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CRYSTAL CHEMISTRY OF CANCRINITE-GROUP MINERALS WITH AN *AB*-TYPE FRAMEWORK: A REVIEW AND NEW DATA. I. CHEMICAL AND STRUCTURAL VARIATIONS

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ABSTRACT

Chemical and structural variations of 11 minerals of the cancrinite group having an Al,Si,O framework of the *AB* type are summarized and discussed. The total number of chemically studied samples is 360 (our data and literature data): cancrinite 192 and 35, vishnevite 21 and 13, cancrisilite 19 and 10, kyanoxalite and oxalate-rich intermediate members of the cancrinite–kyanoxalite series 12 and 0, davyne 10 and 23, depmeierite 2 and 0, balliranoite 1 and 0, hydroxycancrinite 0 and 1, quadridavyne 0 and 10, microsommite 0 and 8, and pitiglianoite 0 and 3. We provide original structural data for nine samples of distinct varieties of cancrinite and one sample of cancrisilite, as well as published structural data on the above-listed minerals. The major topics are the distribution and ratios of extra-framework components, cations (Na^+, Ca^{2+}, K^+), anions (CO_3^{2-}, SO_4^{2-}, Cl^-, $C_2O_4^{2-}$, PO_4^{3-}) and H_2O, with special emphasis on oxalate and phosphate anions. The idealized formula of cancrinite has been refined: $Na_7Ca[Al_6Si_6O_{24}](CO_3)_{1.5}•2H_2O$. The solid-solution series with coupled substitutions in the framework and extra-framework portions are discussed, as is the genetic aspect of crystal chemistry of cancrinite-group minerals with a *AB*-type framework.

Keywords: cancrinite group, cancrinite, cancrisilite, vishnevite, kyanoxalite, depmeierite, davyne, balliranoite, composition of minerals, crystal structure, oxalate in silicate minerals, alkaline intrusive complexes.

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Sommaire

Nous résumons ici les variations chimiques et structurales de 11 minéraux du groupe de la cancrinite ayant une charpente Al,Si,O du type *AB*, et nous en discutons la portée. Le nombre total des échantillons dont la composition a été étudiée atteint 360 (nos données et celles prises de la littérature): cancrinite 192 et 35, vishnévite 21 et 13, cancrisilite 19 et 10, membres intermédiaires riches en oxalate de la série cancrinite–kyanoxalite ainsi que kyanoxalite 12 et 0, davyne 10 et 23, depmeïerite 2 et 0, balliranoïte 1 et 0, hydroxycancrinite 0 et 1, quadridavyne 0 et 10, microsommite 0 et 8, et pitiglianoïte 0 et 3. Nous présentons des données structurales originales pour neuf échantillons de variétés distinctes de cancrinite et un échantillon de cancrisilite, de même que les données publiées antérieurement portant sur ces espèces. Les sujets majeurs de notre analyse portent sur la distribution et les rapports des composantes externes à la charpente, les cations (Na^+, Ca^{2+}, K^+), anions (CO_3^{2-}, SO_4^{2-}, Cl^-, $C_2O_4^{2-}$, PO_4^{3-}) et H_2O, avec emphase particulière portée sur les anions oxalate et phosphate. La formule idéale de la cancrinite a été affinée: $Na_7Ca[Al_6Si_6O_{24}](CO_3)_{1.5}•2H_2O$. On discute de la série de solutions solides avec substitutions couplées impliquant la charpente et les composantes externes à celle-ci, et de l'aspect génétique de la cristallochimie des minéraux du groupe de la cancrinite ayant une charpente de type *AB*.

(Traduit par la Rédaction)

Mots-clés: groupe de la cancrinite, cancrinite, cancrisilite, vishnévite, kyanoxalite, depmeïerite, davyne, balliranoïte, composition des minéraux, structure cristalline, oxalate dans les minéraux silicatés, complexes intrusifs alcalins.

Introduction

Feldspathoids of the cancrinite group are hexagonal or trigonal tecto-aluminosilicates with frameworks consisting of layers containing six-membered rings of Si- and Al-centered tetrahedra perpendicular to the **c** axis. The rings centered by 6-fold or 3-fold axes [1/3 2/3 *z*], [2/3 1/3 *z*] and [0 0 *z*] are usually denoted by the letters *A*, *B* and *C*, respectively. Rings of each type form layers (levels). Every ring is linked to three rings of the preceding layer and to three rings of the succeeding layer. The stacking of the *A*, *B*, *C* layers along the **c** axis determines the type of framework that contains zeolitic cavities forming channels running along [001]. The channels host extra-framework cations (major: Na^+, Ca^{2+}, K^+), anions (species-defining: CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-, S^{2-}, $C_2O_4^{2-}$, PO_4^{3-}) and, in many cases, H_2O molecules. The diversity of cancrinite-group minerals (CGM) is determined by 1) the type of Al,Si,O framework and 2) the composition and distribution of extra-framework cations and anions. Various data on types of frameworks and the configuration of cavities for CGM were summarized by Bonaccorsi & Merlino (2005).

Cancrinite-subgroup minerals are widespread in nature. It seems paradoxical, but their crystal chemistry has been poorly studied in comparison with rarer CGM with other types of frameworks or unit cells. As our data show, cancrinite-subgroup minerals, especially carbon-bearing ones, are very diverse chemically and demonstrate wide structural variations in their extra-framework components. In particular, we recently discovered in these minerals two earlier unknown extra-framework anions, $C_2O_4^{2-}$ and PO_4^{3-}, and some new continuous solid-solution series in this subgroup. We found that cancrinite as a mineral species is represented by several distinct chemical and structural varieties, and its idealized formula was refined. The present paper addresses the chemical and structural diversity of CGM with an *AB*-type framework, especially in terms of the distribution and ratios of extra-framework constituents in cancrinite-subgroup members.

Infrared spectroscopy, earlier used for this group rather rarely, has turned out to be a very effective tool in crystal-chemical studies of the CGM. A companion paper (Chukanov *et al.* 2011) is devoted to this aspect.

Background Information

At present, the cancrinite group includes 25 minerals with 13 types of frameworks. Eleven CGM have a framework with the simplest stacking of layers: *...ABABAB...* (Table 1). This framework contains channels of two types: so-called narrow channels (in fact, columns of "cancrinite" cages, or ε cages) and zeolitic wide channels (Fig. 1). Members with the *AB*-type framework have the smallest possible unit-cell parameter *c*, in the range 5.1–5.4 Å, for cancrinite-like aluminosilicates. Eight of these minerals also have the smallest *a* parameter, in the range 12.55–12.85 Å, whereas three others are characterized by larger values of the *a* parameter caused by the distribution of extra-framework components (Bonaccorsi & Merlino 2005). These three rare minerals, namely pitiglianoite, microsommite and quadridavyne, are well studied in their crystal-chemical aspects (Merlino *et al.* 1991, Bonaccorsi *et al.* 1994, 2001), and each of them has a relatively stable chemical composition (Table 2). Another eight CGM with the *AB*-type framework can be subdivided on the basis of the content of the narrow channel, into a subgroup of cancrinite *sensu stricto* (below: the cancrinite subgroup), and the davyne–balliranoite solid-solution series (below: the davyne series) (Table 1). Such a distinction also makes geological and genetic sense (see the Discussion).

Earlier published original data on CGM with an *AB*-type framework, especially on cancrinite, a

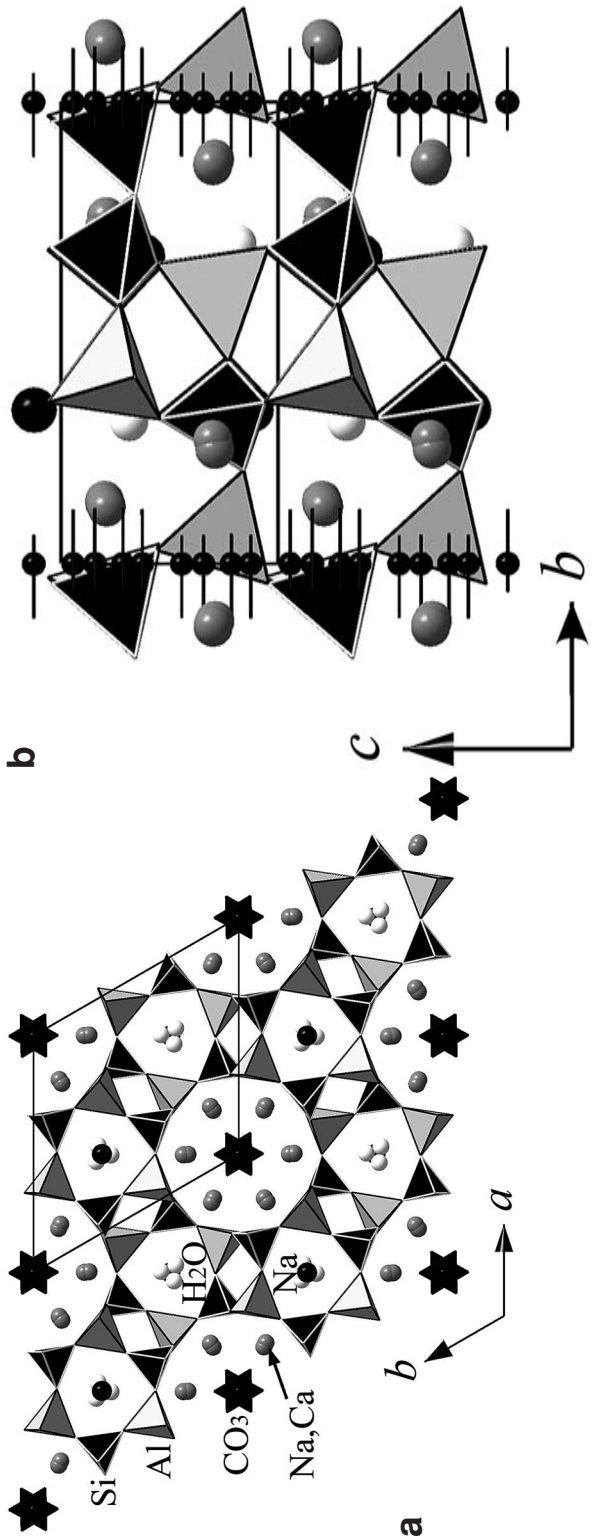

FIG. 1. Crystal structure of cancrinite from its type locality: Ilmeny Mountains, southern Urals, Russia (sample mmf28962): **a–b** and **b–c** projections.

