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CANCRINITE-LIKE MINERALS: NEW DATA AND CRYSTAL CHEMICAL CONSIDERATIONS

ABSTRACT. — New findings of cancrinite-like minerals from various localities of the volcanic region of Latium and South Tuscany are described: franzinite from Sacrofano and Ariccia, afghanite from Sacrofano and Pitigliano, microsommite from Pitigliano.

Crystallographic, physical and chemical properties are compared with the literature data.

The minerals of the group are characterized by Si/Al ratio always near one, similar distribution of sodium, calcium and potassium; as regards the anionic contents, franzinite is the sulphate richest phase. On the basis of the exhisting data, remarkable compositional or genetic differentiation among the various minerals seems to be excluded.

RIASSUNTO. — Vengono segnalati nuovi ritrovamenti di minerali del gruppo della cancrinite, da varie località della regione vulcanica tosco-laziale; in particolare viene descritta franzinite da Sacrofano e Ariccia, afghanite da Pitigliano e Sacrofano, microsommite da Pitigliano.

I campioni sono stati caratterizzati dal punto di vista delle propretà cristallografiche, fisiche e chimiche.

Di particolare rilievo sono il rapporto Si/Al costantemente vicino ad uno, una distribuzione di sodio, calcio e potassio simile in liottite, afghanite e franzinite, un arricchimento in solfato, con minori tenori di carbonato e cloro, nella franzinite. I dati esistenti sembrano escludere la possibilità di differenziare i minerali del gruppo da un punto di vista composizionale o genetico.

Introduction

Many new phases, structurally and chemically related to cancrinite, were reported in the last years. All of them are framework silicates, built up by six-membered rings of tetrahedra; the rings are stacked according to a close packing sequence (MERLINO and MELLINI, 1976). The most significant data, reported in Table 1, show the different *c* periods, which are multiple values of the tetrahedral edge length (nearly 2.64 Å) and the corresponding stacking sequences. Other structures can be devised, with different stacking sequences and larger translation periods: it is worthwhile to recall the results of RINALDI and WENK (1978), who have observed, by high resolution electron microscopy, domains with 42 and 64 Å *c*-translation inside crystals of afghanite, thus revealing the exhistence, at least in small domains, of 16-layers and 24-layers structures.

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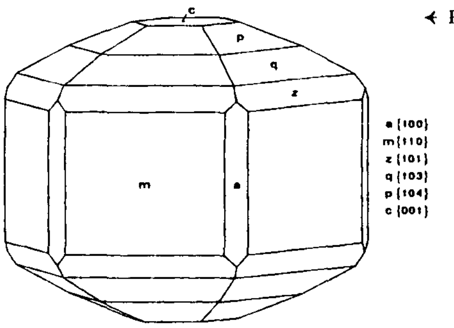
Aim of this paper is to report some results of the work developed in this laboratory on natural cancrinite-like minerals, mainly as regards the chemical and physical properties of specimens we found in various localities of Latium and South Tuscany (Italy). Our discussion will concern mainly liottite, afghanite and franzinite, with few data about a new finding of microsommite, without any comprehensive approach to other phases in the group as cancrinite, davyne or microsommite itself.

The identification of all the phases we studied was led either by X-ray single crystal methods or careful powder diffraction patterns. Hereafter we report data about two new findings of franzinite (from Sacrofano and Ariccia), two of afghanite (from Sacrofano and Pitigliano), one of microsommite (from Pitigliano), comparing them with the data given in literature.

Occurrence and paragenesis

The mineral specimens were collected in various localities belonging to the volcanic region of Latium and South Tuscany (Italy). All of them occur in ejected metasomatized blocks, product of reaction between carbonate rocks and magma.

Afghanite from Pitigliano: the mineral occurs as small crystals, 2-3 mm in diameter, with the crystal morphology described in fig. 1, inside the cavities of large metasomatized ejected blocks, almost completely built up by vesuvianite and grossular, with minor amounts of phlogopite in small packets of lamellar crystals and sanidine; very rare minute crystals of hellandite were also identified in the blocks. The ejected blocks were found in a pumice deposit in the locality Casa Collina, not far from Pitigliano.



← Fig. 1 — Morphology of a well developed crystal of afghanite from Pitigliano.

