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THE CRYSTAL STRUCTURE OF LIOTTITE, A SIX-LAYER MEMBER OF THE CANCRINITE GROUP

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ABSTRACT

Liottite, ideally $[(Na,K)_{16}Ca_8][Si_{18}Al_{18}O_{72}](SO_4)_5Cl_4$, is the six-layer member of the cancrinite group. The structure of liottite has been refined in space group $P\bar{6}$ to R = 2.7% using single-crystal X-ray-diffraction data. The hexagonal-system cell parameters are a 12.870(1), c 16.096(2) Å. The structure consists of a perfectly (Si,Al)-ordered framework, as shown by an average Si–O bond distance of 1.610(5) Å, and an average Al–O bond distance of 1.730(9) Å. Within a unit cell, three base-sharing cancrinite cages are stacked along $[\frac{1}{3}\ \frac{2}{3}\ z]$, 17-hedra ("losod" cages) alternate with cancrinite cages along $[\frac{2}{3}\ \frac{1}{3}\ z]$, and 23-hedra ("liottite" cages) are stacked along $[0\ 0\ z]$. The small cancrinite cage contains Ca at the center of the hexagonal base and Cl within the cage, except for the cancrinite cage stacked along $[\frac{2}{3}\ \frac{1}{3}\ z]$, which shows a disordered distribution of F and Cl. The "losod" and "liottite" cages are occupied by two and three sulfate groups, respectively. The sulfate groups are separated by triplets of cations (Na, K, and Ca) around the axes of symmetry. The complex distribution of anions inside the cages is strongly influenced by the position of the extra-framework cations, which are disordered over various sites, and particularly by that of the Ca atoms near the center of the six-member rings of aluminosilicate tetrahedra.

Keywords: liottite, cancrinite group, feldspathoid, structure refinement, stacking sequence.

SOMMAIRE

La liottite, de composition idéale $[(Na,K)_{16}Ca_8][Si_{18}Al_{18}O_{72}](SO_4)_5Cl_4$, est le membre à six couches du groupe de la cancrinite. Sa structure a été affinée dans le groupe spatial $P\bar{6}$ jusqu'à un résidu R de 2.7% par diffraction X au moyen de données obtenues sur cristal unique. Les paramètres réticulaires de la maille hexagonale sont a 12.870(1), c 16.096(2) Å. La structure est faite d'une trame de tétraèdres Si,Al parfaitement ordonnée, comme le révèlent une longueur Si–O moyenne de 1.610(5) Å, et une longueur Al–O moyenne de 1.730(9) Å. Dans la maille élémentaire, trois cages de type cancrinite, à bases partagées, sont empilées le long de $[\frac{1}{3}\ \frac{2}{3}\ z]$, des polyèdres à dix-sept côtés (cages de type "losod") alternent avec les cages de type cancrinite le long de $[\frac{2}{3}\ \frac{1}{3}\ z]$, et des polyèdres à vingt-trois côtés (cages de type "liottite") sont empilés le long de $[0\ 0\ z]$. La petite cage de type cancrinite contient un atome de Ca au centre d'une base hexagonale, et un atome de Cl à l'intérieur, à l'exception de celle qui se trouve le long de $[\frac{2}{3}\ \frac{1}{3}\ z]$, qui fait preuve d'une distribution désordonnée de F et Cl. Les cages de types "losod" et "liottite" renferment deux et trois groupes sulfatés, respectivement. Ces groupes sulfatés sont séparés par des triplets de cations (Na, K, et Ca) autour des axes de symétrie. La distribution complexe des anions à l'intérieur des cages est fortement influencée par la position des cations à l'extérieur de la trame, qui sont désordonnés sur plusieurs sites, et en particulier par les atomes de Ca situés près du centre des anneaux de six tétraèdres à Al, Si.

(Traduit par la Rédaction)

Mots-clés: liottite, groupe de la cancrinite, feldspathoïde, affinement de la structure, séquence d'empilement.

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INTRODUCTION

Liottite is a six-layer member of the cancrinite family. This group of feldspathoids has a framework obtained by the stacking of layers of six-member rings of AlO_4 and SiO_4 tetrahedra along the *z* direction. The stacking can be described on an *ABC*-based scheme (Merlino 1976): up to now, seven different topologies are known (Table 1), with the *c* parameters ranging from 5 Å (two-layer structures) to 74 Å (28-layer structure). Each of the different frameworks contains structural subunits as cages and channels (Ballirano *et al.* 1994) that are filled by interstitial cations and anions. Some of the two-layer cancrinites show different types of superstructures, whose occurrence was explained in terms of vacancies or cation ordering inside the channels (Grundy & Hassan 1982, Merlino *et al.* 1991, Hassan & Buseck 1992, Bonaccorsi *et al.* 1994). Complete structure-refinements have been done only for the natural two-layer, four-layer, and eight-layer members of the family (see Table 1). Problems encountered during the structure refinement include complex twinning and the occurrence of domains with opposite schemes of ordering, simulating a disordered Si, Al pattern (Merlino 1984).

Liottite was described from Pitigliano, Tuscany, Italy (Merlino & Orlandi 1977a); its cell parameters (*a* 12.84, *c* 16.09 Å) indicated a six-layer structure (Merlino 1976). Recently, liottite has been examined by X-ray powder diffraction, Selected Area Electron Diffraction (SAED), infrared (IR) spectroscopy, and electron-microprobe analysis (Ballirano *et al.* 1995a), which gave the formula [calculated on the basis of 36 (Si+Al)] $(Na_{9.78}K_{4.68}Ca_{9.12})[Si_{18.24}Al_{17.76}O_{72.27}](SO_4)_{5.16}Cl_{3.39}F_{0.69}$. No CO_3- or OH-stretching bands were observed in the IR spectrum.

