

Crystal structure of afghanite, the eight-layer member of the cancrinite-group: evidence for long-range Si,Al ordering

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Abstract: Afghanite, ideally $[(\text{Na},\text{K})_{22}\text{Ca}_{10}][\text{Si}_{24}\text{Al}_{24}\text{O}_{96}](\text{SO}_4)_6\text{Cl}_6$, is the eight-layer member of the cancrinite-group (ABABACAC stacking sequence). Its structure was refined in the $P31c$ space group to $R = 4.5\%$ by means of single-crystal X-ray diffraction data. The cell parameters are $a = 12.8013(7)$ Å, $c = 21.4119(18)$ Å. The $P6_3mc$ space group proposed in a previous structure refinement is not consistent with the ordered Si,Al pattern suggested by an Si/Al ratio equal to 1 shown by afghanite and other members of the cancrinite-group. The Si-O and Al-O bond distances, 1.61(2) Å and 1.72(2) Å respectively, found in the structure refinement, are in accordance with an ordered Si,Al distribution which is allowed by the $P31c$ space group, a maximal non isomorphic subgroup of $P6_3mc$.

Afghanite contains six 11-hedra (cancrinite) cages and two 23-hedra (liottite) cages. Four cancrinite cages are stacked along $[0\ 0\ z]$. They contain a regular ...Ca-Cl-Ca-Cl... chain similar to that observed in davynite and related phases: in particular Ca is located near the center of the bases whereas Cl is near the center of the cage. A liottite cage with a base-sharing cancrinite cage is stacked along $[2/3\ 1/3\ z]$ and $[1/3\ 2/3\ z]$. The liottite cage hosts a maximum of three sulphate groups which alternate regularly with cation-containing planes. The cancrinite cage, that shares the bases with the liottite cages, presents a disordered distribution of Cl and F leading to two possible configurations similar to those observed in liottite.

Key-words: afghanite, cancrinite-group, feldspathoids, structure refinement, stacking sequence.

Introduction

Afghanite is the eight-layer member of the cancrinite-group. The cancrinite-group minerals are feldspathoids showing a stacking along z of layers made up of six-membered rings of silico-aluminate tetrahedra. A complete description

may be found in Ballirano *et al.* (in press). Afghanite was discovered in the lapis-lazuli mine of Sar-e-Sang, Afghanistan (Bariand *et al.*, 1968) and later described by Ivanov & Sapozhnikov (1975) from a lapis-lazuli mine in the Lake Baikal region. The ABABACAC stacking sequence of afghanite was determined by Merlino (1976).

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Merlino & Mellini (1976) tried to refine the structure in the space group $P6_3mc$ assuming a completely disordered distribution of Si and Al ($R = 0.16$). However, because of the poor reliability index, they postulated the presence of small domains with opposite Al/Si ordering schemes suggesting a possible lowering of the symmetry. Additional chemical data were presented by Leoni *et al.* (1979) and Hogarth (1979). The latter showed that afghanite has an SO_4/Cl ratio close to one and indicated some compositional ranges for the various cancrinite-group minerals.

A complete structure refinement was finally done in the space group $P6_3mc$ ($R = 0.069$) by Pobedinskaya *et al.* (1991), apparently using the sample of Ivanov & Sapozhnikov (1975). The structural data confirmed the ABABACAC stacking sequence determined by Merlino (1976). More recent work includes an attempt to correlate the structural features of afghanite with those of the other cancrinite-like minerals (Rastsvetaeva *et al.*, 1993), an X-ray, SAED, IR study of afghanite from Vesuvius (Ballirano *et al.*, 1994a), and a crystal chemical study of the cancrinite-group (Maras & Ballirano, 1994). Moreover Ballirano *et al.* (1994b) explained, on the basis of a sub-unit model and geometrical constraints, the reason why afghanite must have an SO_4/Cl ratio equal to one.

The aim of this work is to obtain more accurate structural information on afghanite, especially with respect to the long-range Si,Al distribution. In this regard the recent structure refinement of liottite (the six-layer member of the cancrinite-group) showed a perfectly ordered distribution of Si and Al tetrahedra. This result is in accordance with the general feature of the cancrinite-group minerals (with the exception of cancrisilite; Khomyakov *et al.*, 1991) of an Si/Al ratio equal to one.

Experimental

A colorless, transparent crystal (0.4 x 0.3 x 0.3 mm) from the sample MMUR (Museo di Mineralogia dell'Università di Roma "La Sapienza") 24336 from Pitigliano, Tuscany, and examined by Maras & Ballirano (1994), was used for this study. The electron-microprobe analysis, recalculated on a (Si + Al = 48) basis, gave an empirical formula of $[(Na_{17.4}K_{3.4}Ca_{10.7})[Si_{24.3}Al_{23.7}O_{96}](SO_4)_{6.3}Cl_{5.7}F_{0.1}]$. Intensity data were measured on a Siemens P4 four-circle diffractometer oper-

ating at 50 kV and 30 mA using graphite monochromatized $MoK\alpha$ radiation. Data were collected in ω scan-mode up to a 2θ value of 60° ; 3317 unique reflections were collected and 2174 were considered as observed $F_{obs} > 4\sigma$ (F_{obs}). The cell parameters ($a = 12.8013(7)$, $c = 21.412(2)$ Å) were derived by least-square refinement using 36 reflections ($15^\circ < 2\theta < 30^\circ$). Three reference reflections were monitored every 47 measurements: they did not show any significant intensity variation. A psi-scan empirical absorption correction was done. Structure refinement was carried out using SHELXL-93 (Sheldrick, 1993).

