American Mineralogist, Volume 62, pages 321–326, 1977

Liottite, a new mineral in the cancrinite–davyne group

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Abstract

A new mineral, liottite, was found in Pitigliano (Tuscany, Italy). It occurs, as flattened hexagonal prisms up to 1 cm in diameter, inside cavities of ejected blocks in a pumice deposit. The space group is $P\bar{6}m2$; a = 12.842, c = 16.091 Å. Optical data $\omega = 1.530$, $\epsilon = 1.528$. The density is 2.56 g cm^{-3}. The strongest lines in the powder patterns are: 4.84(36), 3.715(100), 3.315(75), 2.686(10), 2.471(10), 2.141(24), 1.801(10). The chemical formula $(Ca_{10.76}Na_{9.29}K_{3.82}Fe^{+3}_{0.16})(Si_{18.34}Al_{17.66})O_{72}(SO_4)_{3.91}(CO_3)_{1.72}Cl_{2.61}(OH)_{3.58}\cdot 1.83H_2O$, the hexagonal symmetry, and the lattice dimensions show that liottite is a new member of the cancrinite group.

Introduction

Pitigliano (Tuscany, Italy) is a locality well known to collectors and students of minerals, because of the occurrence of a rich variety of well-crystallized minerals. Within a program of reexamination of Tuscan mineralogy, a study of the various mineral phases of that locality was undertaken. The study was fruitful because at least three different minerals of the cancrinite–davyne group were found: one was identified as afghanite and two appeared to be new mineral species on the basis of space group and cell dimensions. The aim of the present paper is the description and discussion of one of these new minerals, which was named *liottite* in honor of Luciano Liotti, enthusiast and well-informed collector, who kindly gave us the material in which liottite was first found.

The new mineral and its name were approved by the New Minerals and Mineral Names Commission of I.M.A. Type material is deposited in the museums of Instituto di Mineralogia e Petrografia dell' Università di Pisa (Italy) and Istituto di Mineralogia dell' Università di Modena (Italy).

Paragenesis

The sample studied is one of numerous ejected blocks found in a pumice deposit, which is indicative of the explosive activity of a small volcanic center set up in the Pleistocene on the rims of the great Latera caldera. These blocks are the product of a syntexis between the carbonate rocks which make up the walls of the vent of the magmatic reservoir and a trachytic magma. The most common mineral assemblage, which is also characteristic of the specimen from which the new species was obtained, is vesuvianite, garnet (grossular and andradite), pyroxene, and, subordinately, melilite, latiumite, anorthite, and brandisite.

Crystallographic and physical properties

Liottite is transparent and colorless. The crystals occur as well-developed flattened hexagonal prisms, up to one centimeter in diameter, inside the cavities of the blocks. Measurement by two-circle optical goniometer indicated hexagonal symmetry. No evidence contrary to dihexagonal dipyramidal symmetry was discovered in morphology; the various forms were then indexed assuming $6/mmm$ symmetry. The habit of the crystals is illustrated in Figure 1. Other minor forms appearing in the crystal on which we made our goniometric measurements were: {120}, {121}, {112}, {113}. They were not included in the drawing because of their minor development.

Weissenberg and precession photographs indicated Laue symmetry $6/mmm$, with $a \simeq 12.9$ and $c \simeq 16.1$ Å. As no systematic absences were observed, possible space groups are $P6/mmm$, $P6mm$, $P\bar{6}2m$, $P\bar{6}m2$, and $P622$.