widespread rock-forming mineral, are "scattered" in numerous papers, and it will be impossible to cite the complete list in the context of this article. A summary of data on CGM were recently given in the reference books (Minerals 2003, Deer *et al*. 2004) and in the article by Bonaccorsi & Merlino (2005). As far as crystal-structure refinements are concerned, we will cite only the key publications of the last thirty years (Table 1) and the review by Bonaccorsi & Merlino (2005). For chemical compositions, we first note the reference book (Minerals 2003), which contains scrupulously collected published analytical data on CGM, and the later paper by Binon *et al*. (2004) for davyne and quadridavyne.

The synthetic analogues and "relatives" of CGM are numerous. All known synthetic aluminosilicates belonging to this structural family (>20) have the *AB* framework and are diverse chemically, mostly in their extra-framework anions (*e.g.*, CO_3^{2-}, HCO_3^-, OH^-, NO_3^-, $S_2O_3^{2-}$, SO_4^{2-}, S^{2-} and Se^{2-}). Reviews of these compounds were given by Sirbescu & Jenkins (1999) and Bonaccorsi & Merlino (2005). Synthetic phases are not discussed in this paper.

The Materials Studied and Experimental Conditions

Chemical study

We have studied 257 samples of cancrinite-subgroup and davyne-series minerals (329 analyses). For purposes of comparison, chemical data for CGM with the *AB*-type frameworks taken from the literature (103 analyses) were used (Table 2). Thus, the total number of chemically studied samples involved in this work

TABLE 1. CANCRINITE-GROUP MINERALS WITH AN *AB*-TYPE FRAMEWORK

Mineral	Space group	*a*, Å	*c*, Å	*Z*	Simplified formula			References
					framework	narrow channel	wide channel	
Cancrinite subgroup								
Cancrisilite	$P6_3mc$	12.57-12.60	5.10-5.11	1	$Si_{6.7-7.6}Al_{5.3-4.4}O_{24}$	$Na_2(H_2O)_2$	$Na_5(CO_3)_{1-1.4}(H_2O)_{1-0}$	Khomyakov *et al.* (1991a,b), this work
Cancrinite	$P6_3$*	12.61-12.67	5.11-5.18	1	$Si_{6.0-6.8}Al_{6.0-5.2}O_{24}$	$Na_{1.6-2}(H_2O)_{0-2}$	$(Na_{5.8-4}Ca_{0.2-2})(CO_3)_{1.4-1.6}$	Grundy & Hassan (1982), Ballirano & Maras (2004), Hassan *et. al*. (2006), Chukanov *et al.* (2009b), this work
Vishnevite	$P6_3$	12.62-12.83	5.14-5.27	1	$Si_{6.0-6.4}Al_{6.0-5.6}O_{24}$	$Na_2(H_2O)_2$	$(Na_{6-3}K_{0-3}Ca_{0-0.9})(SO_4)_{0.6-1.3}$	Hassan & Grundy 1984, Pushcharovskii *et al.* (1989), Della Ventura *et al.* (2007), this work
Hydroxycancrinite	$P3$	12.74	5.18	1	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$Na_6(OH)_2$**	Nadezhina *et al.* (1991), Khomyakov *et al.* (1992)
Depmeierite	$P6_3$	12.73	5.18	1	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$Na_6(PO_4)_{0.67}(H_2O)$**	Pekov *et al.* (2010)
Kyanoxalite	$P6_3$	12.74	5.21	1	$Si_{6-7}Al_{6-5}O_{24}$	$Na_2(H_2O)_2$	$Na_6(C_2O_4)_{0.5-1}(H_2O)_{3-2}$	Chukanov *et al.* (2009a), this work
Davyne series								
Davyne	$P6_3/m$ or $P6_3$	12.70-12.85	5.33-5.37	1	$Si_6Al_6O_{24}$	Ca_2Cl_2	$(Na,K,Ca)_6(SO_4)_{0.5-1}Cl_{1-0}$	Bonaccorsi *et al*. (1990), Hassan & Grundy (1990), Ballirano *et al.* (1996, 1998), Rozenberg *et al.* (2009), this work
Balliranoite	$P6_3$	12.695	5.325	1	$Si_6Al_6O_{24}$	Ca_2Cl_2	$Na_6(CO_3)$**	Chukanov *et al.* (2010)
Others								
Quadridavyne	$P6_3$	25.77	5.37	4	$Si_6Al_6O_{24}$	Ca_2Cl_2	Na_6Cl_2**	Bonaccorsi *et al*. (1994),
Microsommite	$P6_3/m$	22.14	5.35	3	$Si_6Al_6O_{24}$	Ca_2Cl_2	$Na_4K_2(SO_4)$**	Bonaccorsi *et al*. (2001)
Pitiglianoite	$P6_3$	22.12	5.22	3	$Si_6Al_6O_{24}$	$Na_2(H_2O)_2$	$Na_4K_2(SO_4)$**	Merlino *et al*. (1991)

* Note that for a variety intermediate between cancrinite and hydroxycancrinite, space group *P*3 was reported (Rastsvetaeva *et al*. 2007);
** end-member formula.

TABLE 2. GENERALIZED CHEMICAL DATA (RANGES AND AVERAGED VALUES) FOR CANCRINITE-GROUP MINERALS WITH AN *AB*-TYPE FRAMEWORK