Structure refinement

The refinement of the framework was started assuming an ordered distribution of Si and Al with framework symmetry $P31c$, a maximal non-isomorphous subgroup of $P6_3mc$. A few cycles of refinement confirmed this model. The positions of the remaining anions and cations were located on difference-Fourier maps. Similarly to liottite, the cancrinite cage, which shares its bases with the liottite cages, shows a disordered distribution of the Ca atoms. As in liottite this disordered distribution of Ca atoms is coupled with the presence of a subsidiary maximum inside the cancrinite cage; this maximum was attributed, according to the microprobe analysis, to F atoms. This type of disordered distribution was not observed in the previous structure refinement of afghanite (Pobedinskaya *et al.*, 1991). According to their chemical data, Pobedinskaya *et al.* (1991) attributed the Cl2 and Cl3 sites to molecular water: the sample of afghanite of the present study does not show any IR absorption band in the 4000-3000 cm^{-1} and 1800-1400 cm^{-1} regions attributable to H_2O (Maras & Ballirano, 1994). The occupancies of the oxygen sites of the sulphate groups of the liottite cages were fixed as requested by the correct geometry of the SO_4 tetrahedra, as explained in the following chapter. As for liottite the cation site occupancies were refined assuming the scattering power of K.

The final conventional R index is 4.5 % for 2174 $F_{obs} > 4\sigma F_{(obs)}$, and 7.8 % for all 3317 data; the wR^2 index is 10.2 % for 2174 $F_{obs} > 4\sigma F_{(obs)}$, and 12.8 % for all 3317 data. Fractional coordinates, occupancies, and displacement parameters are listed in Table 1. Bond distances are reported in Table 2.

Table 1. Fractional coordinates, site occupancies, and mean displacement parameters in afghanite.

Atoms	x	y	z	Site multiplicity	Occupancy	U _{eq} (× 10 ⁴)
Si1	0.2530(3)	0.0000(1)	0.4950(4)	1	1	49(9)
Al1	0.7412(4)	0.0000(1)	0.9952(4)	1	1	117(12)
Si2	0.9234(3)	0.5849(3)	0.3687(4)	1	1	91(8)
Al2	0.0784(3)	0.4033(3)	0.8684(4)	1	1	88(9)
Si3	0.0056(3)	0.2570(4)	0.2445(4)	1	1	91(10)
Al3	0.0040(3)	0.7424(4)	0.7450(4)	1	1	57(10)
Si4	0.9232(3)	0.5851(3)	0.1217(4)	1	1	75(7)
Al4	0.0783(3)	0.4033(3)	0.6220(4)	1	1	70(8)
O1	0.342(1)	0.333(1)	0.6773(5)	1	1	254(25)
O2	0.669(1)	0.680(1)	0.1820(6)	1	1	194(22)
O3	0.348(1)	0.345(1)	0.8062(5)	1	1	161(22)
O4	0.663(1)	0.668(1)	0.3020(5)	1	1	194(22)
O5	0.122(1)	0.887(1)	0.7462(7)	1	1	147(12)
O6	0.336(1)	0.335(1)	0.4281(5)	1	1	266(25)
O7	0.674(1)	0.677(1)	0.9335(5)	1	1	214(23)
O8	0.3516(9)	0.3424(9)	0.0554(5)	1	1	153(21)
O9	0.658(1)	0.669(1)	0.5508(5)	1	1	153(21)
O10	0.121(1)	0.883(1)	0.0028(6)	1	1	220(22)
O11	0.117(1)	0.887(1)	0.4947(6)	1	1	310(26)
O12	0.118(1)	0.884(1)	0.2491(7)	1	1	217(20)
O13	0.4580(8)	0.5465(8)	0.6257(6)	1	1	223(15)
O14	0.4562(8)	0.5482(8)	0.8750(5)	1	1	293(26)
O15	0.2113(8)	0.7732(9)	0.6264(5)	1	1	202(20)
O16	0.2128(8)	0.7715(8)	0.8660(6)	1	1	208(22)
Ca1	0	0	0	1/3	1	188(22)
Ca2	0	0	0.2500(7)	1/3	1	175(9)
Ca3	1/3	2/3	0.6296(4)	1/3	1	163(9)
Ca3a	1/3	2/3	0.660(1)	1/3	0.90(1)	131(13)
Ca4	1/3	2/3	0.8791(6)	1/3	0.10(1)	131(13)
Ca4a	1/3	2/3	0.853(2)	1/3	0.90(1)	147(17)
Y1	0	0	0.1237(5)	1/3	0.10(1)	147(17)
Cl2	0	0	0.3739(5)	1/3	1	701(43)
Cl3	1/3	2/3	0.7527(5)	1/3	1	796(52)
F	0.4018	0.5995	0.7527(5)	1	0.90(1)	1157(42)
K1*	0.4432	0.2235(5)	0.7452	1	0.03(1)	500
			0.8651(5)	1	0.675(9)	387(17)
K1a	0.386(4)	0.199(3)	0.860(2)	1	0.10(1)	387(17)
K2 (0.45 (K,Ca) + 0.55 Na)	0.5054(6)	0.5014(6)	0.9912(5)	1	0.769(7)	377(11)
K3 (0.03 (K,Ca) + 0.97 Na)	0.5211(6)	0.4845(7)	0.7412(5)	1	0.591(7)	399(15)
K4	0.423(1)	0.210(1)	0.6238(6)	1	0.401(6)	341(24)
	(0.18 (K,Ca) + 0.82 Na)					
K4a	0.456(2)	0.236(1)	0.6163(9)	1	0.26(1)	341(24)
S1	1/3	2/3	0.2475(6)	1/3	1	429(12)
S2	1/3	2/3	0.4625(5)	1/3	1	445(17)
S3	1/3	2/3	0.0301(6)	1/3	1	532(21)
OS1a	0.444(4)	0.744(3)	0.278(3)	1	1/3	920(165)
OS1b	0.400(6)	0.619(6)	0.208(4)	1	1/3	1173(288)
OS1c	0.40(1)	0.64(1)	0.296(2)	1	1/3	1387(353)
OS1d	0.432(5)	0.762(6)	0.214(5)	1	1/3	1895(438)
OS2a	1/3	2/3	0.5231(9)	1/3	1	1255(149)
OS2b	0.211(2)	0.608(2)	0.442(1)	1	1	875(55)
OS3a	0.206(7)	0.587(9)	0.073(2)	1	1/3	1621(405)
OS3b	0.215(2)	0.608(2)	0.042(2)	1	2/3	1251(160)
OS3c	0.265(5)	0.635(4)	0.970(3)	1	1/3	1596(302)