The X-ray powder data (Table 1) were obtained by means of a Phillips diffractometer, scanning speed 1/2° 2ϑ per min, Ni-filtered Cu radiation (λ = 1.54051 Å). The powder pattern was readily indexed using prominent reflections on the single-crystal pho-

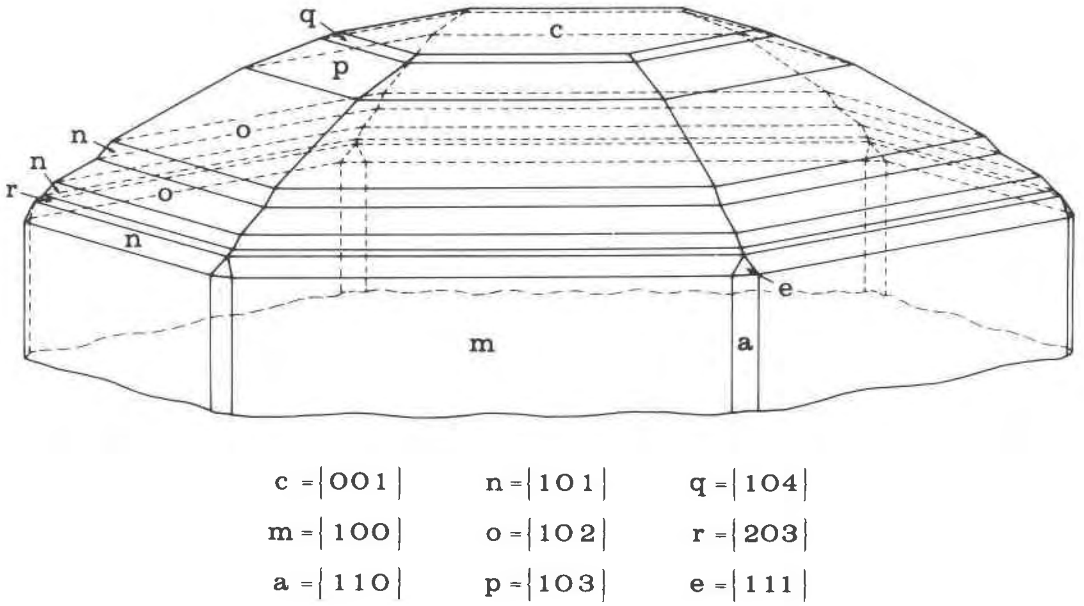

FIG. 1. Drawing of a well-developed crystal of liottite.

tographs. The cell parameters derived from single-crystal study and refined by a least-squares method, using the indexed powder data, are given in Table 3. Refractive indices, $\omega = 1.530$, $\epsilon = 1.528$, were measured by a double variation method using *o*-nitrotoluene as liquid. The density of liottite, also reported in Table 3, was determined by suspension in a mixture of bromoform and acetone as 2.56 ± 0.02 g cm^{-3}. The hardness of the mineral is 5 in the Mohs scale.

Chemical composition

The chemical composition was obtained in the following way: CaO, Na_2O, and K_2O were determined by atomic absorption spectrometry using a Perkin Elmer 303 instrument. CO_2 and H_2O were obtained by the microdetermination of carbon and hydrogen carried out with the Carlo Erba elemental microanalyzer 1104 instrument. Cl and SO_3 were determined by X-ray fluorescence spectrometry, using as reference standard samples of analyzed cancrinite to which known quantities of sulphur and chlorine were added. Starting from the known quantities of the other elements, SiO_2, Al_2O_3, and Fe_2O_3 were determined by X-ray fluorescence spectrometry according to the method of Franzini and Leoni (1972), introducing the appropriate correction factors for sulphur and chlorine and assuming that the sum of the weight percentages was 100.0. The results of the analyses are given in the first column of Table 2.

Related compounds and structural considerations

The chemical data reported in Table 2, together with the hexagonal symmetry and the cell parameters, clearly show a close relationship with the minerals of the cancrinite–vishnevite–davyne series with chemical composition $(Na,Ca,K)_{6-8}Al_6Si_6O_{24}$ $(CO_3, SO_4,Cl,OH)_{1-2}\cdot 1\text{–}5H_2O$. On this basis the unit-cell contents of liottite were calculated assuming 36(Si + Al) and are given in Table 2. From the excess of oxygen atoms over 72, a content of 3.58 hydroxyl anions can be inferred; in fact, hydroxyl ions are present in cancrinite minerals as indicated by chemical analyses and structural studies and were actually found in liottite by crystal-structure determination (Merlino and Mellini, 1976). The following chemical formula was thus calculated for liottite: $(Ca_{10.76}Na_{9.29}K_{3.82}Fe^{+3}_{0.16})(Si_{18.34}Al_{17.66})O_{72}(SO_4)_{3.91}(CO_3)_{1.72}Cl_{2.61}(OH)_{3.58}\cdot 1.83\ H_2O$. Liottite contains calcium as its dominant cation, a relation which was not found in any mineral of the cancrinite group except one microsommite, as shown in Figure 2.