Constituent	Cancrisilite				Cancrinite				Vishnevite				Depmeierite		Kyanoxalite*	
	o.d. (21 anal.)		l.d. (10 anal.)		o.d. (243 anal.)		l.d. (35 anal.)		o.d. (30 anal.)		l.d. (13 anal.)		o.d. (2 anal.)		o.d. (16 anal.)	
	range	av.	range	av.	range	av.	range	av.	range	av.	range	av.	range	av.	range	av.
Na_2O wt.%	14.7 - 23.3	22.1	20.9 - 22.7	21.9	13.7 - 23.7	19.7	9.8 - 23.6	18.4	10.1 - 22.7	17.1	12.4 - 20.8	17.6	19.6 - 23.0	21.3	12.3 - 23.7	18.6
K_2O	0.0 - 0.5	-	0.0 - 0.4	-	0.0 - 1.3	-	0.0 - 1.8	0.6	0.0 - 14.5	6.6	0.7 - 12.8	4.4	0.3 - 0.5	0.4	0.0 - 1.9	1.2
CaO	0.0 - 1.2	0.3	0.0 - 0.8	0.3	0.9 - 10.1	5.3	1.3 - 11.7	5.6	0.0 - 4.8	1.3	0.0 - 3.9	1.4	b.d.l.	-	0.0 - 1.2	0.4
SrO	0.0 - 1.2	0.15			0.0 - 1.7	0.1	0.0 - 2.1	0.8	0.0 - 1.2	-			b.d.l	-	0.0 - 0.6	-
MgO	b.d.l.	-	0.0 - 0.1	-	0.0 - 0.4	-	0.0 - 0.5	0.4	b.d.l.	-	0.0 - 0.3	-	b.d.l.	-	b.d.l.	-
Fe_2O_3	0.0 - 0.4	-	0.1 - 0.5	-	0.0 - 1.1	-	0.0 - 0.8	0.3	0.0 - 0.7	-	0.0 - 1.8	0.4	b.d.l.	-	0.0 - 0.4	-
Al_2O_3	22.8 - 26.0	24.7	22.3 - 27.2	23.9	26.2 - 31.9	28.8	24.6 - 30.0	28.4	25.5 - 29.8	28.1	27.3 - 30.8	29.1	29.1 - 29.4	29.2	26.0 - 28.8	27.3
SiO_2	40.7 - 45.9	43.2	40.4 - 46.0	43.2	32.8 - 45.5	37.6	33.6 - 40.3	36.3	32.1 - 38.6	34.4	33.4 - 37.2	35.2	36.5 - 37.5	36.9	37.0 - 43.2	40.0
P_2O_5	0.0 - 0.6	-			0.0 - 0.5	-	0.0 - 0.2	-	0.0 - 0.4	-			3.3 - 3.8	3.5	0.0 - 2.2	0.3
SO_3	0.0 - 1.2	0.1	0.0 - 0.4	0.1	0.0 - 2.7	0.4	0.0 - 4.7	0.6	4.8 - 8.9	6.9	4.4 - 7.0	6.1	0.0 - 0.2	0.1	0.0 - 1.7	0.7
Cl	b.d.l.	-	0.0 - 0.1	-	0.0 - 1.4	-	0.0 - 0.5	0.1	0.0 - 1.0	0.1	0.0 - 0.4	0.2		-	0.0 - 1.1	0.1
F	b.d.l.	-			b.d.l.	-	0.0 - 0.5	-	b.d.l.	-	0.0 - 0.3	-	b.d.l.	-	b.d.l.	-
CO_2	4.3	4.3	4.0 - 4.8	4.4	3.4 - 4.9	4.0	3.2 - 7.0	5.9			0.0 - 2.16	1.2	1	1	3.2§	3.2§
H_2O	4.6	4.6	5.0 - 5.8	5.4	3.3 - 5.5	4.3	1.5 - 9.3	4.3			2.5 - 8.2	5.7	5.9	5.9	8.4	8.4
Si *apfu*	6.84 - 7.59	7.16	6.66 - 7.63	7.24	6.00 - 6.85	6.29	5.29 - 6.72	6.09	5.93 - 6.46	6.14	5.78 - 6.23	6.03	6.19 - 6.23	6.21	6.50 - 6.96	6.65
Al	4.34 - 5.16	4.84	4.36 - 5.28	4.76	5.15 - 6.00	5.70	5.23 - 6.71	5.87	5.54 - 6.07	5.86	5.73 - 6.13	5.92	5.77 - 5.81	5.79	5.00 - 5.48	5.35
Fe	0.00 - 0.05	-	0.01 - 0.06	-	0.00 - 0.14	-	0.00 - 0.10	0	0.00 - 0.11	-	0.00 - 0.22	0.05	b.d.l.	-	0.00 - 0.04	-
Na	6.21 - 7.48	7.09	6.68 - 7.35	7.11	4.18 - 7.32	6.40	3.32 - 7.83	6.12	3.60 - 7.54	5.74	4.32 - 7.71	5.86	6.32 - 7.58	6.95	4.18 - 7.41	5.97
K	0.00 - 0.11	-	0.00 - 0.08	-	0.00 - 0.23	-	0.00 - 0.38	0.13	0.00 - 3.33	1.65	0.15 - 2.93	0.99	0.07 - 0.12	0.09	0.00 - 0.43	0.25
Ca	0.00 - 0.23	0.05	0.00 - 0.13	0.05	0.16 - 1.83	0.97	0.24 - 2.18	1.03	0.00 - 0.88	0.16	0.00 - 0.70	0.28	b.d.l.	-	0.00 - 0.21	0.06
Sr	0.00 - 0.12	0.01			0.00 - 0.22	0.01	0.00 - 0.22	-	0.00 - 0.12	0.01			b.d.l.	-	0.00 - 0.05	-
Mg	b.d.l.	-			0.00 - 0.11	-	0.00 - 0.13	0	b.d.l.	-	0.00 - 0.08	-	b.d.l.	-	b.d.l.	-
Σe.f.c.		*7.15*		*7.16*		*7.38*		*7.32*		*7.56*		*7.13*		*7.04*		*6.28*
PO_4	0.00 - 0.09	-			0.00 - 0.07	-	0.00 - 0.02	-	0.00 - 0.07	-			0.47 - 0.53	0.49	0.00 - 0.30	0.05
SO_4	0.00 - 0.15	0.01	0.00 - 0.04	0.01	0.00 - 0.36	0.1	0.00 - 0.61	0.12	0.64 - 1.15	0.92	0.56 - 1.31	0.79	0.00 - 0.02	0.00	0.00 - 0.21	0.09
Cl	b.d.l.	-	0.00 - 0.03	-	0.00 - 0.37	-	0.00 - 0.16	0.00	0.00 - 0.29	0.00	0.00 - 0.12	0.04	b.d.l.	-	0.00 - 0.31	0.02
F	b.d.l.	-			b.d.l.	-	0.00 - 0.26	-	b.d.l.	-			b.d.l.	-	b.d.l.	-
CO_3	1.05	1.05	0.91 - 1.10	1.01	1.16 - 1.37	1.26	0.76 - 1.80	1.37			0.00 - 0.50	0.27	0.22	0.22	0.46§	0.46§
OH**	0.2	0.2	0.02 - 0.30	0.16	0.00 - 0.31	0.10	0.00 - 0.20	0.12					0.02	0.02	0.01	0.01
H_2O	2.55	2.55	2.79 - 3.20	2.99	2.30 - 3.01	2.61	1.03 - 5.17	2.35			1.41 - 4.77	3.33	3.35	3.35	4.74	4.74
Al/Si	*0.57 - 0.75*	*0.68*	*0.57 - 0.80*	*0.66*	*0.75 - 1.01*	*0.91*	*0.79 - 1.04*	*0.97*	*0.86 - 1.02*	*0.95*	*0.93 - 1.04*	*0.99*	*0.93 - 0.94*	*0.93*	*0.73 - 0.85*	*0.80*

The chemical data are calculated on the basis of (Si + Al + Fe) = 12 atoms per formula unit (*apfu*). NOTE. Empty cell means that a constituent was not detected (for our analyses) or no data presented (for analyses taken from the literature); dash means that averaged value is less than 0.05 wt.%; b.d.l.: below detection limit (for our analyses); o.d.: our data (including our recently published data: Chukanov *et al*. (2009a, 2010), Pekov *et al*. (2010); *l.d.:* data taken from literature; *Σ e.f.c.*: sum of extra-framework cations; *: including intermediate members of the cancrinite–kyanoxalite series with significant content of $C_2O_4^{2-}$ (as documented with IR spectroscopy data); §: C_2O_3/C_2O_4 instead of CO_2/CO_3; **: calculated from charge balance.

TABLE 2 (cont'd). GENERALIZED CHEMICAL DATA (RANGES AND AVERAGED VALUES) FOR CANCRINITE-GROUP MINERALS WITH AN *AB*-TYPE FRAMEWORK

	Hydroxy-cancrinite	Davyne				Balli-ranoite	Pitiglia-noite		Micro-sommite		Quadri-davyne	
	l.d. (1 anal.)	o.d. (16 anal.) range	av	l.d. (23 anal.) range	av.	o.d. (1 anal.)	l.d. (3 anal.) range	av.	l.d. (8 anal.) range	av.	l.d. (10 anal.) range	av.
Na_2O wt.%	23.4	11.3 - 22.8	13.6	8.0 - 18.3	13.5	13.1	15.4 - 18.7	17.1	8.5 - 12.4	10.3	10.9 - 14.1	11.7
K_2O	0.4	0.3 - 9.1	5.1	0.3 - 8.0	2.7	3.1	6.8 - 9.4	8.4	4.3 - 11.5	7.6	3.4 - 8.0	6.0
CaO	0.9	0.9 - 12.8	10.3	0.6 - 13.8	11.9	12.7	0.0 - 0.1	-	10.1 - 14.7	11.5	9.0- 11.3	9.9
SrO		0.0 - 1.2	0.2	0.0 - 0.2	-	b.d.l.						
MgO	0.2	0.0 - 1.1	-	0.0 - 0.2	-	b.d.l.						
Fe_2O_3		0.0 - 0.9	-			b.d.l.						
Al_2O_3	31.1	26.4 - 34.1	27.7	26.9 - 29.2	27.4	27.3	26.0 - 31.2	28.7	27.5 - 32.1	29.7	27.1 - 28.3	27.7
SiO_2	36.3	31.6 - 40.6	33.4	31.4 - 33.9	32.2	32.4	33.9 - 37.7	35.5	30.7 - 33.0	32.0	32.6 - 33.4	32.9
SO_3		3.3 - 6.7	4.6	0.4 - 8.8	5.2	2	5.6 - 7.6	6.9	1.7 - 7.2	4.7	0.0 - 1.1	0.5
C1		7.9 - 6.4	6.9	5.2 - 11.5	7.7	7.4			6.2 - 9.1	7.4	10.4 - 12.1	10.9
F		b.d.l.	-	0.0 - 0.5	0.2	b.d.l.					0.0 - 0.6	0.2
CO_2	1.6					3.2						
H_2O	5.4					0.2						
Si *apfu*	5.97	5.97 - 6.14	6.06	5.80 - 6.11	5.99	6.02	6.07 - 6.30	6.15	5.43 - 6.03	5.73	5.96 - 6.11	6.02
Al	6.03	5.74 - 5.99	5.94	5.88 - 6.20	6.01	5.98	5.70 - 5.93	5.85	5.97 - 6.57	6.27	5.89 - 6.03	5.98
Fe	0.02	0.00 - 0.12	-			b.d.l.						
Na	7.46	4.07 - 7.19	4.75	2.92 - 5.63	4.89	4.70	5.57 - 5.84	5.72	2.90 - 4.25	3.57	3.77 - 4.91	4.16
K	0.10	0.00 - 2.19	1.2	0.07 - 1.90	0.63	0.73	1.40 - 2.16	1.88	0.94 - 2.62	1.73	0.78 - 1.90	1.40
Ca	0.16	0.15 - 2.46	2.02	1.90 - 2.77	2.37	2.53	0.00 - 0.02	-	2.01 - 2.72	2.20	1.74 - 2.22	1.94
Sr		0.00 - 0.13	0.02			b.d.l.						
Mg		0.00 - 0.32	-			b.d.l.						
Σ e.f.c.	*7.72*		*7.99*		*7.89*	*7.96*		*7.60*		*7.5*		*7.5*
SO_4		0.47 - 0.95	0.63	0.05 - 1.23	0.74	0.27	0.68 - 1.06	0.91	0.23 - 0.98	0.64	0.01 - 0.15	0.06
Cl		0.97 - 2.23	2.13	1.64 - 3.57	2.44	2.34			1.91 - 2.75	2.26	3.18 - 3.76	3.39
F		b.d.l.	-	0.00 - 0.29	0.11	b.d.l.					0.00 - 0.33	0.14
CO_3	0.36					0.82						
OH	1.23					0.00						
H_2O	2.35					0.12						
Al/Si	*1.01*	*0.96 - 1.01*	*0.98*	*0.96 - 1.07*	*1.00*	*0.99*	*1.02 - 1.11*	*0.95*	*0.83 - 1.01*	*1.09*	*0.97 - 1.01*	*0.99*