* Cation occupancies were derived assuming that the sum of the occupancy of the couples of split sites is equal to one, and the scattering power of 19 electrons was considered for both Ca and K.

Table 2. Selected bond-distances (Å) in afghanite.

Si1	-O7(<i>a</i>)	1.60(1)		Al1	-O6(<i>d</i>)	1.74(1)	
	-O9(<i>b</i>)	1.61(1)			-O8(<i>e</i>)	1.72(1)	
	-O10(<i>c</i>)	1.61(1)			-O10(<i>f</i>)	1.71(1)	
	-O11	1.62(1)			-O11(<i>g</i>)	1.71(1)	
mean value		1.61(1)		mean value		1.72(1)	
Si2	-O3(<i>h</i>)	1.65(1)		Al2	-O4(<i>g</i>)	1.74(1)	
	-O6(<i>f</i>)	1.61(1)			-O7(<i>i</i>)	1.70(1)	
	-O14(<i>i</i>)	1.62(1)			-O14(<i>f</i>)	1.72(1)	
	-O16(<i>d</i>)	1.60(1)			-O16(<i>k</i>)	1.73(1)	
mean value		1.62(2)		mean value		1.73(2)	
Si3	-O2(<i>j</i>)	1.62(1)		Al3	-O1(<i>f</i>)	1.76(1)	
	-O4(<i>j</i>)	1.60(1)			-O3(<i>f</i>)	1.72(1)	
	-O5(<i>l</i>)	1.63(1)			-O5(<i>m</i>)	1.71(1)	
	-O12(<i>k</i>)	1.59(1)			-O12(<i>n</i>)	1.73(1)	
mean value		1.61(2)		mean value		1.73(2)	
Si4	-O1(<i>h</i>)	1.61(1)		Al4	-O2(<i>g</i>)	1.70(1)	
	-O8(<i>f</i>)	1.65(1)			-O9(<i>j</i>)	1.73(1)	
	-O13(<i>i</i>)	1.62(1)			-O13(<i>f</i>)	1.71(1)	
	-O15(<i>d</i>)	1.60(1)			-O15(<i>k</i>)	1.73(1)	
mean value		1.62(2)		mean value		1.72(1)	
Ca1	-O10	2.64(1)		Ca2	-O5(<i>i</i>)	2.61(1)	
	-O10(<i>k</i>)	2.64(1)			-O5(<i>l</i>)	2.61(1)	
	-O10(<i>o</i>)	2.64(1)			-O5(<i>p</i>)	2.61(1)	
	-O11(<i>i</i>)	2.55(1)			-O12	2.59(1)	
	-O11(<i>l</i>)	2.55(1)			-O12(<i>k</i>)	2.59(1)	
	-O11(<i>p</i>)	2.55(1)			-O12(<i>o</i>)	2.59(1)	
	-Cl1	2.65(1)			-Cl1	2.70(1)	
	-Cl2(<i>l</i>)	2.70(1)			-Cl2	2.65(1)	
Ca3	-O13(<i>f</i>)	2.72(1)		Ca3a	-O13(<i>f</i>)	2.81(1)	
	-O13(<i>k</i>)	2.72(1)			-O13(<i>k</i>)	2.81(1)	
	-O13(<i>q</i>)	2.72(1)			-O13(<i>q</i>)	2.81(1)	
	-O15(<i>f</i>)	2.54(1)			-O15(<i>f</i>)	2.64(1)	
	-O15(<i>k</i>)	2.54(1)			-O15(<i>k</i>)	2.64(1)	
	-O15(<i>q</i>)	2.54(1)			-O15(<i>q</i>)	2.64(1)	
	-OS2a	2.28(2)			-OS2a	2.93(4)	
	-Cl3	2.64(1)			-F	2.36	x 1/3
					-F(<i>e</i>)	2.36	x 1/3
					-F(<i>j</i>)	2.36	x 1/3
Ca4	-O14(<i>f</i>)	2.68(1)		Ca4a	-O14(<i>f</i>)	2.72(1)	
	-O14(<i>k</i>)	2.68(1)			-O14(<i>k</i>)	2.72(1)	
	-O14(<i>q</i>)	2.68(1)			-O14(<i>q</i>)	2.72(1)	
	-O16(<i>f</i>)	2.52(1)			-O16(<i>f</i>)	2.52(1)	
	-O16(<i>k</i>)	2.52(1)			-O16(<i>k</i>)	2.52(1)	
	-O16(<i>q</i>)	2.52(1)			-O16(<i>q</i>)	2.52(1)	
	-OS3c(<i>r</i>)	2.09(8)	x 1/3		-OS3c(<i>r</i>)	2.61(8)	x 1/3
	-OS3c(<i>s</i>)	2.09(8)	x 1/3		-OS3c(<i>s</i>)	2.61(8)	x 1/3
	-OS3c(<i>t</i>)	2.09(8)	x 1/3		-OS3c(<i>t</i>)	2.61(8)	x 1/3
	-Cl3	2.71(1)			-F	2.76	x 1/3
					-F(<i>e</i>)	2.76	x 1/3
					-F(<i>j</i>)	2.76	x 1/3
K1	-O3	2.72(1)		K1a	-O3	2.44(4)	
	-O4(<i>u</i>)	2.77(1)			-O4(<i>u</i>)	2.55(4)	
	-O6(<i>v</i>)	2.79(1)			-O6(<i>v</i>)	2.61(4)	
	-O7(<i>b</i>)	2.91(1)			-O7(<i>b</i>)	2.79(4)	
	-OS1a(<i>u</i>)	2.27(5)	x 1/3		-O12(<i>c</i>)	2.91(4)	
	-OS1c(<i>u</i>)	2.44(10)	x 1/3		-OS1a(<i>u</i>)	2.59(7)	x 1/3
	-OS1c(<i>v</i>)	2.79(12)	x 1/3		-OS1c(<i>u</i>)	2.89(12)	x 1/3

