C polyhedra are ideally stacked along the z direction by face-sharing, however this is not the case for a “real” cancrinite because of the occurrence of short C-C contacts.

Moreover the presence of the sulphate group has to be taken in account. In fact, according to EMPA, there are 0.07 SO_4 *pfu*. Difference Fourier maps do not show any significant electron density residual along the axis of the channel to be attributed to the sulphur atom of the sulphate group. A model that includes the presence of the sulfate group may be however derived. In fact a suitable geometry for an SO_4 polyhedron may be obtained considering that C1 (or C2) is partly substituted by S and that C2 (or C1) may be substituted by an apical (OS) oxygen atom (Fig. 4). Such coordination may be obtained whenever C1 and C2 are separated by

Table 7. M-C contacts (Å) resulting in different possible M₆C polyhedra. Ca-C contacts of Ca₆C polyhedron for aragonite (Dal Negro & Ungaretti, 1971) are reported for comparison.

C1	-M1	x3	2.760(4)	C2	-M1	x3	2.718(4)
	-M1	x3	3.248(4)		-M1	x3	3.360(4)
	-M2	x3	2.808(4)		-M2	x3	2.866(4)
	-M2	x3	3.463(4)		-M2	x3	3.307(4)
C	-Ca		2.911(6)				
	-Ca	x2	2.939(6)				
	-Ca		3.242(6)				
	-Ca	x2	3.413(6)				

1.34 Å. In this case the S-(OS, OC1, OC2) bond distances are in the 1.30-1.34 Å range but more realistic distances of 1.40-1.50 Å may be obtained within the frame of the observed oxygen and carbon U₃₃ displacement parameters. This behaviour is different from that reported for carbonate-bearing davyne (Ballirano *et al.*, 1998), in fact in that case the sulphur of the sulphate anion has been clearly located midway between the two C1 and C2 carbon atoms separated by 1.13(4) Å and the apical oxygen between those separated by 1.54(4) Å. It should be reminded that the geometry of the carbonate groups was constrained to be planar in the case of davyne. An attempt to constrain the geometry of the carbonate group was therefore carried out in the case of cancrinite. The only result was an increase of the carbon U₃₃ displacement parameters without the appearance of any further electron density maxima. The different behaviour of the two structures may be attributed to the expanded *c* parameter of davyne (5.3333(5) Å) as compared to that of cancrinite (*c* = 5.1293 Å).

Accordingly we may hypothesise that the displacement of the carbon atoms from the plane of the oxygen atoms of the carbonate groups should reflect more realistically a distortion of the electron density due to the presence of a sulfur (or oxygen) atom located off-plane to realise the correct tetrahedral coordination. The displacement of both C1 and C2 seems to indicate that both orientation (“upward” with apical oxygen pointing up, and “downward” with apical oxygen pointing down) are statistically observed. Bond distances (C1-OC1 = 1.299(3) Å; C2-OC2 = 1.310(4) Å) and off-plane displacements (C1 = 0.027 Å; C2 = 0.037 Å) seems to point out that the downward orientation should be slightly more probable than the upward one.

The structural investigation of Grundy & Hassan (1982) was carried out with the constraint of the planarity of the carbonate group. Moreover the occupancy of C1-OC1 and C2-OC2 was arbitrarily fixed to 0.38 (corresponding to a content of 1.52 CO₃ *pfu*) whereas the wet chemical analysis pointed out to a 1.57 CO₃ and 0.06 Cl *pfu* content (see Table 1 in Grundy & Hassan, 1982). This omission as well as the constrain on the planarity of the carbonate group may be the reason for the different displacement parameters behaviour.

A possible model for the present sample of cancrinite points out to a C1 site that contains 0.03 S, 0.04 O and 0.81 C whereas C2 contains 0.04 S, 0.03 O and 0.62 C (Table 8). Such model is therefore consistent with the presence of 1.43 CO₃ and 0.07 SO₄ *pfu*. As can be seen the agreement is quite good, the only exception being OC1, whose observed *s.s.* is

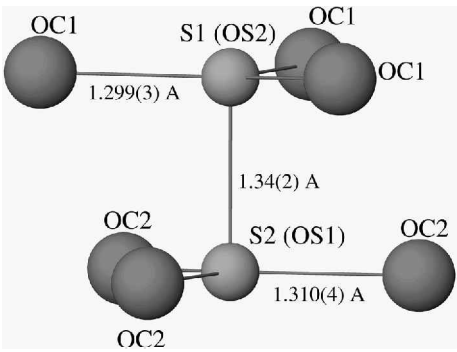


Fig. 4. Possible coordinations for the sulphate group. The first “downward” coordination is built-up by S1 OC1 x 3 and OS1. The second “upward” coordination consists of S2 OC2 x 3 and OS2.

Table 8. Possible site partition for M1, M2, C1-OC1 and C2-OC2 sites.

	Na	Ca	C	S	O	s.s. (calc.)	s.s. (obs.)
M1	2.464	0.536				37.8	37.8(3)
M2	2.670	0.330				36.0	36.0(4)
C1			0.805	0.030	0.040	5.6	5.6(1)
OC1					2.505	20.1	24.0(2)
C2			0.620	0.040	0.030	4.6	4.6(1)
OC2					1.980	15.8	14.9(2)

s.s. (calc.) refers to site scattering calculated from the model;
s.s. (obs.) refers to site scattering from structure refinement.

larger than that arising from the model, maybe because of correlation among occupancy and displacement parameters. If we admit that the lower *s.s.* of cations from EMPA with respect to that from structure refinement is due to alcalies’ loss, the difference of 2 electrons may be attributed to about 0.2 Na (corresponding to *ca.* 0.7 wt%). Considering this extra content we obtain a total of 7.13 Na *pfu* that is a value consistent with a fully occupation (Na_{7.13}Ca_{0.87})_{Σ=8.00} of the cationic sites. Based on this content the following cationic partitions M1 = 2.46 Na + 0.54 Ca and M2 = 2.67 Na + 0.33 Ca may be derived. The final formula from refinement may be therefore expressed as Na_{7.13}Ca_{0.87}(Si₆Al₆O₂₄)(SO₄)_{0.07}(CO₃)_{1.43} · 2H₂O and compares reasonably with Na_{6.91}Ca_{0.89}(Si_{6.13}Al_{5.87}O₂₄)(SO₄)_{0.07}(CO₃)_{1.32} · 2H₂O from EMPA.

Acknowledgements: Thanks are due to Dr. G.C. Parodi for the sample and to Dr. F. Bosi for the help in single-crystal data acquisition. Electron Microprobe analyses were carried out with the facilities of the CNR – Istituto di Geologia Ambientale e Geoingegneria in Roma. The authors very appreciated the careful revision and the constructive comments of two anonymous reviewers and Associate Editor Marco Pasero. This research has been carried out with the financial support of the Programma Nazionale di Ricerche in Antartide (PNRA) for the FT-IR spectroscopic work and of the CNR 98.00280.CT05 for the X-ray single-crystal work.

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Received 30 June 2003

Modified version received 26 July 2003

Accepted 6 October 2003