TABLE 1. LIST OF THE KNOWN STACKING SEQUENCES OF NATURAL CANCRINITE-LIKE MINERALS

Stacking sequence	N° of layers	Mineral species and references
AB	2	Cancrinite[1], vishnevite[2], davyne[3] hydroxyl-cancrinite[4], pitiglianoite[5] microsommite[5], quadridavyne[6]
ABAC	4	Bystrite[7]
ABABAC	6	Liottite[8,9]
ABABACAC	8	Afghanite[10,11]
ABCABACABC	10	Franzinite[12,13]
?	12	Tunkite[14]
ABABABACBABABABC	16	Giuseppettite[15,16]
ABCABCABACACABAC BACBACABABAC (?)	28	Sacrofanite[17,18]

By means of transmission electron microscopy (TEM) a few more domains were observed, showing 12, 14, 18, and 24 layers for the unit-cell (Rinaldi & Wenk 1979; Rinaldi, personal communication to Merlino, in Merlino 1984).

(1) Jarchow (1965); Grundy & Hassan (1982); (2) Hassan & Grundy (1984); (3) Bonaccorsi *et al.* (1990); (4) Nadezhina *et al.* (1991); (5) Merlino *et al.* (1991); (6) Bonaccorsi *et al.* (1994); (7) Pobedimskaya *et al.* (1991a); (8) Merlino & Mellini (1976); (9) Merlino & Orlandi (1977a); (10) Bariand *et al.* (1968); (11) Pobedimskaya *et al.* (1991b); (12) Merlino & Orlandi (1977b); (13) The reported sequence has been recently determined by Ballirano *et. al.* (in preparation); (14) Ivanov & Sapozhnikov (1985); (15) Mazzi & Tadini (1981); (16) Mazzi, pers. comm., in Merlino (1984); (17) Burragato *et al.* (1980); (18) Ballirano *et al.* (1994).

Refinement of the structure in space group $P\bar{6}m2$ led to an *R* index of 15% (Merlino & Mellini 1976). Recently, an average structure was refined by means of Rietveld analysis, in order to overcome problems encountered during single-crystal studies (Ballirano *et al.* 1995b). Owing to the number of parameters involved in the refinement and to strong correlation of variables, no attempt was made to model the degree of Si,Al order.

EXPERIMENTAL

A fragment of a crystal 0.4 × 0.3 × 0.3 mm from sample MMUR 24333 (Museo di Mineralogia dell'Università di Roma "La Sapienza"), part of the hand sample originally studied by Merlino & Mellini (1976) and Merlino & Orlandi (1977a) and subsequently studied by Ballirano *et al.* (1995a, b), was chosen for this investigation. The colorless transparent crystal was mounted on a Siemens P4 four-circle automated diffractometer; the instrument uses graphite-monochromatized Mo*K*α X-radiation and was operated at 50 kV and 30 mA. The following unit-cell parameters were derived from least-square refinement using 36 reflections ($15° < 2\theta < 30°$): *a* 12.870(1), *c* 16.096(2) Å. Intensity data were collected in ω-scan mode up to a 2θ value of 60°; a total of 2601 unique reflections were measured. Three reference reflections monitored every 47 measurements did not show significant variation in intensity. The intensities were corrected for Lorentz and polarization effects and absorption, and the refinement was done using SHELXL–93 (Sheldrick 1993).

STRUCTURE REFINEMENT

For $P\bar{6}$, $R_{int} = 0.014$, compared with $R_{int} = 0.066$ for $P\bar{6}m2$; note that $P\bar{6}$ is the maximal non-isomorphic subgroup of $P\bar{6}m2$ allowing an ordered distribution of Si and Al. All cancrinite-group minerals (except cancrisilite: Khomyakov *et al.* 1991) show an Si:Al ratio equal to 1, which suggests an ordered distribution of Si and Al. The refinement started with only the framework atoms, and interstitial cations were located on difference-Fourier maps. The occupancy of each site was refined in terms of the scattering power of K. The actual chemical contents were subsequently derived by assuming full occupancy of the single site (K4) and of each pair of sites (K1 + K1a, K2 + K2a, K3 + K3a) and obtaining the contents of Na on one side and of K + Ca on the other side from the refined occupancies; the resulting chemical content is in accord with the analytical data. Ten different maxima were found corresponding to the oxygen atoms of the sulfate groups, indicating a substantially disordered distribution of SO_4. In the last cycles of refinement, the occupancies of the oxygen atoms in SO_4 groups were fixed as discussed below.

The final conventional R index is 2.75% for 2168 $F_{obs} > 4\sigma(F_{obs})$, and 3.65% for all 2601 data; the wR^2 factor is 7.48 % for 2168 $F_{obs} > 4\sigma(F_{obs})$, and 8.29% for all 2601 data. The Flack x parameter is 0.04(6).

TABLE 2. FRACTIONAL COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS IN LIOTTITE