The crystal structure of cancrinite, space group $P6_3$, $a = 12.75$, $c = 5.14$ Å, was determined by Pauling (1930) and refined by Jarchow (1965). It is made up of six-fold rings of tetrahedra: each ring is linked to three rings in the preceding layer and to

TABLE 1. X-ray powder diffraction data for liottite

hkl[a]	I/Io	d obs (Å)	d calc (Å)	hkl	I/Io	d obs (Å)	d calc (Å)
100	2	11.12	11.12	423	2	1.957	1.957
101	1	9.17	9.15	307			1.954
102*	1	6.52	6.52	406*	6	1.932	1.930
003*	1	5.37	5.36	513*	3	1.872	1.872
103*	36	4.84	4.83	227			1.869
210*	2	4.210	4.204	431	<1	1.816	1.817
113*	2	4.114	4.116	218			1.815
211*	2	4.077	4.067	416*	10	1.801	1.800
104*	8	3.790	3.783	432	1	1.782	1.783
300*	100	3.715	3.707	335			1.782
302*	2	3.375	3.367	520*			1.781
213*	75	3.315	3.309	308	1	1.768	1.768
005	2	3.217	3.218	109			1.765
220*			3.211	603*	1	1.753	1.752
105	1	3.095	3.091	433*	2	1.732	1.731
303	1	3.058	3.050	219*	1	1.646	1.645
311*	3	3.033	3.029	613*	1	1.618	1.617
312*	4	2.885	2.880	605	6	1.606	1.606
205	9	2.787	2.785	440*			1.605
400*			2.780	531	<1	1.581	1.581
223*	2	2.760	2.755	701			1.581
401*	5	2.745	2.740	328			1.580
006*	10	2.686	2.682	702	1	1.559	1.559
313*	7	2.678	2.674	532			1.559
402*	3	2.630	2.628	525			1.558
106	<1	2.610	2.607	606	2	1.525	1.525
116	10	2.471	2.475	533			1.523
403*			2.468	703			1.523
314*	2	2.456	2.449	409*	1	1.505	1.504
305	2	2.427	2.430	2 1 10			1.503
410			2.427	534	<1	1.478	1.478
404*	2	2.290	2.287	704			1.478
315	2	2.225	2.227	3 0 10			1.476
500			2.224	710*	1	1.474	1.473
306*	1	2.174	2.173	4 0 10	1	1.391	1.393
324*	2	2.155	2.155	625			1.391
330*	24	2.141	2.140	800			1.390
405	4	2.102	2.104	446*	4	1.378	1.377
420			2.102	543			1.376
226	5	2.060	2.058	803*	4	1.346	1.346
325	1	1.999	1.999	804	1	1.314	1.315
510			1.997	1 1 12			1.314

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[a] Only the reflexions marked with a star were used for the refinement of the unit cell dimensions. (220), (400), (403), (513), (520), (440), (409), (446) were used because their intensities in the single crystal photographs were much greater than (005), (205), (116), (227), (432) and (335), (605), (2110), (543).

three other rings in the succeeding one, in a three-dimensional framework. The layers succeed each other along the *c* axis, according to the stacking sequence *ABAB* . . .