Table 2. (continued).

-OS2b(v)	2.71(2)				
-OS2b(w)	2.71(2)				
K2 -O6(<i>l</i>)	2.54(2)		K3 -O1	2.54(2)	
-O7(<i>x</i>)	2.53(1)		-O2(v)	2.55(1)	
-O8	2.43(1)		-O3	2.47(1)	
-O9(<i>l</i>)	2.42(1)		-O4(v)	2.48(1)	
-O14(<i>y</i>)	2.71(1)		-O13(<i>q</i>)	2.84(1)	
-OS2b(<i>h</i>)	2.52(2)		-OS1a	2.72(5)	x 1/3
-OS3a(<i>e</i>)	2.92(7)	x 1/3	-OS1b(v)	2.16(4)	x 1/3
-OS3b(<i>e</i>)	2.66(4)	x 1/3	-OS1c(v)	2.53(5)	x 1/3
-OS3c(<i>e</i>)	3.01(6)	x 1/3	-OS1d(<i>u</i>)	2.41(9)	x 1/3
			-F	2.60	x 1/3
K4 -O1	2.54(1)		K4a -O1	2.68(2)	
-O2(<i>u</i>)	2.54(1)		-O2(<i>u</i>)	2.87(2)	
-O8(v)	2.89(1)		-O8(v)	2.86(2)	
-O9(<i>b</i>)	2.92(1)		-OS1b(<i>u</i>)	2.77(6)	x 1/3
-OS1b(<i>u</i>)	2.84(6)	x 1/3	-OS1b(v)	2.86(10)	x 1/3
-OS1d(<i>u</i>)	2.58(7)	x 1/3	-OS1d(<i>u</i>)	2.48(8)	x 1/3
-OS3a(v)	2.38(8)	x 1/3	-OS3a(v)	2.11(8)	x 1/3
-OS3a(w)	2.77(10)	x 1/3	-OS3a(w)	2.37(10)	x 1/3
-OS3b(w)	2.92(3)	x 1/3	-OS3b(w)	2.53(3)	x 1/3
-OS3b(v)	2.92(5)	x 1/3	-OS3b(v)	2.64(5)	x 1/3
S1 -OS1a	1.41(5)		S2 -OS2a	1.30(2)	
-OS1b	1.52(6)		-OS2b	1.43(2)	
-OS1c(<i>e</i>)	1.50(5)		-OS2b(<i>e</i>)	1.43(2)	
-OS1d(<i>e</i>)	1.43(4)		-OS2b(<i>j</i>)	1.43(2)	
mean value	1.47(5)		mean value	1.40(6)	
S3 -OS3a	1.70(7)				
-OS3b(<i>e</i>)	1.34(2)				
-OS3b(<i>j</i>)	1.34(2)				
-OS3c(<i>e</i>)	1.50(5)				
mean value	1.47(15)				
SYMMETRY CODES					
(a) $-x + 1, -x + y, z - 1/2$		(n) $-x + 1, -x + y + 1, z + 1/2$			
(b) $-y + 1, x - y, z$		(o) $-x + y, -x, z$			
(c) $x - y, -y, z + 1/2$		(p) $-x, -x + y, -z - 1/2$			
(d) $-x + 1, -x + y + 1, z - 1/2$		(q) $x, y + 1, z$			
(e) $-y + 1, x - y + 1, z$		(r) $x, y, z + 1$			
(f) $-x + y + 1, -x + 1, z$		(s) $-x + y, -x + 1, z + 1$			
(g) $x - y, -y + 1, z + 1/2$		(t) $-y + 1, x - y + 1, z + 1$			
(h) $x - y + 1, -y + 1, z - 1/2$		(u) $-x + 1, -x + y, z + 1/2$			
(i) $x - y, -y, z - 1/2$		(v) $y, x, z + 1/2$			
(j) $-x + y, -x + 1, z$		(w) $x - y + 1, -y + 1, z + 1/2$			
(k) $-y, x - y, z$		(x) $x, y, z - 1$			
(l) $y, x, z - 1/2$		(y) $x, y + 1, z - 1$			
(m) $x + 1, y + 1, z$					