Atoms	x	y	z	U_{eq} (x 10^4)
Si1	0.9954(1)	0.7437(1)	0	77(3)
Al1	0.3339(1)	0.4088(1)	0.83304(8)	81(2)
Si2	0.67182(9)	0.08217(9)	0.66374(6)	75(2)
Al2	0.3364(1)	0.4097(1)	1/2	71(3)
Si3	0.58517(9)	0.66611(9)	0.83287(7)	77(2)
Al3	0.7378(1)	0.7488(1)	0	76(3)
Si4	0.5873(1)	0.6700(1)	1/2	72(3)
Al4	0.9282(1)	0.3431(1)	0.66345(7)	79(3)
O1	0.8771(4)	0.1258(4)	0	250(10)
O2	0.1025(4)	0.8798(4)	0	207(9)
O3	0.9943(3)	0.6706(3)	0.9182(2)	190(8)
O4	0.6631(3)	0.6698(3)	0.9119(2)	203(8)
O5	0.2179(3)	0.7886(3)	0.8253(2)	209(7)
O6	0.4501(3)	0.5552(3)	0.8386(2)	209(7)
O7	0.3463(3)	0.3310(3)	0.7491(2)	179(8)
O8	0.6574(3)	0.6560(3)	0.7543(2)	193(8)
O9	0.5464(3)	0.4367(4)	0.6545(2)	170(6)
O10	0.7933(3)	0.2105(3)	0.6632(2)	266(8)
O11	0.6772(3)	0.0062(3)	0.5856(2)	179(8)
O12	0.6659(3)	0.6735(3)	0.5794(2)	177(8)
O13	0.2173(4)	0.7836(4)	1/2	197(9)
O14	0.4540(4)	0.5557(4)	1/2	148(8)
Ca1	1/3	2/3	1/2	162(5)
Ca2	1/3	2/3	0.8330(1)	172(3)
Ca3	0	0	0.9783(2)	219(7)
Ca4	2/3	1/3	0.3915(2)	191(6)
Ca5	2/3	1/3	0.3436(3)	294(8)
K1	0.8463(5)	0.1651(3)	1/2	170(7)
K1a	0.857(1)	0.143(1)	1/2	170(7)
K2	0.1125(2)	0.8864(2)	0.6651(1)	392(6)
K2a	0.145(2)	0.851(2)	0.675(1)	392(6)
K3	0.8364(3)	0.1722(2)	0.8313(2)	248(6)
K3a	0.816(2)	0.191(3)	0.847(2)	248(6)
K4	0.5543(2)	0.4458(2)	0	338(6)
F	0.7476(8)	0.2700(8)	1/2	256(16)
Cl1	1/3	2/3	0	732(19)
Cl2	2/3	1/3	1/2	1608(73)
Cl3	1/3	2/3	0.3335(2)	742(12)
S1	0	0	0.7971(8)	172(23)
S1'	0.977(3)	0.013(4)	0.7874(9)	338(41)
S2	0.0357(5)	0.017(1)	1/2	348(16)
S3	2/3	1/3	0.8568(2)	410(7)
OS1a	0	0	0.886(1)	1005(78)
OS1b	0.1213(8)	0.0582(9)	0.7676(7)	738(26)
OS1c	0.056(7)	0.094(3)	0.723(2)	1154(188)
OS1d	0.119(2)	0.054(2)	0.845(1)	864(61)
OS2a	0.119(2)	0.058(2)	0.426(1)	649(52)
OS2b	0.110(2)	0.051(4)	0.479(3)	1349(224)
OS3a	2/3	1/3	0.2409(9)	350(30)
OS3b	0.7285(7)	0.4595(6)	0.8789(5)	366(16)
OS3c	0.692(5)	0.298(5)	0.211(2)	931(150)
OS3d	0.728(4)	0.288(3)	0.913(2)	1281(140)

TABLE 3. POPULATION OF ALL THE EXTRAFRAMEWORK SITES

Site	Occupancy [on the basis of the scattering power of K]	Multiplicity	total number of electrons	% K+Ca	% Na	atoms K+Ca	atoms Na
K1	0.572(5)	3	14.33	0.42	0.58	1.26	1.74
K1a	0.182(5)	3					
K2	0.684(4)	6	14.40	0.43	0.57	2.58	3.42
K2a	0.074(4)	6					
K3	0.694(4)	6	14.29	0.41	0.59	2.46	3.54
K3a	0.058(7)	6					
K4	0.822(3)	3	15.62	0.58	0.42	1.74	1.26

Site	Occupancy	Multiplicity	Site	Occupancy	Multiplicity
Ca1	1	1	OS1a	0.5	2
Ca2	1	2	OS1b	0.667	6
Ca3	0.5	2	OS1c	0.167	6
Ca4	0.5	2	OS1d	0.333	6
Ca5	0.5	2			
Cl1	1	1	OS2a	0.333	6
Cl2	0.5	1	OS2b	0.333	6
Cl3	1	2			
F	0.167	3	OS3a	0.5	2
S1	0.5	2	OS3b	0.667	6
S1'	0.167	6	OS3c	0.167	6
S2	0.333	3	OS3d	0.333	6
S3	1	2			

Fractional coordinates, occupancies, and isotropic-displacement parameters are listed in Table 2, and the population of all extra-framework sites is given in Table 3. A list of selected bond-distances is reported in Table 4. A table of structure factors is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

Framework

The liottite framework shows a perfectly ordered distribution of Si and Al, as indicated by the <Si–O> and <Al–O> bond distances, 1.610(5) and 1.730(9) Å, respectively (standard deviations refer to the dispersion of the observed values). According to Hassan & Grundy (1990), a perfectly ordered member of the cancrinite family has a $d_{Si–O}/d_{Al–O}$ value of 0.93, as observed in the present refinement. As already pointed out (Ballirano *et al.* 1994), the liottite framework contains a number of different subunits: a column of base-sharing cancrinite cages runs along [⅓ ⅔ *z*] (Fig. 1a), "losod" and cancrinite cages follow each