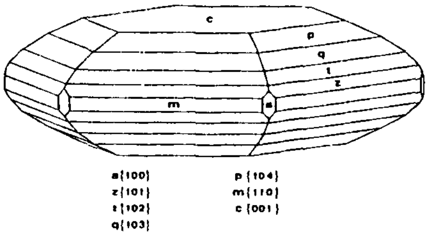


Fig. 2. — Morphology of a well developed crystal of franzinite from Ariccia.

Microsommite from Pitigliano: the mineral was found as milky white hexagonal prisms nearly four millimeters long and one millimeter in diameter. It was found in a little fragment from an ejected block closely similar to those where afghanite was found. Apatite, as thin acicular milky white prisms and diopside were also identified in the same fragment.

Afghanite from Sacrofano: the specimen where afghanite was found has a coarse grained matrix of phlogopite, diopside, sanidine and anorthite. A large geode in the centre of the block is almost completely covered by large crystals of afghanite without well developed morphology and by euhedral and clear crystals of sanidine. Thin section exhamination of a fragment from a large crystal of afghanite indicates presence of other phases of the same structural family. An accurate study of all the minerals in the specimen is now in progress.

TABLE 1
Crystallographic data of cancrinite-like phases

	a	c	Space Group	Stacking Sequence	Selected Reference
Cancrinite	12.75	5.14	$P6_3$	AB	Jarchow (1965)
Losod syn	12.906	10.541	$P6_3/mmc$	ABAC	Sieber and Meier (1974)
Liottite	12.842	16.091	$P\bar{6}m2$	ABABAC	Merlino and Orlandi (1977a)
Afghanite	12.77	21.35	$P6_3mc$	ABABACAC	Bariand,Cesbron and Giraud (1968)
Franzinite	12.884	26.580	$P\bar{3}m1$	ABCABCBACB	Merlino and Orlandi (1977b)
Microsommite syn	22.138	5.248	$P6_3$	AB	Klaska and Jarchow (1977)

TABLE 2
Chemical analyses

	Afghanite Pitigliano	Afghanite Sacrofano	Franzinite Sacrofano	Franzinite Ariccia	Microsommite Pitigliano
SiO_2	31.92	31.21	30.92	31.85	33.87
Al_2O_3	24.55	25.51	25.51	25.13	26.00
Fe_2O_3	0.11	0.05	0.10	0.10	n.d.
MgO	0.29	0.40	0.63	0.26	n.d.
Na_2O	11.33	11.56	13.79	10.99	15.45
K_2O	4.89	4.90	4.73	7.23	9.10
CaO	13.12	9.72	9.81	10.44	0.09
H_2O	1.79	2.81	2.43	1.70	n.d.
CO_2	1.80	2.73	1.83	1.98	n.d.
Cl	2.40	3.75	1.12	0.13	n.d.
SO_3	8.33	8.19	9.38	10.22	7.60
-O=Cl	0.54	0.85	0.25	0.03	92.11
	99.99	99.98	100.00	100.00	

n.d. = not determined

Franzinite from Ariccia: the specimen was found near Ariccia. It was a large ejected block with a middle grained matrix built up by augite, grossular, sanidine, phlogopite and wollastonite: the minerals are listed in order of decreasing abundance. Inside little cavities in the matrix rounded crystals of calcite and leucite were found, as well as perfectly euhedral, clear and colourless crystals of franzinite, with dimensions up to 3-4 mm in diameter (fig. 2).

Franzinite from Sacrofano: the specimen was found in a layer of pyroclastic products near Sacrofano. It was an ejected block built up by large crystals of phlogopite, diopside, anorthite and franzinite. The last phase is rather abundant, milky white in colour and without well developed morphology.

Chemical analyses

Chemical analyses were carried out by atomic absorption spectrometry for Na_2O; CO_2 and H_2O were determined by gas-chromatographic separation using a Carlo Erba 1104 elemental microanalyzer. K_2O, CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3 and Cl were analyzed by X-ray fluorescence spectrometry, following the method developed by FRANZINI and LEONI (1972), later modified by LEONI and SAITTA (1973). Owing to the low available amount, microsommite was analyzed by electron microprobe (analyst R. RINALDI). The results are reported in Table 2.

Optical properties

Refractive indices (n_D) were determined by comparison with standard liquids; they are reported in Table 3, together with the literature data. Microsommite from Pitigliano and liottite have negative birefringence ($\omega > \varepsilon$), whereas the other members of the cancrinite group have positive birefringence.