The chemical data are calculated on the basis of (Si + Al + Fe) = 12 atoms per formula unit (*apfu*). NOTE. Empty cell means that a constituent was not detected (for our analyses) or no data presented (for analyses taken from the literature); dash means that averaged value is less than 0.05 wt.%; b.d.l.: below detection limit (for our analyses); o.d.: our data (including our recently published data: Chukanov *et al*. (2009a, 2010), Pekov *et al*. (2010); *l.d.:* data taken from literature; *Σ e.f.c.*: sum of extra-framework cations.

is 360 (our data and literature data): cancrinite 192 and 35, vishnevite 21 and 13, cancrisilite 19 and 10, kyanoxalite and oxalate-rich intermediate members of the cancrinite–kyanoxalite series 12 and 0, davyne 10 and 23, depmeierite 2 and 0, balliranoite 1 and 0, hydroxycancrinite 0 and 1, quadridavyne 0 and 10, microsommite 0 and 8, and pitiglianoite 0 and 3.

The samples chemically studied by us represent close to 50 localities belonging to three major geological formations. I. Alkaline intrusive and related contact rocks (only members of the cancrinite subgroup): Khibiny, Lovozero, Kovdor, Gremyakha–Vyrmes (Kola Peninsula), Vuoriyarvi (northern Karelia), Ilmeny Mountains, Vishnevye Mountains (southern Urals), Botogol (eastern Sayan, Siberia), Dakhuunur, Ulan–Erge, Pichekhol' (Tyva, Siberia), Murun, Gornoe Ozero (Sakha–Yakutia, Siberia) [all in Russia], Mariupol' complex (Ukraine), Dzhelisu (Kyrgyzstan), Darai–Pioz, Tutek, Tagoby–Sobakh, Rokhshiv–Sobakh, Shahi–Safet (Tadjikistan), Samarkand (Uzbekistan), Kishengarh (India), Dodo (Korea), Tamazeght (Morocco), Langesundsfjord, Tvedalen, Brevik, Sørøya, Mørje (Norway), Loch Borrolan (U.K.), Mont Saint-Hilaire, Bancroft, French River, Ice River, Blue Mountain, Big Spruce Lake, Gooderham, Cancrinite Hill, Nephton (Canada), Bigwood, Litchfield (U.S.A). II. Alkaline volcanic and related contact rocks: Vesuvius – Monte Somma complex in Italy (davyne series), Laacher See in Eifel, Germany (H_2O-poor variety of cancrinite). III. Alkali-rich metamorphic and metasomatic rocks (davyne series): Slyudyanka (Siberia, Russia), Sar-e-Sang (Afghanistan), Mogok (Myanmar), Zabargad (Egypt).

The contents of cations, S and Cl were determined by means of an electron microprobe. The EDS mode was used because of the instability of C- and H_2O-bearing samples and the strong tendency for Na to migrate under the electron beam, even with as low a current as 2–3 nA. A VEGA TS 5130MM electron microscope equipped with an energy-dispersive X-ray microanalyzer with a semiconductor Si(Li) detector INCA Energy was used for the majority of analyses (15.7 kV, 0.5 nA; the beam raster had an area of 16 × 16 mm^2). Both CO_2 and H_2O were determined by selective sorption from gaseous products obtained by heating the mineral at 1080°C in oxygen; for CO_2, we used the askarite sorbent (an asbestiform matter saturated with NaOH), and for H_2O, we used $Mg(ClO_4)_2$. We detected $C_2O_4^{2-}$ by means of anion chromatography.

Descriptions of all studied samples and full quantitative chemical data, both original and from the literature, are presented in the Ph.D. thesis of Olysych (2010). This material is too extensive and cannot be published in the context of this paper; we give here only the summarized results (Table 2, Figs. 2–4). All CGM formulae given in the present paper were calculated on the basis of a sum of framework-forming atoms Si + Al + Fe = 12 atoms per formula unit (*apfu*).

The measured Na content in the majority of electron-probe analyses of CGM (Table 2) can be somewhat lower than in reality because of the above-mentioned strong effect of its migration under the electron beam. This becomes apparent by the somewhat higher Na content determined in CGM from structure-refinement data (Table 3) in comparison with the electron-microprobe data for the same samples.

Structural study

In this paper, we present new structural data for ten samples of carbonate-dominant cancrinite-subgroup minerals that differ one from another in chemical composition and IR spectra: nine are samples of different varieties of cancrinite and one is a sample of cancrisilite. The structures were solved by direct methods and refined using the SHELX–97 package of programs (Sheldrick 2008). Details of the collection of single-crystal X-ray data and the structure refinement, crystal data and structural formulae for the samples studied are given in Table 3. The coordinates and equivalent isotropic displacement parameters of the atoms and selected interatomic distances are presented in Tables 4–7. Tables of structure factors are available from the Depository of Unpublished Data on the MAC website [document Cancrinite CM49_1129].

Chemical Variations

Chemical variations of CGM with an *AB*-type framework are shown in Table 2 and in Figures 2–4. First, we summarize data on the cationic compositions.

1. In the cationic composition diagrams, cancrinite-subgroup minerals form broad fields, including pitiglianoite, dimorphous with the K-rich variety of vishnevite. Members of the davyne series, quadridavyne and microsommite, minerals containing Ca instead of Na in the narrow channel, occupy a separate field (Figs. 2, 3).

2. Each of the cancrinite-subgroup members occupies an individual field in a diagram showing framework composition (Al:Si ratio) and Ca content (Fig. 2). The fields of the various minerals are separate or only insignificantly overlapping.

3. Cancrinite-subgroup minerals with high contents of carbon-bearing extra-framework anions (CO_3^{2-}, $C_2O_4^{2-}$) are characterized by the widest variations in Si:Al ratio: from $Si_{6.0}Al_{6.0}$ to $Si_{7.6}Al_{4.4}$. Other CGM (Olysych 2010) typically show only insignificant deviations from the stoichiometric ratio $Si_{6.0}Al_{6.0}$ ($Si_{6.1}Al_{5.9}$ – $Si_{5.9}Al_{6.1}$). An increase of the Si:Al ratio is typical in the CO_3-bearing variety of vishnevite.

4. Sodium prevails over K or Ca in all samples. Almost Na end-member varieties are typical of all members of the cancrinite subgroup except cancrinite itself, which shows the strongest affinity for Ca in this subgroup. The carbonate-dominant members of

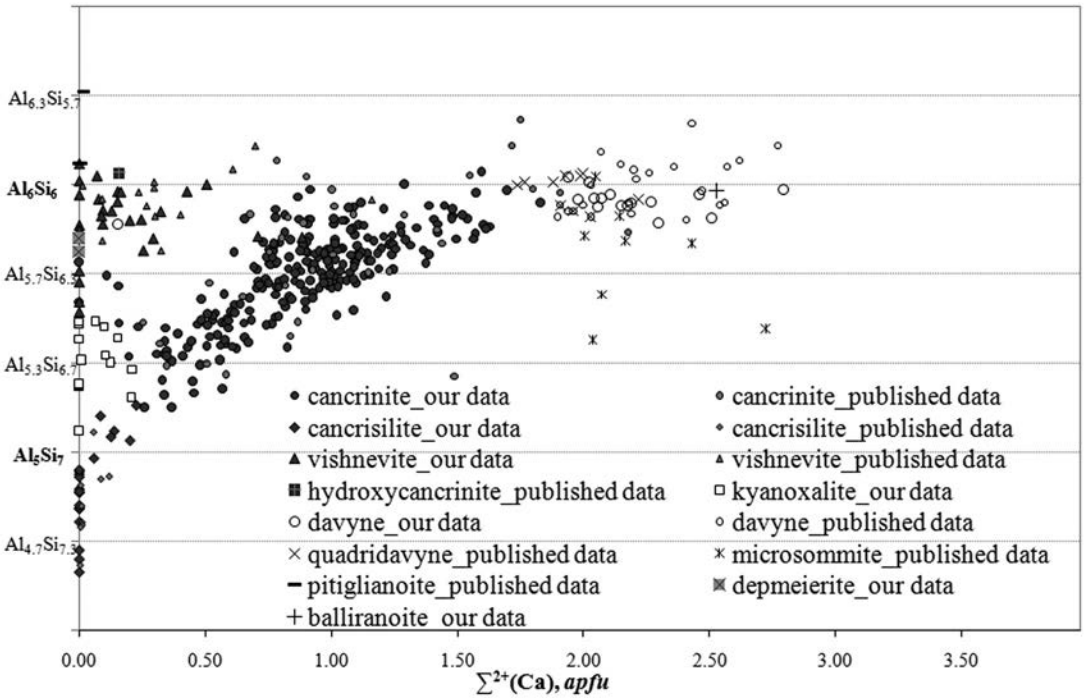

FIG. 2. Correlation between contents of framework atoms (Si, Al) and Ca (*apfu*) in cancrinite-group minerals with an *AB*-type framework.