TABLE 4. SELECTED BOND DISTANCES (Å) IN LIOTTITE

Si1	–O1(a)	1.611(5)	Al1	–O3(a)	1.738(4)
	–O2(b)	1.599(5)		–O5(e)	1.729(3)
	–O3(c)	1.613(3)		–O6	1.725(4)
	–O3(d)	1.613(3)		–O7	1.736(4)
Si2	–O7(a)	1.612(4)	Al2	–O11(f)	1.747(4)
	–O9(a)	1.610(3)		–O11(g)	1.747(4)
	–O10	1.609(3)		–O13(e)	1.720(5)
	–O11	1.616(3)		–O14	1.726(5)
Si3	–O4	1.607(4)	Al3	–O1(a)	1.739(5)
	–O5(h)	1.599(3)		–O2(h)	1.716(5)
	–O6	1.609(4)		–O4(c)	1.729(4)
	–O8	1.613(4)		–O4(d)	1.729(4)
Si4	–O12	1.616(4)	Al4	–O8(f)	1.722(4)
	–O12(c)	1.616(4)		–O9(f)	1.724(3)
	–O13(h)	1.603(5)		–O10	1.722(3)
	–O14	1.607(5)		–O12(f)	1.734(3)
Ca1	–O13	2.597(5)	Ca2	–O5	2.648(4)
	–O13(e)	2.597(5)		–O5(e)	2.648(4)
	–O13(h)	2.597(5)		–O5(h)	2.648(4)
	–O14	2.583(5)		–O6	2.546(4)
	–O14(e)	2.583(5)		–O6(e)	2.546(4)
	–O14(h)	2.583(5)		–O6(h)	2.546(4)
	–Cl3	2.680(3)		–Cl3(c)	2.679(4)
	–Cl3(c)	2.680(3)		–Cl1(i)	2.689(2)
Ca3	–O1(j)	2.794(5)			
	–O1(k)	2.794(5)			
	–O1(l)	2.794(5)			
	–O2(m)	2.509(5)			
	–O2(n)	2.509(5)			
	–O2(o)	2.509(5)			
	–OS1a(p)	2.19(2)			
	–OS1d	2.53(2) x 2/3			
	–OS1d(q)	2.53(2) x 2/3			
	–OS1d(r)	2.53(2) x 2/3			
Ca4	–O9(c)	2.603(3)	Ca5	–O9(c)	2.496(3)
	–O9(g)	2.603(3)		–O9(g)	2.496(3)
	–O9(s)	2.603(3)		–O9(s)	2.496(3)
	–O10(c)	2.917(4)		–O10(c)	2.784(4)
	–O10(g)	2.917(4)		–O10(g)	2.784(4)
	–O10(s)	2.917(4)		–O10(s)	2.784(4)
	–OS3a	2.42(1)		–Cl2	2.517(6)
	–F	2.376(6) x 1/3		–OS3c	2.25(3) x 1/3
	–F(a)	2.376(6) x 1/3		–OS3c(a)	2.25(3) x 1/3
	–F(f)	2.376(6) x 1/3		–OS3c(f)	2.25(3) x 1/3
K1	–O10	2.846(4)	K1a	–O10	3.003(7)
	–O10(c)	2.846(4)		–O10(c)	3.003(7)
	–O11	2.523(5)		–O11	2.51(1)
	–O11(c)	2.523(5)		–O11(c)	2.51(1)
	–O12(f)	2.481(5)		–O12(f)	2.58(1)
	–O12(g)	2.481(5)		–O12(g)	2.58(1)
	–OS2a(a)	2.53(2) x 1/3		–OS2a(a)	2.21(2) x 1/3
	–OS2a(s)	2.53(2) x 1/3		–OS2a(s)	2.21(2) x 1/3
	–OS2b(a)	2.36(2) x 1/6		–F	2.63(1) x 1/6
	–OS2b(s)	2.36(2) x 1/6			
	–F	2.27(1) x 1/6			
K2	–O7(h)	2.928(4)	K2a	–O5	2.85(2)
	–O8(e)	2.952(4)		–O7(h)	2.62(2)
	–O11(q)	2.724(4)		–O8(e)	2.64(2)
	–O12(e)	2.755(4)		–O11(q)	2.59(2)
	–OS1b(t)	2.71(1) x 1/2		–O12(e)	2.63(2)
	–OS1b(h)	2.76(1) x 1/2		–O13	3.22(2)
	–OS2a(u)	2.62(3) x 1/3		–OS1b(t)	3.20(3) x 1/2
	–OS2a(v)	2.64(3) x 1/3		–OS1b(h)	3.23(2) x 1/2
				–OS1c(h)	2.35(4) x 1/6
K3	–O1(i)	2.883(3)	K3a	–O1(i)	2.835(3)
	–O3(f)	2.525(4)		–O3(f)	2.44(2)
	–O4(f)	2.517(4)		–O4(f)	2.46(3)
	–O7(a)	2.475(4)		–O7(a)	2.63(3)
	–O8(f)	2.476(4)		–O8(f)	2.64(2)
	–O10	2.855(4)		–O10	3.00(3)
	–OS1b(a)	2.60(1) x 1/3		–OS1b(a)	3.11(4) x 1/3
	–OS1d(a)	2.43(2) x 1/6		–OS1d(a)	2.86(4) x 1/6
	–OS3b(f)	2.407(9) x 1/3		–OS3c(c)	2.73(4) x 1/6
	–OS3c(c)	3.09(3) x 1/6		–OS3d	2.32(4) x 1/6
	–OS3d	2.83(3) x 1/6			
K4	–O3(s)	2.834(4)	S1	–OS1a	1.43(2)
	–O3(w)	2.834(4)		–OS1b	1.43(1)
	–O4(c)	2.871(4)		–OS1b(q)	1.43(1)
	–O4(d)	2.871(4)		–OS1b(r)	1.43(1)
	–OS3b(c)	2.909(9) x 1/6			
	–OS3b(d)	2.909(9) x 1/6	S1'	–OS1b(b)	1.67(3)
	–OS3b(s)	2.933(9) x 1/6		–OS1c(a)	1.32(4)
	–OS3b(w)	2.933(9) x 1/6		–OS1d(a)	1.31(3)
	–OS3d(s)	2.49(4) x 1/6		–OS1d(y)	1.76(4)
	–OS3d(w)	2.49(4) x 1/6			
	–OS3d(g)	2.67(4) x 1/6	S2	–OS2a	1.50(2)
	–OS3d(x)	2.67(4) x 1/6		–OS2a(c)	1.50(2)
				–OS2b(q)	1.49(3)
				–OS2b(z)	1.51(3)
S3*	–OS3a(c)	1.57(1) x 1/2	S3*	–OS3b	1.451(7) x 1/2
	–OS3b	1.451(7) x 1/2		–OS3c(g)	1.28(2) x 1/2
	–OS3b(a)	1.451(7) x 1/2		–OS3d	1.50(3) x 1/2
	–OS3b(f)	1.451(7) x 1/2		–OS3d(f)	1.50(3) x 1/2