X-ray crystallography

The unit cell parameters of the various minerals we studied were refined by least squares fitting either of $2\,\vartheta$ values from X-ray powder diffraction patterns or of the crystal settings in the single crystal automatic diffractometer. They are reported in Table 3, together with the unit cell contents. In our opinion, at present it is not possible to put down any significant correlation between lattice parameters and chemical variables.

The Table 3 gives also V_c, values of the unit cell volume normalized to the smaller cancrinite unit cell; it shows some spread for afghanite, from 747.1 to 767.0 Å^3, nearly constant value for franzinite, not dissimilar from the unique datum for liottite, and the smallest specific volume for microsommite.

The agreement among observed and calculated densities is good, with the measured values always smaller than the calculated ones.

Crystal chemistry of the cancrinite-like minerals

The crystal chemical formulae reported in Table 3 were calculated on the basis of the number of silicon and aluminum atoms in the unit cell: this number is obviously six times the number of layers in the stacking sequence. As in any other framework silicate we assumed a (Si+Al)/O ratio equal to 1/2 and the excess oxygen atoms were used, together with the analytical water content, to obtain the number of hydroxyl anions.

TABLE 3

Chemical formulae, crystallographic and optical properties of cancrinite-like minerals

	1	2	3	4	5	6	7	8	9	10	11
Si	18.34	25.18	24.45	24.53	24.11	24.82	25.13	31.32	30.42	31.09	18.90
Al	17.66	22.82	23.55	23.47	23.89	23.18	22.87	28.68	29.58	28.91	17.10
Fe	0.16	0.07	0.03	n.d.	n.d.	n.d.	b.d.	0.03	0.07	0.07	n.d.
Mg	n.d.	0.34	0.47	n.d.	b.d.	0.03	b.d.	0.20	0.92	0.38	n.d.
Na	9.29	17.32	17.55	19.46	18.10	20.13	18.51	21.53	26.30	20.80	16.71
K	3.82	4.91	4.90	2.74	0.83	2.19	2.99	5.22	5.93	9.00	6.48
Ca	10.76	11.08	8.16	14.08	9.93	9.78	9.79	12.50	10.34	10.92	0.05
$CO_3^=$	1.72	1.94	2.92	0.43	0.78	n.d.	n.d.	2.03	2.46	2.64	n.d.
$SO_4^=$	3.91	4.93	4.81	5.08	5.46	6.15	6.19	7.72	6.93	7.49	3.18
Cl^-	2.61	1.21	4.98	6.21	5.28	4.76	5.14	0.59	1.87	0.22	n.d.
H_2O	1.81	1.97	7.35	0.00	5.28	n.d.	n.d.	4.31	5.61	3.93	n.d.
OH^-	3.58	5.50	0.00	3.72	0.00	n.d.	n.d.	3.48	4.72	3.22	n.d.
$O^=$	72.00	96.00	93.90	98.96	94.32	96.85	96.34	120.00	120.00	120.00	71.91

n.d. = not determined b.d. = below detection limit

a	12.842(3)	12.847(3)	12.796(2)	12.77(3)	12.74	-	-	12.884(9)	12.861(5)	12.906(5)	22.156(5)
c	16.091(5)	21.464(5)	21.361(3)	21.35(4)	21.26	-	-	26.58(2)	26.62(3)	26.45(2)	5.237(2)
V	2298.1	3067.8	3031.0	3015.1	2988.3	-	-	3821.0	3813.1	3815.3	2226.4
V_c	766.0	767.0	757.8	753.8	747.1	-	-	764.2	762.6	763.1	742.1
d_{calc}	2.61	2.56	2.60	2.65	2.53	-	-	2.52	2.57	2.55	> 2.30
d_{obs}	2.56(2)	2.44(2)	2.53(2)	2.55(2)	2.517	-	-	2.49	2.46(2)	2.52(2)	2.37(4)
ω	1.530	1.521	1.510	1.523	1.528	-	1.522	1.510	1.504	1.505	1.508
ε	1.528	1.525	1.512	1.529	1.533	-	1.528	1.512	1.506	1.507	1.506

1 - Liottite Pitigliano (MERLINO and ORLANDI, 1977 a); 2 - Afghanite Pitigliano (present work); 3 - Afghanite Sacrofano (present work); 4 - Afghanite Sar-e-Sang (BARIAND et al., 1968); 5 - Afghanite Tultuisk (IVANOV and SAPOZHNIKOV, 1975); 6 - Afghanite Lyadzhuar-Darinsk (HOGARTH, 1979); 7 - Afghanite Edwards (HOGARTH, 1979); 8 - Franzinite Pitigliano (MERLINO and ORLANDI, 1979 b); 9 - Franzinite Sacrofano (present work); 10 - Franzinite Ariccia (present work); 11 - Microsommite Pitigliano (present work).