The *e.s.d.* are reported in parenthesis; the letters in italics refer to the symmetry codes for equivalent positions, listed at the end of the table. For each cation only the bond distances which may actually occur are reported; if an anion site is only partly occupied, the fraction in the last column indicates how many times the bond occurs. Because the cation sites K1, K1a, K4 and K4a are partly occupied, the number of bonds in the structure is lower than the fractions indicated.

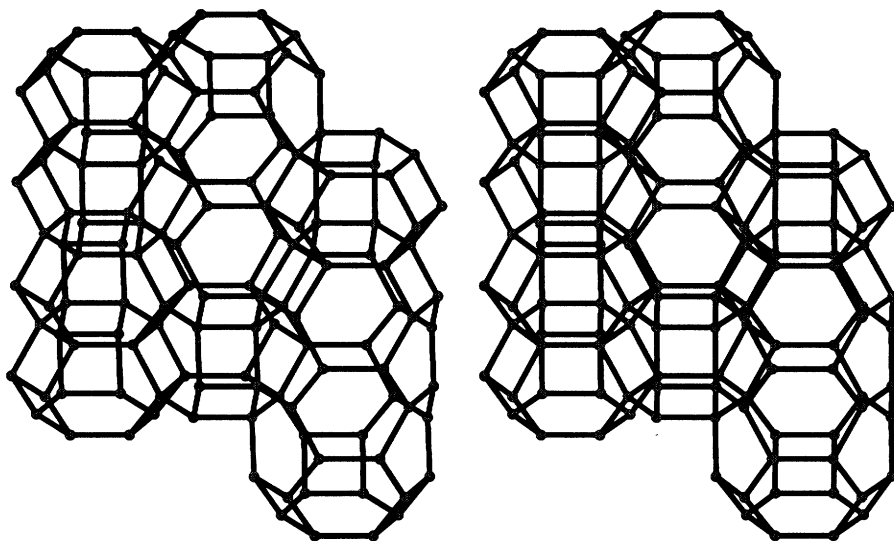


Fig. 1. Stereoscopic drawing of the afghanite framework, depicted as a 4-connected net.

Framework

The afghanite framework (Fig. 1) has a perfectly ordered distribution of Si and Al: $\langle \text{Si-O} \rangle = 1.61(2) \text{ \AA}$ and $\langle \text{Al-O} \rangle = 1.72(2) \text{ \AA}$. The calculated $d_{\text{Si-O}}/d_{\text{Al-O}}$ ratio is 0.936, corresponding closely to the value 0.93 found by Hassan & Grundy (1990) for a perfectly ordered member of the cancrinite group, and 0.931 for liottite (Ballirano *et al.*, in press). Afghanite contains six cancrinite and two liottite cages. Cancrinite cages are stacked along $[0\ 0\ z]$ (Fig. 2a), and liottite and cancrinite cages stack along $[2/3\ 1/3\ z]$ and $[1/3\ 2/3\ z]$ (Fig. 2b).

Cancrinite cages

There are six undecahedral or cancrinite cages in the afghanite structure. The cancrinite cages stacked along $[0\ 0\ z]$ show a regular $\dots\text{Ca-Cl-Ca-Cl}\dots$ chain similar to that observed in davyne, microsommite and quadridavyne (Bonaccorsi *et al.*, 1994). The previous structure-refinement of afghanite (Pobedinskaya *et al.*, 1991) showed a $\dots\text{Ca-Cl-Ca-H}_2\text{O}\dots$ chain, a model suggested by the chemical data. According to the model of Ballirano *et al.* (1994b), afghanite may host six sulphate groups and six chlorine atoms per unit cell, with limited $2\text{Cl} \leftrightarrow \text{SO}_4$ substitution.