The diffraction pattern of the specimen used by Jarchow (1965) to refine the structure of cancrinite showed diffuse spots symmetrically disposed relative to the sharp ones at ± 3/7 c^* in reciprocal space

TABLE 2. Chemical data and unit-cell contents in liottite

	wt.%	cell contents	
SiO_2	30.51	Si	18.34
Al_2O_3	24.92	Al	17.66
Fe_2O_3	0.36	Fe^{+3}	0.16
CaO	16.71	Ca	10.76
Na_2O	7.97	Na	9.29
K_2O	4.98	K	3.82
SO_3	8.66	SO_4	3.91
CO_2	2.1	CO_3	1.72
Cl	2.57	Cl	2.61
H_2O	1.8	H_2O	3.62
	-----	O	73.79
	100.58		
-Cl=O	0.58		

	100.00		

(satellite reflections), thus indicating some kind of superstructure. Foit *et al.* (1973) and Brown and Cesbron (1973) studied "cancrinites" from different sources, finding superstructures characterized by values of *c* parameter equal to 5*c*, 8*c*, 11*c*, 16*c*, and 21*c*, where *c* = 5.13 Å. The diffraction patterns of all these cancrinites differ as regards the much weaker diffuse reflections but do not differ in the positions and intensities of the sharp spots. This indicates, as the authors remark, that they have the same aluminosilicate framework structure, differing only in the ordering of the cations outside the framework, which leads to the appearance of the satellite reflections.

Natural and synthetic compounds exist which, although structurally related to cancrinite, have a different aluminosilicate framework. Bariand *et al.* (1968) found and studied afghanite, a new aluminosilicate with unit-cell content $(Na,Ca,K)_{36}(Si,Al)_{48}O_{102}(Cl,SO_4,CO_3)_{12} \cdot 1.8H_2O$. Chemical composition and crystallographic data, reported in Table 3, indicated afghanite as a member of the cancrinite group, with an 8-layer sequence of six-membered rings. Recently Sieber and Meier (1974) prepared and studied *Losod*, a compound with idealized formula $Na_{12}Al_{12}Si_{12}O_{48} \cdot 18H_2O$. Its cell data, also reported in Table 3, indicated it is a member of the cancrinite group with a 4-layer sequence *ABAC*.

Liottite is another member of this group. Cell data pointed to a 6-layer sequence of six-membered rings; this has been confirmed by a crystal structure determination (Merlino and Mellini, 1976), which has led to the space group $P\bar{6}m2$ and indicated the stacking sequence *ABABAC*. The structure refinement is in progress.

TABLE 3. Crystallographic data of compounds in the cancrinite group

	Davyne	"Losod"	Liottite	Afghanite
Source	Bariand et al. (1968)	Sieber and Meier (1974)	This paper	Bariand et al. (1968)
Space group	$P6_3$	$P6_3/mmc$	$P\bar{6}m2$	$P6_3/mmc, P6_3mc$ $P\bar{6}2c$
a(Å)	12.70(0.03)	12.906(0.003)	12.842(0.003)	12.77(0.03)
c(Å)	5.33(0.02)	10.541(0.003)	16.091(0.005)	21.35(0.04)
$D_{calc.}$ $(g.cm^{-3})$	-	2.21	2.61	2.65
$D_{meas.}$ $(g.cm^{-3})$	-	2.15	2.56	2.55
z*	2	4	6	8

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* *number of layers of six-membered rings in the sequence.*