In our opinion three main points deserve discussion: 1) the Si/Al ratio; 2) the cationic content in the various minerals; 3) the content of water and anions.

1) All the analyses of natural cancrinite-like minerals give a Si/Al ratio near one; this is a strong indication for ordered distribution of these cations, in agreement with the results of the structural studies of natural cancrinite (JARCHOW, 1965) and synthetic microsommite (KLASKA and JARCHOW, 1977). Crystal structure analyses of liottite, afghanite and franzinite (MERLINO and MELLINI, 1976) indicate that these minerals do not present any long range order in the distribution of the tetrahedral cations. These minerals thus appear characterized by short range ordering of tetrahedral cations with development of antiphase domains. In this context it seems interesting the observation that while the Si/Al ratio is nearly one for all the analyzed specimens, it is always greater than one, ranging from 1.009 to 1.105, with a mean value of 1.06, which is in keeping with the so called Lowenstein's avoidance rule.

2) We shall consider only the sodium, calcium and potassium contents, as magnesium and iron are present in very low quantity. The ternary diagram reported in Fig. 3 indicates that afghanite cannot be distinguished from franzinite on the

basis of the cationic content, whereas liottite seems sodium depleted and more calcic than afghanite and franzinite; however, the availability of only one analysis for liottite gives limited statistical significance to this last observation.

The diagram reports also the point representative for microsommite from Pitigliano, the only locality, at present, where microsommite was found apart from the type locality Monte Somma. The comparison of our data with those collected by Hogarth (1979) indicates that the calcium free microsommite from Pitigliano is very different from all the previously analyzed specimens. Its chemical composition is similar to the theoretical $K_9Na_{15}Al_{18}Si_{18}O_{72}(OH)_2(SO_4)\cdot 7\text{-}8\ H_2O$ given by Klaska and Jarchow (1977) for their synthetic microsommite.

3) Fig. 4 gives the sulphur, chlorine and carbon content in cancrinite-like minerals, indicating different anionic contents in liottite and afghanite on one side and franzinite on the other side: in fact this last mineral has a lower chlorine content and is enriched in sulphate anions. Such differences cannot be related, in our opinion, neither to the cationic content in the various phases, as we already saw it is similar in the different phases of the group; nor to the genetical conditions, as we are comparing minerals from the same locality and, sometimes, from the same rock specimen. An explanation could be perhaps derived from a careful structural analysis.

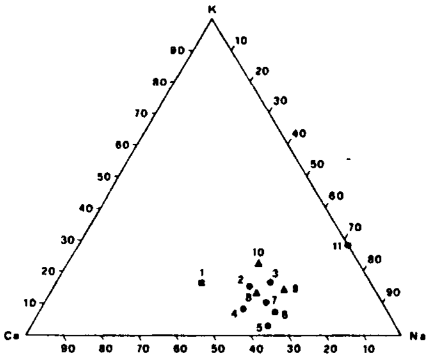


Fig. 3. — Na-Ca-K diagram for cancrinite-like minerals. Code numbers as given in table 3.

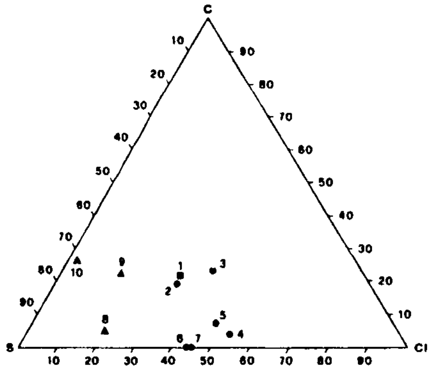


Fig. 4. — Cl-S-C diagram for cancrinite-like minerals. Code numbers as given in table 3.

From the preceding considerations it appears that we have no indication either of different stability fields for the different phases nor of any genetical hierarchy among them. The problem arises of what possible mechanism leads to the development of a crystal of liottite, afghanite or franzinite. Although preliminary structural investigations (Merlino and Mellini, 1976) clearly indicated that these minerals cannot be considered polytypes « stricto sensu » we retain that the problem of their genesis is similar to the genetical problem of the various polytypic structures.

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