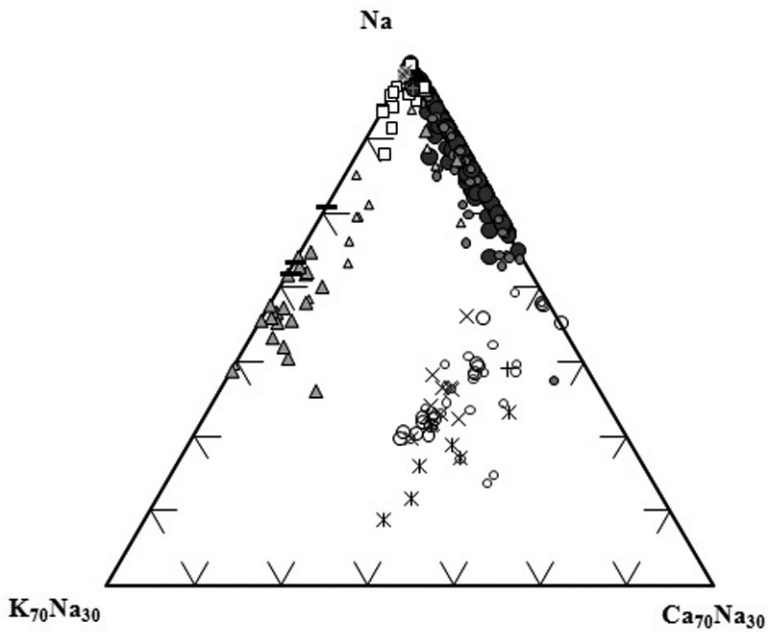

FIG. 3. Ratios of major extra-framework cations (in atom proportions) in cancrinite-group minerals (CGM) with an *AB*-type framework. Legend: see Figure 2.

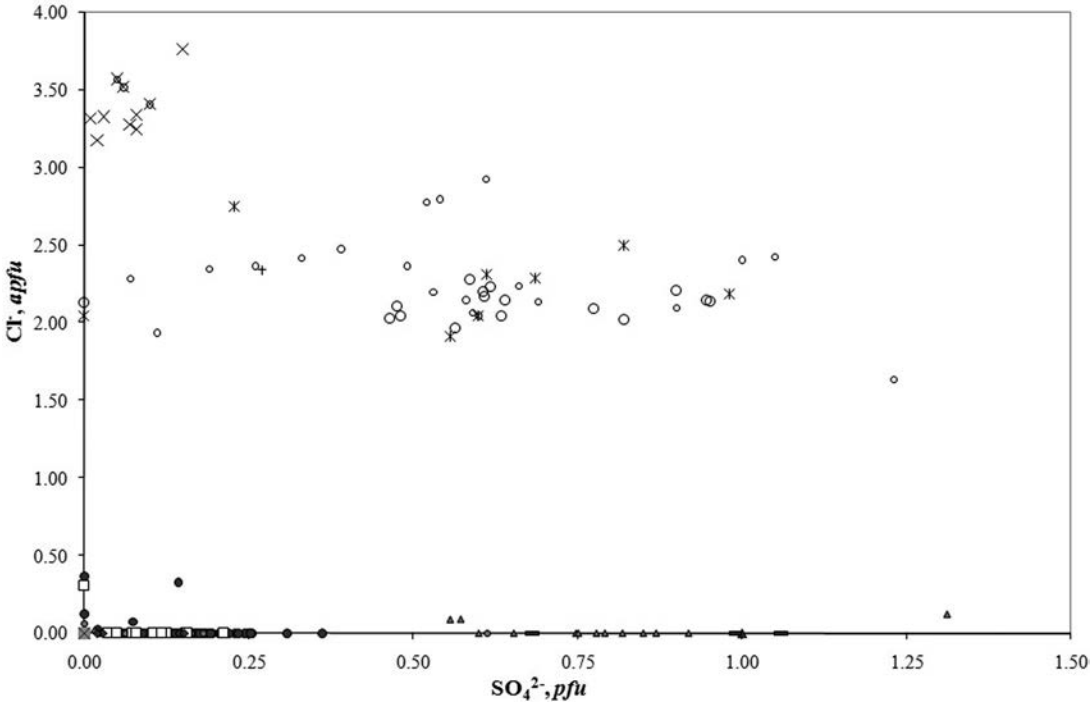

FIG. 4. Correlation between contents of S (SO_4) and Cl (*apfu*) in cancrinite-group minerals with an *AB*-type framework. Legend: see Figure 2.

the subgroup form a continuous solid-solution series with a gradual change in the Na:Ca ratio, from Ca-free varieties of cancrisilite to Ca-rich varieties of cancrinite (Fig. 2).

5. In the cancrinite subgroup, only sulfate-rich minerals show a high affinity for K. Note that K-rich samples of these minerals are Ca-depleted, and *vice versa*. Thus, K and Ca are antipathetic in the members of this subgroup, which is most strikingly illustrated by vishnevite. Other CGM do not show such "antagonism" (Fig. 3).

Figure 4 demonstrates the correlations between S and Cl, the major anions easily determined using routine electron-probe analysis, in CGM with an *AB*-type framework. Sulfur is considered as SO_4. The structural and IR spectroscopic data indicate that the sulfate form strongly prevails in cancrinite-subgroup minerals. The compositions with low contents of both S and Cl mainly correspond to minerals with species-defining C-bearing extra-framework anions.

As one can see from Figure 4 and Table 1, members of the cancrinite subgroup are minerals strongly depleted in Cl (maximum 0.37 *apfu* = 1.2 wt.% Cl; it is very probable that this Cl content is caused by submicroscopic inclusions of sodalite), and the mineral typically is Cl-free. They form two fields with different S contents. One of them corresponds to vishnevite with 0.56–1.15 SO_4 *pfu* (in literature, analyses with SO_4 content up to 1.31 *pfu* were found, but such high values are probably caused by analytical errors: see below). Another field includes S-free samples and those with SO_4 as an impurity anion: for them, no more than 0.36 SO_4 *pfu* is typical. These fields are separate; thus, the cancrinite–vishnevite solid-solution series is probably not continuous as far as the CO_3:SO_4 ratio is concerned.

The field corresponding to the minerals with Cl in the narrow channel, namely members of the davyne series, quadridavyne and microsommite is quite separate in Figure 4 from the field of "common" cancrinite-subgroup minerals.

The sulfate and chlorine–sulfate CGM, unlike the C-bearing members, are characterized by the widest variations of ratios of extra-framework cations (Na, K, Ca) (Figs. 3–4, Table 2): from almost Na-pure vishnevite (Lovozero: our data) to microsommite with $Na_{2.90}K_{2.02}Ca_{2.04}$ (Vesuvius: Zambonini 1935).

The PO_4^{3-} anion turned out as a typical component of cancrinite-subgroup minerals. Before our work, analytical data for only one P-bearing CGM was published: 0.16 wt.% P_2O_5 was reported by Dorfman (1962) for a cancrinite sample from Khibiny. Our data show that P is usual for cancrinite-subgroup minerals

TABLE 3. CRYSTAL DATA, STRUCTURAL FORMULAE, DATA-COLLECTION INFORMATION AND REFINEMENT DETAILS FOR CANCRISILITE (u1631) AND DIFFERENT VARIETIES OF CANCRINITE (OTHER SAMPLES)