(a) $-y+1, x-y, z$; (b) $x+1, y, z$; (c) $x, y, -z+1$; (d) $x, y, z-1$; (e) $-y+1, x-y+1, z$; (f) $-x+y+1, -x+1, z$; (g) $-x+y+1, -x+1, -z+1$; (h) $-x+y, -x+1, z$; (i) $x, y, z+1$; (j) $-x+y+1, -x+1, z+1$; (k) $x-1, y, z+1$; (l) $-y, x-y-1, z+1$; (n) $-y+1, x-y+1, z+1$; (o) $-x+y-1, -x, z+1$; (p) $x, y, -z+2$; (q) $-y, x-y, z$; (r) $-x+y, -x, z$; (s) $-y+1, x-y, -z+1$; (t) $x, y+1, z$; (u) $x, y+1, -z+1$; (v) $-x+y, -x+1, -z+1$; (w) $-y+1, x-y, z-1$; (x) $-x+y+1, -x+1, z-1$; (y) $-x+y+1, -x, z$; (z) $-x+y, -x, -z+1$

* For the S3 tetrahedron, the two possible configurations are listed separately

other, through base-sharing, along [⅔ ⅓ *z*] (Fig. 1b), and a "liottite" cage is located at [0 0 *z*] (Fig. 1c). Because of geometrical restraints, the occurrence of these subunits greatly constrains the number and the type of the extra-framework anions that can be hosted by the structure.

Cancrinite cage

The undecahedral cage (limited by five six-member and six four-member rings) is the smallest subunit observed in the cancrinite-group minerals (Ballirano *et al.* 1994). The base-sharing cancrinite cages stacked along [⅓ ⅔ *z*] show a regular ....Ca–Cl–Ca–Cl.... chain similar to that in davyne (Bonaccorsi *et al.* 1990, 1992, Hassan & Grundy 1990), microsommite (Merlino *et al.* 1991), and quadridavyne (Bonaccorsi *et al.* 1994). Some samples of davyne (Bonaccorsi *et al.* 1990, 1992) show a small displacement of the chlorine atom from the on-axis position, leading to a disordered distribution among three symmetry-related positions; the large flattening of the ellipsoid describing the

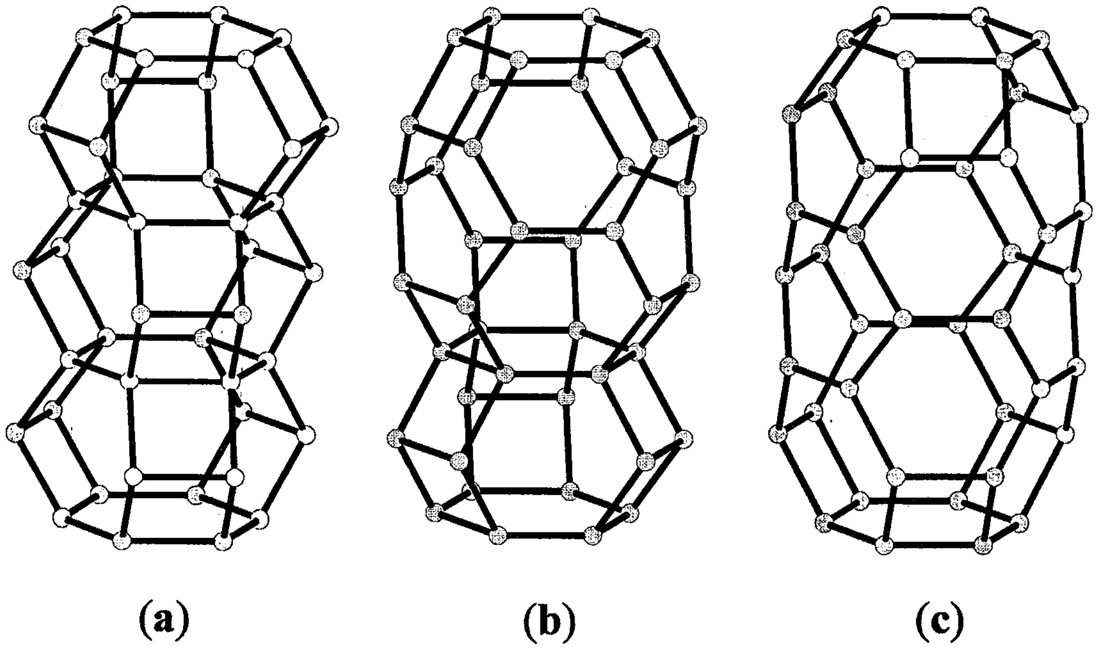
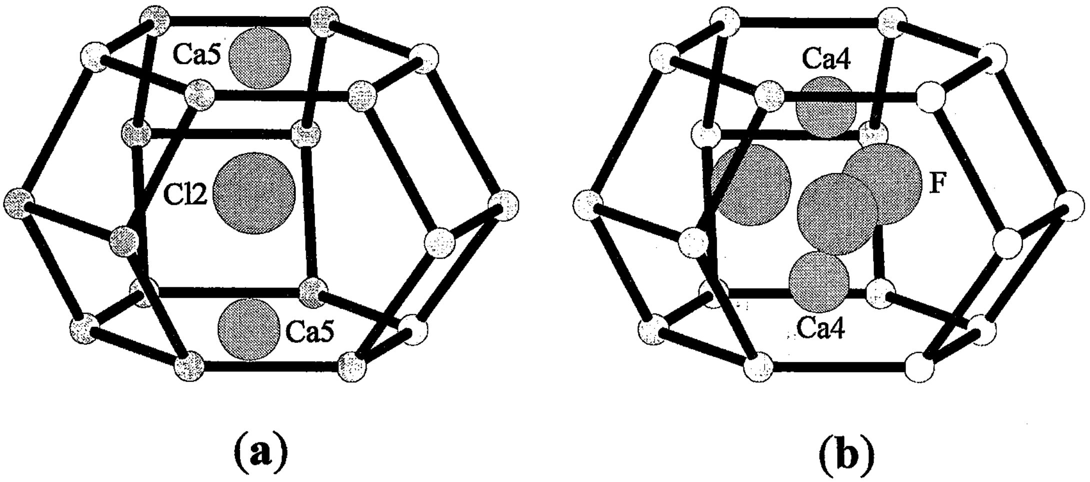