Conversely, the chemical analyses of the sample of Pobedinskaya *et al.* (1991) indicate 5.6 SO_4 , 5.6 Cl, 0.8 CO_3 and 10.4 H_2O to be

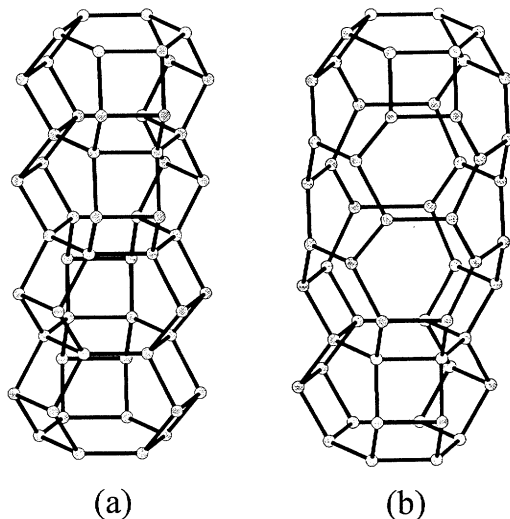


Fig. 2. Drawing of the various sub-units in afghanite; only the connectivity between tetrahedral nodes is represented. (a) Columns of cancrinite cages along $[0\ 0\ z]$; (b) liottite cage and cancrinite cages along $[1/3\ 2/3\ z]$.

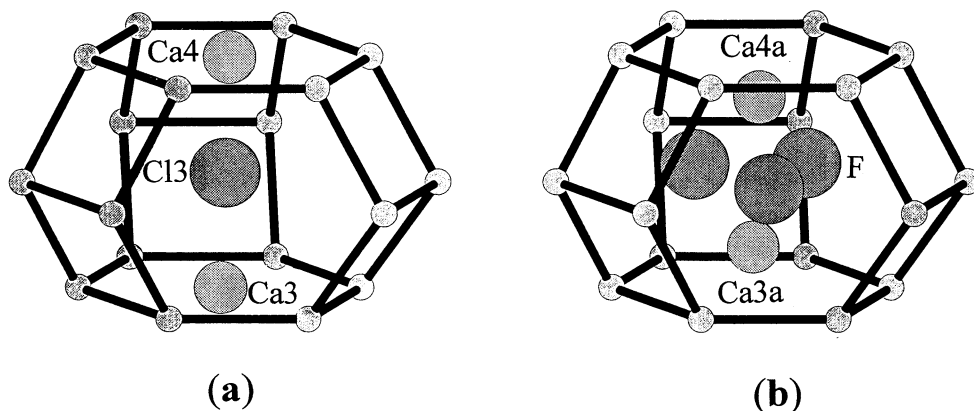


Fig. 3. The two configurations of the cancrinite cage, each sharing its base with the liottite cages: in (b) (configuration with fluorine atom inside the cage,) the three symmetry-related positions of fluorine are represented.

compared with 5.3 SO_4 , 2 Cl, 0.7 CO_3 and 4.0 H_2O obtained from the structure refinement. The very high water content from the chemical analysis may be the result of the strong tendency of all cancrinite-like minerals to adsorb water (Maras & Ballirano, 1994). The Cl \leftrightarrow H_2O substitution suggested by the Pobedismkaya *et al.* from the structure refinement may be due to the fact that the anions have been located exactly on-axis, whereas, from reference data, both Cl and H_2O are significantly displaced from the center of the cancrinite cage. According to this fact, the displacement parameters of the two anions may have increased remarkably and a reduction to "reasonable" values may have been obtained with a decrease of the scattering power of the anion from Cl to O. However there are evidences that such Cl \leftrightarrow H_2O substitution may occur in cancrinite-like minerals (Ballirano *et al.*, in prep.).

The U_{11} and U_{22} displacement parameters of Cl1, Cl2 and Cl3 are high and similar to those of the Cl atoms in liottite (Ballirano *et al.*, in press). This is due to a small off-axis displacement of Cl, as found in davyne (Bonaccorsi *et al.*, 1990). Cl1 and Cl2 make two distinct bonds with Ca1 and Ca2. These distances are similar to those found in davyne and liottite (2.64–2.71 Å), whereas the Cl–Ca distances of Pobedismkaya *et al.* (1991) are more spread out (2.52 and 2.86 Å). Ca1 has two sets of bond distances to oxygen atoms whereas Ca2 has six nearly identical bonds with the framework oxygens (Table 2).

The cancrinite cages of Fig. 2b show two configurations similar to those in liottite (Fig. 3). a) The typical cage configuration (90 % probability) with Cl3 at the center of the cancrinite cage and bonded to Ca3 and Ca4. The Cl3–Ca3 and Cl3–Ca4 bond distances are the same as those in the other cancrinite cages of afghanite. Ca3 forms two different distances with the framework oxygen.

b) The anomalous configuration (10 % probability) with the F atom, located off-axis, bonded to Ca3a and Ca4a both shifted toward the center of the cage. Ca3a and Ca4a form two different distances with the framework oxygens (Ca3a–O15 = 2.64(1) Å; Ca3a–O13 = 2.81(1) Å; Ca4a–O16 = 2.52(1) Å; Ca4a–O14 = 2.72(1) Å). F occupies one of the three symmetry related positions and forms two different bond distances with Ca3a (2.36 Å) and Ca4a (2.76 Å). F is also coordinated by K3 which belongs to the nearby liottite cage, making a bond distance of 2.60 Å.