Sample no. Locality	Space group	*a*, Å *c*, Å	*V*, Å^3	DM	θ range °	*h,k,l* ranges	Reflections measured/ unique/used [$I > 2\sigma(I)$]	*R*1(*F*) / *wR2**(*F*^{2}) / GoF	Structural formula framework	Structural formula narrow channel wide channel
u1631* Lovozero	$P6_3mc$	12.584(2) 5.101(1)	699.5(2)	1**	3.24-48.41	-24/24, -24/26, -9/8	21816 / 2118 / 1865 (R_{int} = 0.0300)	0.0216 / 0.0469 / 1.063	$Si_{7.4}Al_{4.6}O_{24}$	$Na_2(H_2O)_2$ $Na_{5.4}(CO_3)_{1.4}$
kir2343* Khibiny	$P6_3$	12.607(2) 5.111(1)	703.5(2)	1**	3.23-40.49	-23/23, -23/23, -9/6	20213 / 2630 / 2484 (R_{int} = 0.0207)	0.0224 / 0.0557 / 1.089	$Si_{6.6}Al_{5.4}O_{24}$	$Na_2(H_2O)_2$ $Na_{5.5}Ca_{0.4}(CO_3)_{1.5}$
11/1* Khibiny	$P6_3$	12.618(2) 5.116(1)	705.4(2)	1**	1.86-40.57	-23/23,-23/23, -9/9	20257 / 3004 / 2814 (R_{int} = 0.0241)	0.0242 / 0.0524 / 1.083	$Si_{6.45}Al_{5.55}O_{24}$	$Na_2(H_2O)_2$ $Na_{5.45}Ca_{0.55}(CO_3)_{1.5}$
kovd15/1* Kovdor	$P6_3$	12.683(2) 5.190(1)	723.0(2)	1**	4.34-36.93	-21/13, -20/21, -7/8	18032 / 2402 / 2193 (R_{int} = 0.0244)	0.0276 / 0.0796 / 1.130	$Si_{6.7}Al_{5.3}O_{24}$	$Na_2(H_2O)_2$ $Na_{4.8}K_{0.3}(CO_3)_{0.9}$***
kovd5* Kovdor	$P6_3$	12.606(2) 5.118(1)	704.3(2)	1**	3.23-45.84	-23/25, -23/24, -9/9	21598 / 3682 / 3042 (R_{int} = 0.0272)	0.0280 / 0.0630 / 1.057	$Si_{6.65}Al_{5.35}O_{24}$	$Na_2(H_2O)_2$ $Na_{5.8}Ca_{0.2}(CO_3)_{1.4}$
ggm 44331* Vishnevye Mtns.	$P6_3$	12.627(2) 5.136(1)	709.2(2)	2**	3.23-32.64	-18/18, -18/19, -7/7	22106 / 1675 / 1387 (R_{int} = 0.0651)	0.0413 / 0.0866 / 1.008	$Si_{6.4}Al_{5.6}O_{24}$	$Na_2(H_2O)_2$ $Na_{5.0}Ca_{1.0}(CO_3)_{1.7}$
tz3/1* Tamazeght	$P6_3$	12.625(2) 5.122(1)	707.0(2)	1**	1.86-40.71	-23/18, -17/20, -9/9	17259 / 2513 / 1284 (R_{int} = 0.0904)	0.0565 / 0.1093 / 1.012	$Si_{6.3}Al_{5.7}O_{24}$	$Na_{1.7}(H_2O)_2$ $Na_{4.3}Ca_{1.2}(CO_3)_{1.5}$
tz5/1* Tamazeght	$P6_3$	12.618(2) 5.144(1)	709.3(2)	1**	1.86-40.57	-23/23, -23/23, -9/7	20143 / 2866 / 1699 (R_{int} = 0.1193)	0.0472 / 0.1035 / 1.016	$Si_{6.5}Al_{5.5}O_{24}$	$Na_2(H_2O)_2$ $Na_{4.6}Ca_{0.9}(CO_3)_{1.4}$
mmf 62633/2* Dakhuunur	$P6_3$	12.613(1) 5.124(1)	706.0(2)	2**	3.23-34.85	-20/20, -20/20, -8/8	26160 / 2006 / 1666 (R_{int} = 0.0710)	0.0483 / 0.1149 / 1.029	$Si_{6.2}Al_{5.8}O_{24}$	$Na_{1.6}(H_2O)_2$ $Na_{4.2}Ca_{1.6}(CO_3)_{1.6}$
mmf 28962* Ilmeny Mtns	$P6_3$	12.617(2) 5.129(1)	707.1(2)	2**	3.23-34.91	-20/20, -19/20, -8/8	26734 / 2000 / 1750 (R_{int} = 0.0439)	0.0273 / 0.0628 / 0.965	$Si_{6.2}Al_{5.8}O_{24}$	$Na_{1.8}(H_2O)_2$ $Na_{4.7}Ca_{1.2}(CO_3)_{1.5}$

* u1631 $w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.0489P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * kir2343 $w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 0.1701P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * 11/1 $w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 0.0707P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * kovd15/1 $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.1826P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * kovd5 $w = 1/[\sigma^2(F_o^2) + (0.0310P)^2 + 0.0315P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * ggm44331 $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.00P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * tz3/1 $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.00P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * tz5/1 $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.2396P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * mmf62633/2 $w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.00P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. * mmf28962 $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.00P]$; P = ([max of (0 or F_o^2)] + $2F_c^2$)/3. ** DM (diffractometer): 1: KAPPA APEX II, 2: Xcalibur S CCD; Mo$K\alpha_1$ radiation (λ = 0.71073 Å) was used in both cases; *** from IR data, contains admixture of oxalate groups.

from Lovozero, where depmeierite, a new member of this subgroup with PO_4^{3-} as species-defining extra-framework anion was discovered (Pekov *et al.* 2010). In the members of the cancrinite–kyanoxalite series and in cancrisilite from Lovozero, the concentration of P_2O_5 reaches, respectively, 2.2 wt.% (0.30 *apfu* P) and 0.6 wt.% (0.09 *apfu* P). About 0.2–0.5 wt.% P_2O_5 turns out to be a typical component in cancrinite from many alkaline complexes: Kovdor, Ilmeny Mountains, Vishnevye Mountains, Dakhuunur, Mariupol', Darai–Pioz, Tutek, Shakhi–Safet, Rokhshiv–Sobakh, Langesundsfjord, Mørje, and Bancroft. Vishnevite from the Vishnevye Mountains contains up to 0.4 wt.% P_2O_5.

The oxalate group $C_2O_4^{2-}$ is another extra-framework anion typical of the CGM. Before the discovery of kyanoxalite, the first natural silicate with an additional organic anion (Chukanov *et al.* 2009a), no data on $C_2O_4^{2-}$ in CGM, as well as in other silicate minerals, were known. Here, IR spectroscopy plays a key role in the identification of oxalate anion in these minerals, as is discussed in detail by Chukanov *et al.* (2009a) and Olysych *et al.* (2011). Using the IR data, it was found that oxalate-bearing CGM are widespread in nature: more than half of all samples studied by us contain the C_2O_4 component (Fig. 5). In Lovozero, kyanoxalite is a rock-forming mineral of a specific hydrothermally altered poikilitic urtite-like rock (up to 25 vol.% of a rock), and it is also typical of some naujaite pegmatites. The oxalate-rich intermediate members of the cancrinite–kyanoxalite series are widespread in the

Lovozero, Khibiny and Kovdor alkaline complexes in the Kola Peninsula. In addition to these three complexes, CGM with a minor oxalate component were found by us in the Ilmeny Mountains, Vishnevye Mountains, Vuoriyarvi, Botogol, Gornoe Ozero, Pichekhol', Tutek, Darai–Pioz, Shakhi–Safet, Tamazeght, Bellerberg, Monte Somma, Mørjee, Tvedalen, Sørøya, Litchfield, Gooderham, Mont Saint-Hilaire, and Bancroft (Fig. 5). The presence of C_2O_4 in solid solution is mainly typical of the mineral species cancrinite.

A Brief Summary of the Individual Chemical Features of Major Cancrinite-Subgroup Minerals

Cancrinite

Cancrinite occupies the most extensive field in Figure 2. The Al:Si ratio and the Ca content are the major variable values, whereas the CO_3 content does not vary strongly, and the K impurity is insignificant. Calcium and silicon show a negative correlation. In terms of the Al:Si ratio, the majority of cancrinite compositions are located in the range of $Al_{5.5}Si_{6.5}$–$Al_{6.0}Si_{6.0}$, and in terms of the Ca content, between 0.3 and 1.7 *apfu* (Table 2, Figs. 2–3). In the samples studied by us, the maximum Ca content is 1.83 *apfu*. In the literature, we found one old dataset with 2.18 *apfu* Ca ("unusual cancrinite": Meen 1938), and two samples with a Ca content between 1.8 and 2.0 *apfu* (Fig. 2); it is not excluded that these samples are admixed with calcite. The Ca content in cancrinite is typically no less than 0.16 *apfu*; only the intermediate members of the cancrinite–kyanoxalite and cancrinite–hydroxycancrinite series from Lovozero, Khibiny and Kovdor contain less than 0.1 *apfu* Ca.

Cancrisilite

Cancrisilite is the member of the subgroup (and of the cancrinite group as well) richest in silica: the Al:Si ratio varies from $Si_{7.63}Al_{4.37}$ to $Si_{6.66}Al_{5.34}$. Sodium strongly prevails over other extra-framework cations (6.21–7.48 *apfu*), and some samples from Khibiny contain up to 0.23 *apfu* Ca; the K content is typically not more than 0.01, rarely up to 0.11 *apfu*. Some positive correlation between the Ca content and Al:Si ratio is observed (Table 2, Figs. 2–3).

Vishnevite

Vishnevite shows quite different chemical features. The Al:Si ratio varies from $Si_{5.78}Al_{6.22}$ to $Si_{6.46}Al_{5.54}$, and the Ca content varies from 0 to 0.88 *apfu*. The varieties richest in potassium (up to 3.33 *apfu* K) are Ca-depleted (typically almost Ca-free) samples, whereas the Ca-rich samples contain only insignificant amounts of potassium. Unlike the carbonate members of the subgroup, no correlation between the Al:Si ratio and composition of extra-framework cations is found in vishnevite (Table 2, Figs. 2–3).

TABLE 4. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (U_{eq}, Å^2) OF ATOMS AND SITE-OCCUPANCY FACTORS FOR CANCRISILITE§

Atom	*x*	*y*	*z*	U_{eq}	s.o.f.
			Framework		
$Si_{0.62}Al_{0.38}$	0.079337(12)	0.412136(12)	0.7500	0.00796(4)	1
O(1)	0.20219(4)	-0.20219(4)	0.66167(15)	0.01749(12)	1
O(2)	0.44218(4)	-0.44218(4)	0.72436(19)	0.02156(14)	1
O(3)	0.03638(5)	0.35694(5)	0.05218(11)	0.01725(8)	1
			Narrow channel		
Na	0.3333	0.6667	0.6341(4)	0.0348(5)	0.822(6)
Ow	0.3333	0.6667	0.140(4)	0.059(6)	0.22
Ow'	0.3811(8)	0.6905(4)	0.1913(15)	0.0577(17)	0.26
			Wide channel		
Na'	0.12384(18)	-0.12384(18)	0.3022(12)	0.0248(7)	0.49(3)
Na	0.1219(2)	-0.1219(2)	0.263(2)	0.0259(8)	0.47(3)
C(1)	0.0	0.0	0.6524(13)	0.0253(19)	0.278(7)
OC(1)	0.05911(17)	0.1182(3)	0.6524(13)	0.0335(16)	0.278(7)
C(2)	0.0	0.0	0.9146(11)	0.0248(16)	0.274(6)
OC(2)	0.05926(16)	0.1185(3)	0.9146(11)	0.0311(12)	0.274(6)
C(3)	0.0	0.0	0.7820(14)	0.0128(18)*	0.152(7)
OC(3)	0.0594(3)	0.1189(6)	0.7820(14)	0.0162(13)*	0.152(7)

Ow: oxygen atoms belonging to H_2O molecules, OC: oxygen atoms belonging to CO_3 groups. *: U_{iso}. Interatomic distances (Si,Al)–O in tetrahedra vary from 1.6581(6) to 1.6698(6) Å; the averaged value is 1.6632 Å. § Sample u1631.