(a) (b) (c)

FIG. 1. Drawing of the various subunits in liottite; only the connectivity between tetrahedral nodes is represented. (a) Columns of cancrinite cages along [⅓ ⅔ *z*]; (b) "losod" and cancrinite cages along [⅔ ⅓ *z*]; (c) "liottite" cage at [0 0 *z*].

mean-square displacements of Cl1 and Cl3 in liottite may be interpreted as due to this type of static disorder. The Cl1–Ca2 (2.689 Å), Cl3–Ca2 (2.679 Å), and Cl3–Ca1 (2.680 Å) distances are similar to those in davyne, which are in the range 2.64–2.71 Å. Ca1 has six nearly identical bonds with the framework O atoms (Ca1–O14 = 2.583 Å, Ca1–O13 = 2.597 Å), whereas Ca2 has two different sets of bond distances (Ca2–O6 = 2.546 Å, Ca2–O5 = 2.648 Å).

The cancrinite cage that shares its base with the "losod" cage (see below) shows two distinct configurations: (1) Cl2 at the center of the cancrinite cage



(a) (b)

FIG. 2. The two distinct configurations of the cancrinite cage sharing its bases with the "losod" cages: in (b) configuration with F inside the cage), the three symmetry-related F positions are represented.

and Ca5 near the center of the six-member rings of tetrahedra (Fig. 2a), and (2) F located off-axis, and Ca4 appreciably shifted toward the center of the cage (Fig. 2b). The fluorine atom is also coordinated by K1 or K1a. The site populations of K1 and K1a are discussed in the next section.

Losod cage

The losod cage was described by Sieber & Meier (1974) in the synthetic four-layer member losod, $Na_{12}Al_{12}Si_{12}O_{48}\cdot 18H_2O$. The losod cage is a 17-hedron limited by eleven six-member and six four-member rings with dimensions substantially larger than those of the cancrinite cage. This kind of cage occurs also in bystrite (Pobedimskaya *et al.* 1991a), and in franzinite (Ballirano *et al.* 1994).

The losod cage shows two different configurations (Fig. 3): (1) Ca5 is in the plane of the six-member rings. In this case, the sulfate tetrahedra cannot have the apex pointing toward Ca5 because of a short distance of only 1.65 Å. The sulfate groups show three different triangular arrangements of maxima (OS3b, OS3c, OS3d), each with partial occupancy. The resulting SO_4 configuration is similar to that observed in davyne from Zabargad (Bonaccorsi *et al.* 1992) and in afghanite (Pobedimskaya *et al.* 1991b), with one oxygen pointing toward the neighboring cages aligned along [⅓ ⅔ *z*] and [0 0 *z*]. There are three possible orientations of these sulfate groups, each one related to the others by a rotation of 120° around [⅔ ⅓ *z*]. (2) Ca4 is appreciably shifted toward the center of the cancrinite cage, and the normal orientation of SO_4 is with the apex of the tetrahedron pointing along the axis, with Ca4–OS3a equal to 2.42 Å.

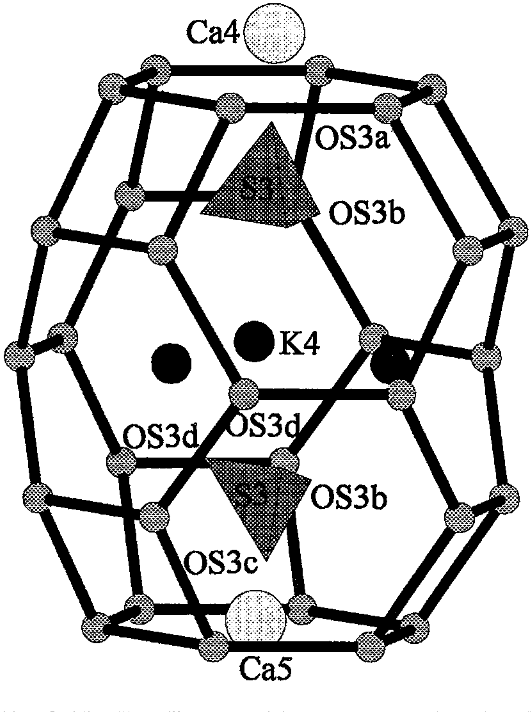


FIG. 3. The "losod" cage and its content. For the sake of simplicity, both possible configurations for the S3 tetrahedra are represented within the same cage.

The distribution of cations shows other interesting features. K4 is between the two sulfate groups with distances of 2.49 and 2.67 Å to OS3d, and 2.91 and 2.93 Å to OS3b. K4 is also coordinated by the framework oxygen atoms O3 and O4, located, respectively, at 2.83 and 2.87 Å. K3 and K3a are located inside the neighboring liottite cage and near the walls of the losod cage. K3a has a short K3a–OS3b distance of 1.91 Å, which is unreasonable whichever cation occupies the K3a site. However, K3a has a relatively low occupancy, and the OS3b site is not fully occupied; therefore, we assume that this contact never occurs.

Liottite cage

The liottite cage is a 23-hedron bounded by 17 six-member and six four-member rings; it also occurs in afghanite. As in afghanite, the liottite cage contains one Ca atom that is slightly displaced from the center of the base (Fig. 4), leading to a disordered distribution of Ca3 at two equivalent positions ($z = -0.02$ and $z = 0.02$). Owing to the short distance between the two positions (0.70 Å), only one of them is locally occupied. As discussed below, this disordered distribution affects the sulfate orientations inside the cage. Three SO_4 groups occur in the liottite cage and, in contrast with the results of the refinement of afghanite (Pobedimskaya *et al.* 1991b), no SO_4 – CO_3 substitution occurs. The three sulfate groups are centered by S1, in two symmetry-related positions at $z = 0.2$ and $z = 0.8$, and S2 is on the mirror plane at $z = 0.5$ and somewhat displaced from the six-fold axis. Furthermore, S1 is split between two positions, S1 and S1′, with half occupancy. S1 is located exactly along [0 0 *z*], whereas S1′ is displaced off-axis; S1 corresponds to the SO_4 orientation with the apical bond pointing along [0 0 *z*], whereas the S1′-centered sulfate groups have a rotated configuration similar to that observed for the S3 sulfate groups inside the losod cage. Ca3 is randomly distributed between two positions at $z \pm 0.02$, related by the symmetry plane. The occupancies of S1 and S1′ are closely related to the actual location of the Ca3 cation.