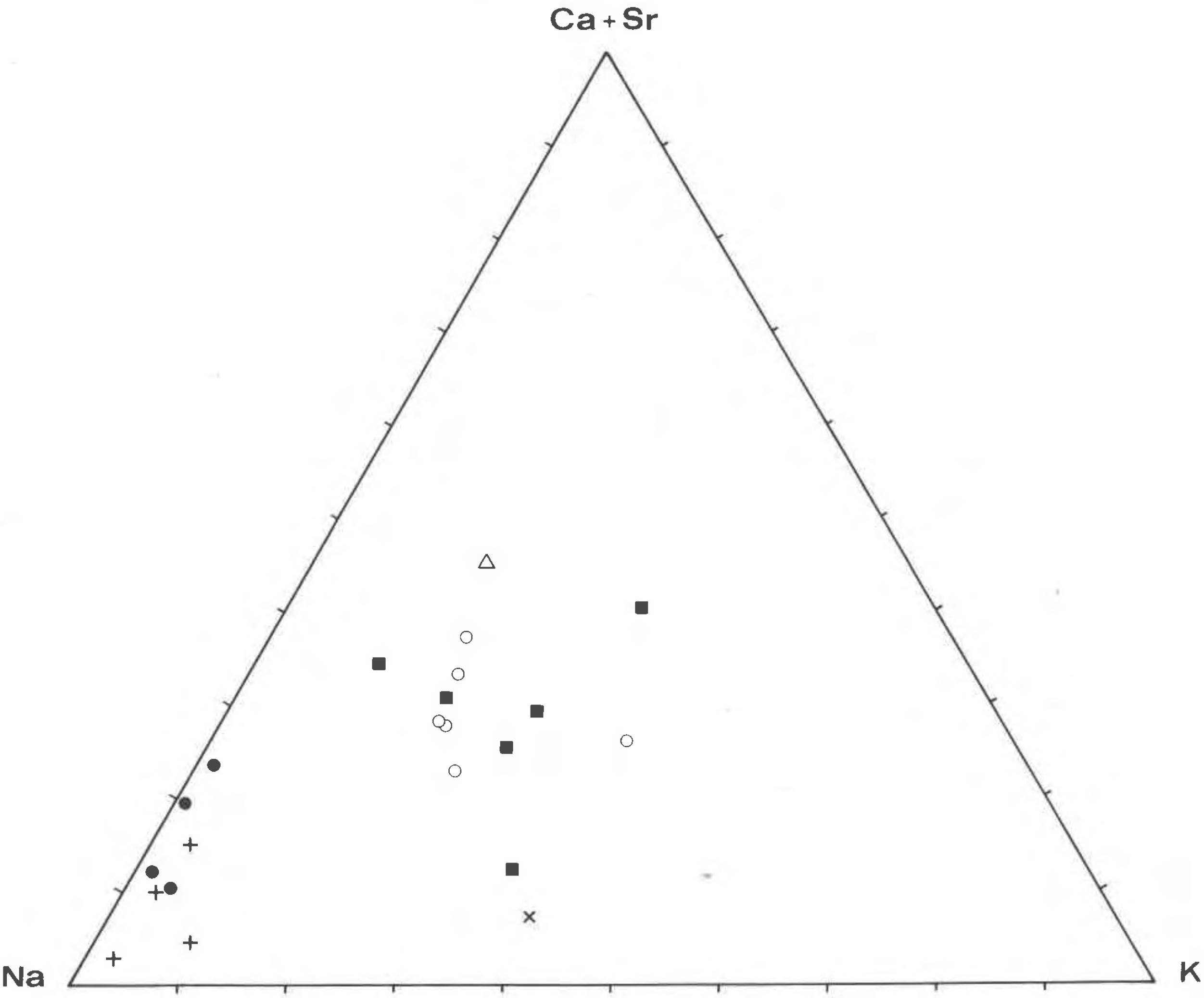

FIG. 2. Cation chemistry of liottite, compared with that of the other minerals in cancrinite group. The data are from Deer *et al.* (1962) and Bariand *et al.* (1968), excluding the analyses with cation sums less than 6 on the basis of 12 (Si + Al).

●	Cancrinite	CO$_3^{2-}$ dominant anion outside the framework
+	Vishnevite	SO$_4^{2-}$ dominant anion outside the framework
■	Microsommite	Cl$^-$ dominant anion outside the framework
○	Davyne	Cl$^-$ dominant anion outside the framework
×	Afghanite	Cl$^-$ dominant anion outside the framework
△	Liottite	SO$_4^{2-}$ dominant anion outside the framework

Acknowledgments

Thanks are due to Mr. R. Cioni and Dr. L. Leoni who made respectively the absorption spectrometry and X-ray fluorescence spectrometry analyses. Particularly helpful were the suggestions and comments by A. Kato. The financial support of Consiglio Nazionale delle Ricerche, Roma, is also kindly acknowledged.

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Manuscript received, April 9, 1976; accepted for publication, September 15, 1976.