Liottite cages

The liottite cage is a 23-hedron bounded by 17 six-member and 6 four-member rings. The liottite cage is able to host a maximum of three sulphate groups and, for this reason, it is favoured in relatively SO_4 -rich members of the cancrinite-group family. The liottite cage shares its bases with the adjacent cancrinite cage which has two different configurations. Consequently, also the liottite

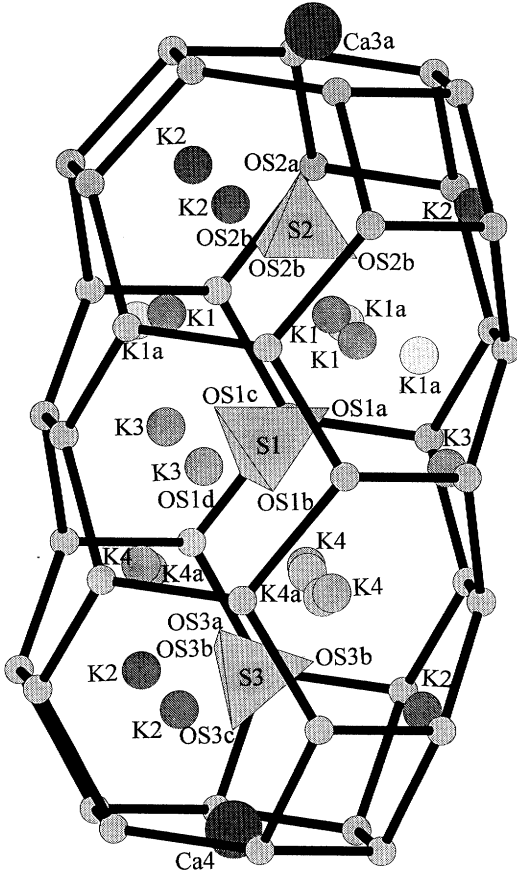


Fig. 4. The liottite cage. The S1 and S3 tetrahedra are represented in one of the three symmetry-related orientations.

cage shows two configurations due to the split Ca3 and Ca4 sites (Fig. 4). However, differently from liottite (Ballirano *et al.*, in press), there is no obvious correlation between the occurrence of the two configurations of the cancrinite cage and the relative orientation of the sulphate group inside the liottite cage.

The sulphate groups show less disorder in afghanite than in liottite (Fig. 5). The S2-centered sulphate group has the typical orientation found in davyne, with the plane of the three basal oxygens normal to z and the apical oxygen located on three-fold axis. The S1-centered sulphate, near the center of the liottite cage, has three equivalent orientations related by 120° rotation around $[1/3\ 2/3\ z]$. The S3-centered sulphate, also has three equivalent orientations related by 120° rotation

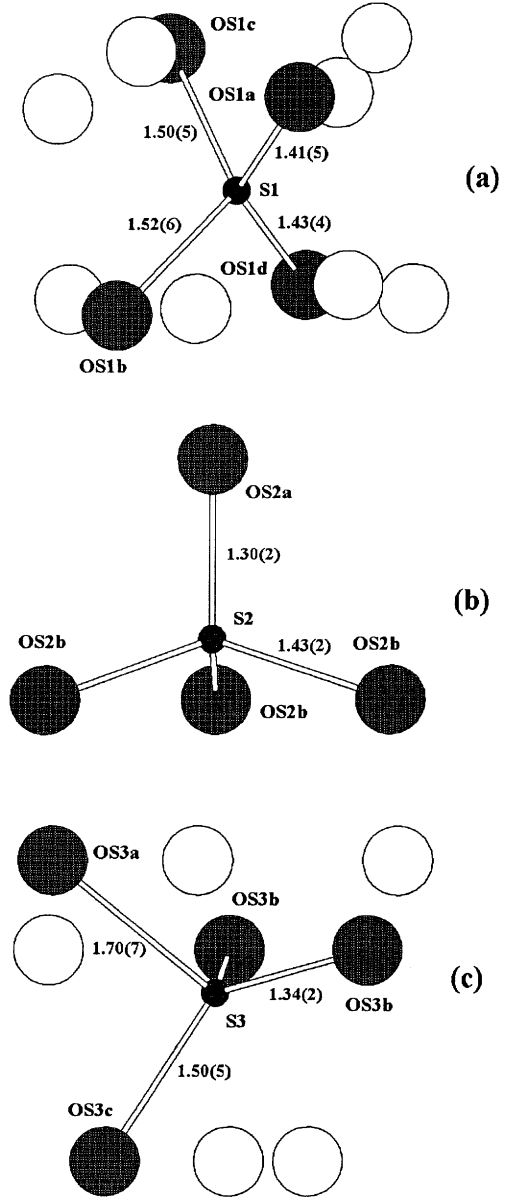


Fig. 5. Coordination of the sulphur atoms S1, S2 and S3 within the liottite cage. For S1 and S3, all the oxygen atoms obtained from the structural refinement are drawn (large circles), but only one of the three possible orientations of the sulphate tetrahedra is emphasized.

along $[1/3\ 2/3\ z]$, but the triangles of oxygens occur at different z elevations: in particular 1/3 of OS3a, 2/3 of OS3b and 1/3 of OS3c represent

the four vertices of the tetrahedron. The large dispersion of the S3-OS3 bond distances (Table 2) may be due to the difficulty in locating the positions of the oxygen atoms because of the partial occupancy of the various sites, and because of the strong correlations between parameters in the refinement.