Two structural schemes are possible, statistically distributed through the structure (Fig. 5): (1) Ca3 is at $z = -0.02$. In this case, only one of the two adjacent OS1a O-atoms located along [0 0 *z*] has a reasonable distance to Ca3: OS1a are located at 0 0 –0.12 and

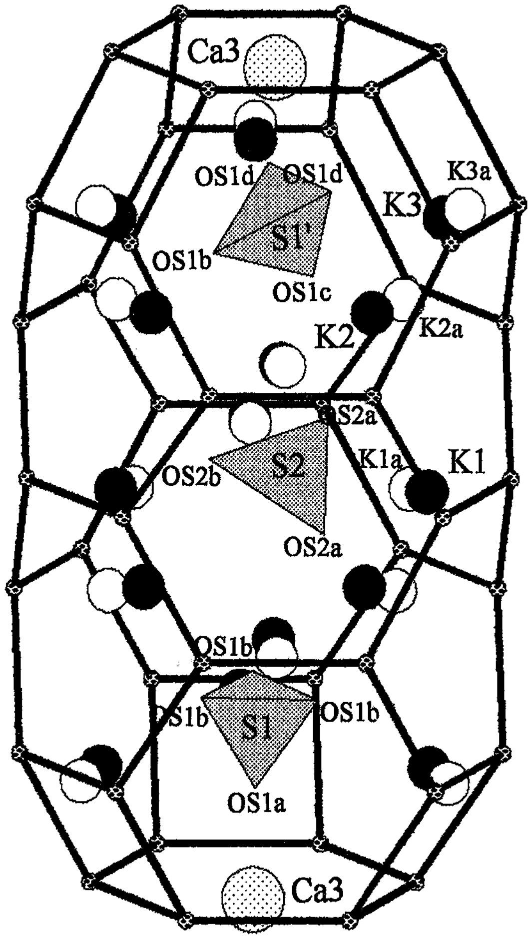


FIG. 4. The "liottite" cage. For the sake of simplicity, the two configurations corresponding to the S1 and S1′ tetrahedra, which are statistically distributed in the structure, are drawn within the same cage. The S1′ and S2 tetrahedra are shown in one of the three symmetry-related orientations. Each pair of filled and open circles represents split cation sites, with high and low occupancy, respectively.

0 0 0.12, and the corresponding distances to calcium Ca3 are 1.49 and 2.19 Å, respectively; accordingly, only the 0 0 0.12 site may be occupied. The tetrahedral coordination of S1 is completed by the three basal O-atoms 1.43 Å from S1. On the other side of the symmetry plane, a S1′ tetrahedron occurs, built up by two OS1d, one OS1c, and one OS1b atoms. As can be seen, OS1b is shared between the two configurations. Three orientations of the S1′ tetrahedron are expected, related by a 120° rotation around the $\bar{6}$ axis. The observed bond-lengths are distributed over a wide range and are obviously inaccurate. (2) Ca3 is located at 0 0 0.02. Also in this case, only one of the OS1a apical oxygen atoms, at $z = -0.12$, is at a reasonable contact distance from Ca3. The structural scheme is reversed relative to that discussed previously.

The S2-centered sulfate group located near the center of the liottite cage has three equivalent orientations related by 120° rotations around [0 0 z]. S2 is slightly displaced off-axis, and the oxygen atoms are arranged in four layers with ⅓ occupancy at each layer. The six cation positions show different degrees of occupancy; K1a, K2a, and K3a have low occupancy. As shown in Table 4, K1 and K1a have similar distances with the framework atoms, with some distances shortened and others lenghtened. K3 and K3a show similar behavior, whereas K2a makes shorter distances than K2 with the framework oxygen atoms. The site populations were calculated from the refined occupancies obtained in terms of the scattering power of K; the results are given in columns 5 and 6 of Table 3. The pairs of sites K1 – K1a, K2 – K2a and K3 – K3a host Na and K + Ca in the proportion of 3 : 2, whereas the proportions are reversed for K4. Taking into account the site multiplicities, we obtain 9.96 Na and 8.04 (K + Ca) atoms per unit cell, which have to be added to the six Ca atoms located at the centers of the bases of the cages. The formula derived from the structure refinement is

$$[\mathrm{Na}_{9.96}(\mathrm{K,Ca})_{8.04}\mathrm{Ca}_6][\mathrm{Si}_{18}\mathrm{Al}_{18}\mathrm{O}_{72}](\mathrm{SO}_4)_5\mathrm{Cl}_{3.5}\mathrm{F}_{0.5}$$

which is similar to $(\mathrm{Na}_{9.78}\mathrm{K}_{4.68}\mathrm{Ca}_{9.12})[\mathrm{Si}_{18.24}\mathrm{Al}_{17.76}\mathrm{O}_{72.27}](\mathrm{SO}_4)_{5.16}\mathrm{Cl}_{3.39}\mathrm{F}_{0.69}$ determined by electron-microprobe analysis (Ballirano *et al.* 1995a). The formula of ideal liottite with 24 extra-framework cations is

$$[(\mathrm{Na,K})_{16}\mathrm{Ca}_8][\mathrm{Si}_{18}\mathrm{Al}_{18}\mathrm{O}_{72}](\mathrm{SO}_4)_5\mathrm{Cl}_4$$

Eight Ca atoms per unit cell are the minimum required in order to balance the negative charge on the framework and interstitial anions. A higher number of Ca may occur if vacancies are present. The electron-microprobe data, showing 9.1 Ca atoms and 23.6 (Na + K + Ca) cations, are in keeping with this statement.