TABLE 5. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (U_{eq}, Å^2) OF FRAMEWORK ATOMS IN VARIOUS CANCRINITE-GROUP MINERALS

Sample	Atom*	*x*	*y*	*z*	U_{eq}
kovd15/1	Si	0.33005(3)	0.41291(3)	0.75	0.00910(7)
kovd5		0.328797(17)	0.411271(18)	0.75	0.00758(4)
kir2343		0.328823(18)	0.411280(18)	0.75	0.00725(4)
tz3/1		0.32817(14)	0.41076(13)	0.75	0.0099(3)
tz5/1		0.32849(6)	0.41087(6)	0.75	0.00881(11)
11/1		0.32841(3)	0.41111(2)	0.75	0.00699(4)
mmf28962		0.32795(3)	0.41047(3)	0.75	0.00926(7)
mmf62633/2		0.32770(5)	0.41029(6)	0.75	0.00911(14)
ggm44331		0.32815(5)	0.41088(5)	0.75	0.01027(14)
kovd15/1	$Al_{0.89}Si_{0.11}$	0.07606(3)	0.41389(3)	0.75067(12)	0.00924(7)
kovd5	$Al_{0.89}Si_{0.11}$	0.07557(2)	0.412385(19)	0.75065(7)	0.00764(4)
kir2343	$Al_{0.90}Si_{0.10}$	0.07563(2)	0.41234(2)	0.75076(9)	0.00719(4)
tz3/1	$Al_{0.94}Si_{0.06}$	0.07537(14)	0.41230(13)	0.7511(7)	0.0088(3)
tz5/1	$Al_{0.92}Si_{0.08}$	0.07534(7)	0.41255(6)	0.7509(3)	0.00886(12)
11/1	$Al_{0.93}Si_{0.07}$	0.07525(3)	0.41236(2)	0.75094(10)	0.00723(5)
mmf28962	$Al_{0.97}Si_{0.03}$	0.07506(3)	0.41250(3)	0.75085(10)	0.00954(8)
mmf62633/2	$Al_{0.97}Si_{0.03}$	0.07504(6)	0.41252(6)	0.7511(2)	0.00991(15)
ggm44331	$Al_{0.94}Si_{0.06}$	0.07515(6)	0.41252(6)	0.7510(2)	0.01077(15)
kovd15/1	O(1)	0.20288(10)	0.40452(11)	0.6721(2)	0.0187(2)
kovd5		0.20304(6)	0.40468(7)	0.65957(16)	0.01530(12)
kir2343		0.20311(6)	0.40467(7)	0.65898(18)	0.01472(12)
tz3/1		0.2028(5)	0.4037(2)	0.6579(6)	0.0156(5)
tz5/1		0.20368(18)	0.40528(18)	0.6629(4)	0.0159(3)
11/1		0.20317(8)	0.40479(7)	0.65897(16)	0.01388(12)
mmf28962		0.20308(9)	0.40495(10)	0.6581(2)	0.0166(2)
mmf62633/2		0.20285(17)	0.40426(19)	0.6582(4)	0.0156(4)
ggm44331		0.20301(16)	0.40490(17)	0.6605(4)	0.0172(4)
kovd15/1	O(2)	0.11904(11)	0.56549(9)	0.7268(3)	0.0238(2)
kovd5		0.11582(7)	0.56377(6)	0.72443(19)	0.01919(14)
kir2343		0.11579(7)	0.56374(6)	0.7243(2)	0.01825(15)
tz3/1		0.1132(2)	0.5635(4)	0.7283(7)	0.0221(6)
tz5/1		0.11412(18)	0.56335(18)	0.7283(5)	0.0214(4)
11/1		0.11541(8)	0.56393(8)	0.7249(2)	0.01830(15)
mmf28962		0.11353(10)	0.56358(9)	0.7273(3)	0.0211(2)
mmf62633/2		0.1127(2)	0.56339(17)	0.7281(5)	0.0204(4)
ggm44331		0.11441(18)	0.56360(16)	0.7266(5)	0.0219(4)
kovd15/1	O(3)	0.02646(10)	0.35346(12)	0.0548(2)	0.0194(2)
kovd5		0.03076(6)	0.35266(7)	0.06175(14)	0.01552(11)
kir2343		0.03099(7)	0.35279(7)	0.06220(16)	0.01511(12)
tz3/1		0.0299(4)	0.3502(4)	0.0618(6)	0.0177(9)
tz5/1		0.02878(18)	0.3506(2)	0.0582(4)	0.0171(4)
11/1		0.03040(8)	0.35195(9)	0.06234(15)	0.01469(14)
mmf28962		0.02942(9)	0.34970(10)	0.0598(2)	0.0174(2)
mmf62633/2		0.02932(19)	0.3487(2)	0.0608(4)	0.0162(4)
ggm44331		0.02867(17)	0.34943(18)	0.0600(4)	0.0168(4)
kovd15/1	O(4)	0.32153(11)	0.36118(11)	0.0386(2)	0.0191(2)
kovd5		0.31616(6)	0.36021(7)	0.04513(13)	0.01569(12)
kir2343		0.31617(7)	0.36021(8)	0.04601(16)	0.01547(12)
tz3/1		0.3141(5)	0.3564(4)	0.0443(7)	0.0177(10)
tz5/1		0.31591(19)	0.3576(2)	0.0422(4)	0.0178(4)
11/1		0.31531(8)	0.35986(9)	0.04496(15)	0.01472(15)
mmf28962		0.31396(9)	0.35719(10)	0.0433(2)	0.0168(2)
mmf62633/2		0.31292(19)	0.3565(2)	0.0430(4)	0.0161(4)
ggm44331		0.31430(17)	0.35775(18)	0.0427(4)	0.0177(4)

Values of the Al:Si ratio in Al-dominant sites are given on the basis of electron-microprobe data, taking into account the (Al,Si)–O distances (Table 7).

Kyanoxalite

Kyanoxalite and oxalate-rich intermediate members of the cancrinite–kyanoxalite series form a compact field in Figure 2. They are Na-rich minerals, with the Ca content not higher than 0.21 *apfu* (the varieties transitional to cancrinite) and the K content in the range 0–0.43 *apfu*. The oxalate-rich members of the subgroup are intermediate in Al:Si ratio between cancrisilite and vishnevite: $Si_{6.05}(Al,Fe)_{5.95}$–$Si_{6.96}(Al,Fe)_{5.04}$. Figures 2–3 and IR spectroscopy data (Chukanov *et al*. 2011) show that kyanoxalite forms a solid-solution series with the most Ca-depleted and Si-rich variety of cancrinite, but not with cancrisilite: the IR spectra of the latter do

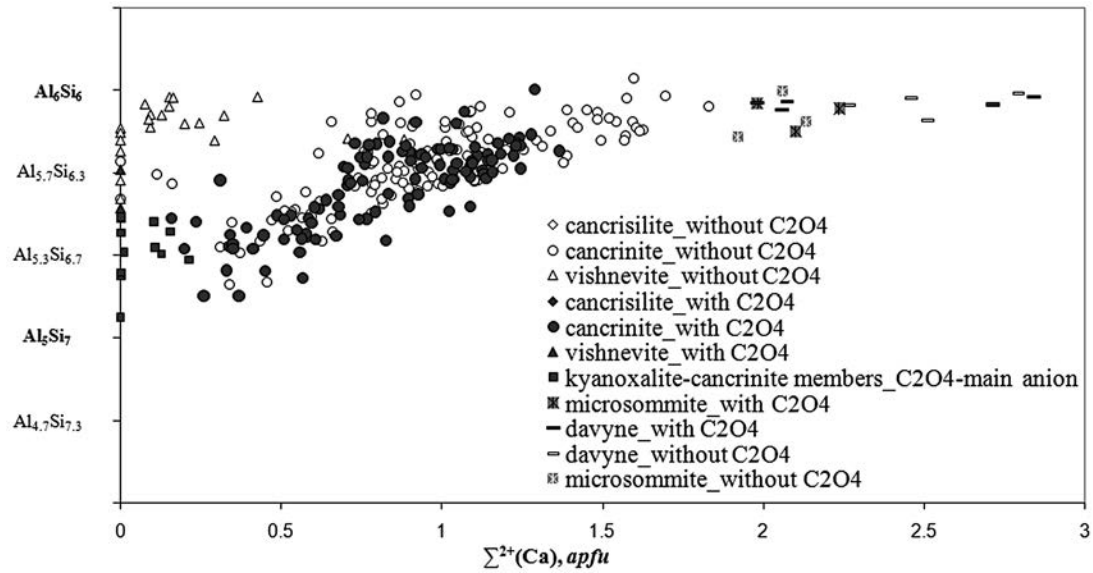

FIG. 5. Distribution of oxalate-bearing varieties of cancrinite-group minerals with an *AB*-type framework.

not contain the intense bands corresponding to oxalate groups.