There are six cation positions similar to those described in Pobedinskaya *et al.* (1991): the only difference is that four pairs of split cation sites were located. In our refinement, only K1 and K4 are split in two sites (K1 and K1a, and K4 and K4a). K4a has a very short K4a-OS3a distance of 2.11 Å, but both K4a and OS3a sites are only partly occupied, and probably this arrangement does not occur.

Site populations and chemical composition

To derive the site-scattering values, we followed the procedure described by Ballirano *et al.* (in press), assuming that the sums of the occupancies of the split sites are equal to one. Sites K3 and K4 + K4a are mainly filled by Na (Table 3), whereas sites K1 + K1a and K2 are approximately half-occupied each by Na and (K + Ca). The resulting crystal-chemical formula is $[\text{Na}_{17.3}(\text{K}, \text{Ca})_{6.7}\text{Ca}_8][\text{Si}_{24}\text{Al}_{24}\text{O}_{96}](\text{SO}_4)_6\text{Cl}_{5.8}\text{F}_{0.2}$

Assignment of 6.7 (K + Ca) atoms to K and Ca contents may be done by charge balance to give $[\text{Na}_{17.28}\text{K}_{4.72}\text{Ca}_{10}][\text{Si}_{24}\text{Al}_{24}\text{O}_{96}](\text{SO}_4)_6\text{Cl}_{5.8}\text{F}_{0.2}$.

This formula agrees closely with $[(\text{Na}_{17.4}\text{K}_{3.4}\text{Ca}_{10.7})][\text{Si}_{24.3}\text{Al}_{23.7}\text{O}_{96}](\text{SO}_4)_{6.3}\text{Cl}_{5.7}\text{F}_{0.1}$ obtained from the electron-microprobe analysis (Maras & Ballirano, 1994). The ideal crystal-chemical formula for afghanite is thus $[(\text{Na}, \text{K})_{22}\text{Ca}_{10}][\text{Si}_{24}\text{Al}_{24}\text{O}_{96}](\text{SO}_4)_6\text{Cl}_6$.

More than ten Ca cations may occur in the structure only by reducing the total number of cations with respect to the maximum possible content of thirty-two. The microprobe data indi-

cate 10.7 Ca cations and 31.5 (Na + K + Ca) cations, in keeping with this argument. On the other hand, less than ten Ca cations may occur through the coupled substitution $\text{Ca} + \text{Cl} \leftrightarrow \text{Na} + \text{H}_2\text{O}$ in the cancrinite cages.

Conclusions

The framework shows perfect Si,Al order resulting in a lowering of the maximal framework symmetry from $P6_3mc$ to $P31c$. It seems probable that similar long-range ordering occurs in all phases of this family with an Si/Al ratio of 1.

The framework of afghanite (ABABACAC stacking sequence) contains six cancrinite and two liottite cages: base-sharing cancrinite cages stack along $[0\ 0\ z]$, and a liottite cage and a base-sharing cancrinite cage stack along $[2/3\ 1/3\ z]$ and $[1/3\ 2/3\ z]$. The presence of these cages limits to six the maximum number of sulphate groups per unit cell. The cancrinite cages along $[0\ 0\ z]$ show a...Ca-Cl-Ca-Cl... chain, as in liottite and the minerals of the davyne group, whereas the cancrinite cages along $[2/3\ 1/3\ z]$ and $[1/3\ 2/3\ z]$ show a disordered distribution of fluorine (10 % probability) and chlorine anions (90 % probability). The disorder is coupled with Ca-site splitting, as previously observed in liottite (Ballirano *et al.*, in press).

Each liottite cage contains three sulphate groups. Unlike liottite, the orientation of the sulphate groups is not influenced by the disorder of the Ca atoms in the disordered cancrinite cages, because the Ca atoms can always make favourable bonds with oxygens of the neighbouring SO_4 groups. All the other extra-framework cations occur in the liottite cages disordered over six sites. The positional disorder of the cations does not influence the orientation of the SO_4 groups. The final crystal-chemical formula

Table 3. Site-scattering value calculation.

Site	Multiplicity	number of electrons	K	Na	at. K	at. Na
K1+K1a	6	14.71	0.46	0.54	2.76	3.24
K2	6	14.61	0.45	0.55	2.70	3.30
K3	6	11.25	0.03	0.97	0.18	3.82
K4+K4a	6	12.46	0.18	0.82	1.08	4.92
			1.12	2.88	6.72	17.28

$[\text{Na}_{17.3}(\text{K},\text{Ca})_{6.7}\text{Ca}_8][\text{Si}_{24}\text{Al}_{24}\text{O}_{96}](\text{SO}_4)_6\text{Cl}_{5.8}\text{F}_{0.2}$ calculated from the structure refinement is in good agreement with the formula $[(\text{Na}_{17.4}\text{K}_{3.4}\text{Ca}_{10.7})[\text{Si}_{24.3}\text{Al}_{23.7}\text{O}_{96}](\text{SO}_4)_{6.3}\text{Cl}_{5.7}\text{F}_{0.1}]$ derived from the electron-microprobe analysis (Maras & Ballirano, 1994).

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