As discussed by Maras & Ballirano (1994) and in accord with the geometrical restraints clearly shown by the present analysis of the structure, there is insufficient room inside the cages to host the large number of anions, H_2O and hydroxyl groups that were reported in early chemical analyses (Merlino & Orlandi 1977a, Leoni *et al.* 1979). In particular, neither the present structural study nor the IR spectroscopic evidence (Ballirano *et al.* 1995a) indicates the presence of H_2O, hydroxyl groups, and carbonate anions in liottite from Pitigliano.

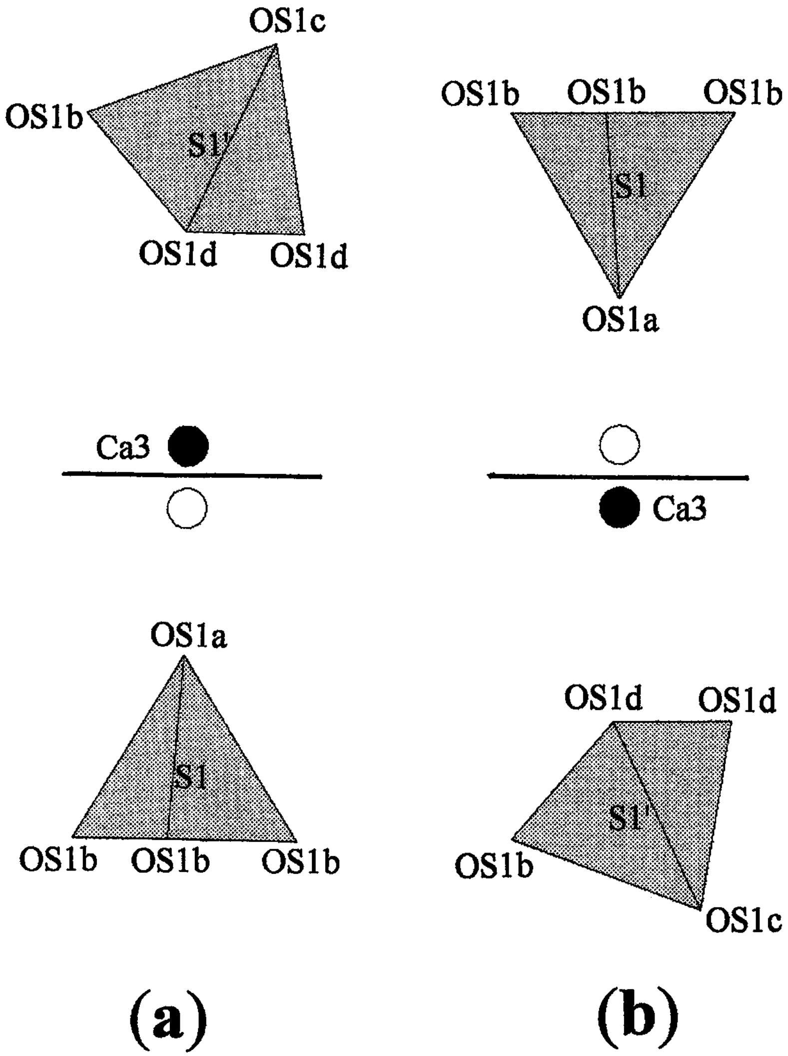


FIG. 5. Schematic drawing of the two possible arrangements of the sulfate groups S1 and S1′, depending on which one of the two split sites at $z = 0.02$ and $z = -0.02$ is actually occupied by the Ca3 cation. The trace of the mirror plane at $z = 0$ is indicated; the filled and open circles represent occupied and empty sites, respectively.

DISCUSSION

The crystal structure of liottite, a six-layer cancrinite-like mineral, consists of a perfectly ordered (Si,Al) framework, in accord with an Si/Al ratio of 1. Three distinct types of cages are formed by the *ABABAC* stacking sequence: cancrinite, losod, and liottite cages. Within the unit cell, three base-sharing cancrinite cages are stacked along [⅓ ⅔ *z*], a losod cage with a base-sharing cancrinite cage is stacked along [⅔ ⅓ *z*], and a liottite cage is located at [0 0 *z*]. The structure hosts, in total, four cancrinite, one losod and one liottite cages. The column of base-sharing cancrinite cages at [⅓ ⅔ *z*] includes ...Ca–Cl–Ca–Cl... chains, and the isolated cancrinite cage stacked along [⅔ ⅓ *z*] has a disordered distribution of fluorine and chlorine anions. The losod and liottite cages are fully occupied, respectively, by two and three sulfate groups, the orientations of which are coupled to the position of Ca atoms at the bases of the cages. The extra-framework cations are disordered over various sites; this distribution also influences the orientation of the SO_4 groups. The structure determination confirms the observation that the SO_4:Cl ratio varies regularly, in the different cancrinite-like minerals, according to the different type of cages that form as a consequence of the distinct sequences of stacking (Ballirano *et al.* 1994). In the case of liottite, the proposed SO_4:Cl ratio, 1.25, derives from five SO_4 groups within the relatively large losod and liottite cages and four Cl within the small cancrinite cages. Minor substitutions are possible [$SO_4 \rightleftharpoons 2Cl$; Bonaccorsi *et al.* (1990), $SO_4 \rightleftharpoons 2CO_3$; Hassan & Grundy (1984), Maras & Ballirano (1994)], but the maximum possible number of sulfate groups is five. According to the refined site-scattering values, we obtain the formula $[Na_{10}(K,Ca)_8Ca_6][Si_{18}Al_{18}O_{72}](SO_4)_5Cl_{3.5}F_{0.5}$, which compares well with $(Na_{9.78}K_{4.68}Ca_{9.12})[Si_{18.24}Al_{17.76}O_{72.27}](SO_4)_{5.16}Cl_{3.39}F_{0.69}$ derived from electron-microprobe analyses (Ballirano *et al.* 1995a). Further structural refinements on cancrinite-like minerals are in progress to confirm the degree of order between tetrahedrally coordinated cations Al and Si and the relation between framework and anion content.

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