STRUCTURAL VARIATIONS

The CGM frameworks are subdivided into Al,Si-disordered and Al,Si-ordered ones. All members of the group, except cancrisilite, have Al,Si-ordered frameworks, with alternating tetrahedra and a strong prevalence of Si over Al and Al over Si (Fig. 1, Tables 3, 5, 7). This pattern of order causes the symmetry to be not higher than $P6_3/m$ (its further lowering in CGM with the Al,Si-ordered *AB*-type framework is caused by the distribution of extra-framework constituents).

Cancrisilite has an Al,Si-disordered framework, which leads to space group $P6_3mc$. Such disorder seems to be the diagnostic criterion defining cancrisilite as an individual mineral species: in its structure, unlike all other CGM, Al-dominant sites are absent. The Al,Si-disorder, discovered first for CGM in the holotype specimen of cancrisilite (Khomyakov *et al*. 1991a, 1991b), has been confirmed by us in another sample of this mineral (u1631: Tables 3–4).

Figure 1 shows the crystal structure of cancrinite from its type locality, Ilmeny Mountains in the southern Urals, Russia, studied by us (sample mmf28962): it is characterized by an Al,Si-ordered framework typical of the species.

Variability in the extra-framework components is very significant for cancrinite-subgroup minerals. This is the main topic of the present section, especially taking into account that this aspect of the crystal chemistry of these minerals was discussed insufficiently earlier, and some of their chemical and structural varieties are first being described here.

The narrow channel in cancrinite-subgroup minerals hosts Na^+ and H_2O. The H_2O molecules are typically shifted from the three-fold axis (Table 6, Figs. 1, 6c–f). Cancrisilite (Khomyakov *et al*. 1991a; our data: Table 4), depmeierite (Pekov *et al*. 2010) and the intermediate member of the cancrinite–hydroxycancrinite series (Rastsvetaeva *et al*. 2007) show splitting of the H_2O site: one of the subsites is located on the three-fold axis, whereas another subsite is shifted away it (Fig. 6f). The amount of H_2O in the narrow channel of cancrinite-subgroup minerals is typically close to the maximum: $(H_2O)_2$ *pfu*. Only a new, unusual variety of cancrinite, found by us in alkaline volcanic rocks at Laacher See, is H_2O-poor. This was initially determined from its IR spectrum; further structural study showed that the composition of narrow channel content is $[Na_{1.90}(H_2O)_{0.18}]$ *pfu*: Fig. 6e (Chukanov *et al*. 2009b).

Sodium atoms in the narrow channel are located on the three-fold axis. The amount of sodium is usually close to the maximum possible: 2 *apfu*; the lowest value found is 1.6 *apfu* (Tables 1, 3–4, 6). Typically, we see a single Na site (Figs. 6c, f); in some cases, it is split into two subsites (mmf28962: Fig. 6d), and only in the above-mentioned H_2O-poor cancrinite from Laacher See (Chukanov *et al*. 2009b) is the Na site split into three subsites (Fig. 6e), which is probably caused by a strong predominance of a vacancy at the H_2O site and, thus, appearance of an additional degree of freedom for Na along the **c** axis.

TABLE 6. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (U_{eq}, Å^2) OF EXTRA-FRAMEWORK ATOMS AND THEIR SITE-OCCUPANCY FACTORS FOR VARIOUS CANCRINITE-GROUP MINERALS

Sample	Atom	*x*	*y*	*z*	U_{eq}	s.o.f.
			Narrow channel			
kovd15/1	Na	0.6667	0.3333	0.1270(4)	0.0346(4)	1.00
kovd5	Na	0.6667	0.3333	0.1315(3)	0.0299(2)	1.00
kir2343	Na	0.6667	0.3333	0.1308(3)	0.0299(2)	1.00
tz3/1	Na	0.6667	0.3333	0.1353(9)	0.0370(13)	0.845(11)
tz5/1	Na	0.6667	0.3333	0.1311(7)	0.0422(6)	1.00
11/1	Na	0.6667	0.3333	0.1323(3)	0.0288(2)	1.00
mmf28962	Na	0.6667	0.3333	0.124(2)	0.0343(19)	0.705(8)
	Na'	0.6667	0.3333	0.187(7)	0.026(7)	0.18
mmf62633/2	Na	0.6667	0.3333	0.1380(10)	0.0382(12)	0.815(12)
ggm44331	Na	0.6667	0.3333	0.1345(6)	0.0374(6)	1.00
kovd15/1		0.6980(8)	0.3874(7)	0.6897(12)	0.0582(17)	
kovd5		0.6873(6)	0.3015(6)	0.6848(8)	0.0562(11)	
kir2343		0.6143(5)	0.3129(7)	0.6849(10)	0.0570(13)	
tz3/1		0.695(6)	0.3756(13)	0.684(2)	0.061(8)	
tz5/1	Ow	0.697(3)	0.378(2)	0.6905(18)	0.073(8)	0.33
11/1		0.6157(4)	0.3146(9)	0.6852(8)	0.0534(12)	
mmf28962		0.6849(16)	0.3068(15)	0.6857(13)	0.066(2)	
mmf62633/2		0.691(3)	0.3741(10)	0.679(3)	0.061(4)	
ggm44331		0.686(3)	0.303(2)	0.6892(18)	0.064(3)	
			Wide channel			
kovd15/1	*A*	0.13129(11)	0.26535(15)	0.2863(2)	0.0522(5)	$Na_{0.81}K_{0.05}$
kovd5	*A'*	0.1249(3)	0.2525(2)	0.2972(7)	0.0254(4)	$Na_{0.62}Ca_{0.02}$
	A	0.1194(4)	0.2418(4)	0.2672(12)	0.0279(10)	$Na_{0.35}Ca_{0.01}$
kir2343	*A'*	0.1236(3)	0.2504(3)	0.2992(8)	0.0230(4)	$Na_{0.57}Ca_{0.05}$
	A	0.1195(5)	0.2410(4)	0.2677(13)	0.0259(10)	$Na_{0.34}Ca_{0.02}$
tz3/1	*A*	0.1230(3)	0.24943(11)	0.2944(5)	0.0269(4)	$Na_{0.77}Ca_{0.20}$
tz5/1	*A*	0.12555(11)	0.25371(11)	0.2955(3)	0.0295(3)	$Na_{0.77}Ca_{0.15}$
11/1	*A'*	0.1248(5)	0.2525(4)	0.2996(8)	0.0209(5)	$Na_{0.55}Ca_{0.05}$
	A	0.1190(8)	0.2411(7)	0.276(2)	0.0263(10)	$Na_{0.35}Ca_{0.04}$
mmf28962	*A*	0.12273(18)	0.24770(19)	0.2913(5)	0.0253(4)	$Na_{0.64}Ca_{0.16}$
	A'	0.1320(10)	0.2699(9)	0.2998(17)	0.038(3)	$Na_{0.15}Ca_{0.04}$
mmf62633/2	*A*	0.12252(11)	0.24759(9)	0.2959(3)	0.0222(3)	$Na_{0.64}Ca_{0.25}$
	A'	0.1424(16)	0.2866(14)	0.288(4)	0.0222(3)	$Na_{0.06}Ca_{0.02}$
ggm44331	*A*	0.1223(5)	0.2452(5)	0.2867(16)	0.0241(12)	$Na_{0.44}Ca_{0.10}$
	A'	0.1269(8)	0.2601(8)	0.301(2)	0.040(2)	$Na_{0.39}Ca_{0.07}$
kovd15/1		0.0	0.0	0.679(2)	0.039(5)*	0.171(10)
kovd5		0.0	0.0	0.644(4)	0.036(4)	0.32(2)
kir2343		0.0	0.0	0.6399(8)	0.0215(13)*	0.289(6)
tz3/1		0.0	0.0	0.669(3)	0.040(6)	0.402(18)
tz5/1	C(1)	0.0	0.0	0.644(2)	0.019(4)*	0.289(13)
11/1		0.0	0.0	0.660(2)	0.0177(17)*	0.225(11)
mmf28962		0.0	0.0	0.715(4)	0.021(3)*	0.211(14)
mmf62633/2		0.0	0.0	0.6751(18)	0.044(5)	0.432(14)
ggm44331		0.0	0.0	0.692(5)	0.016(7)*	0.19(3)
kovd15/1		0.0540(13)	0.1141(12)	0.679(2)	0.055(5)*	0.171(10)
kovd5		0.0575(6)	0.1180(6)	0.644(4)	0.043(3)	0.32(2)
kir2343		0.0579(3)	0.1182(3)	0.6399(8)	0.0233(9)*	0.289(6)
tz3/1		0.0559(19)	0.1178(9)	0.669(3)	0.046(5)	0.402(18)
tz5/1	OC(1)	0.0575(9)	0.1178(8)	0.644(2)	0.024(3)*	0.289(13)
11/1		0.0577(5)	0.1187(4)	0.660(2)	0.0163(13)*	0.225(11)
mmf28962		0.0575(5)	0.1202(5)	0.715(4)	0.022(2)*	0.211(14)
mmf62633/2		0.0578(6)	0.1186(6)	0.6751(18)	0.046(4)	0.432(14)
ggm44331		0.0574(12)	0.1194(12)	0.692(5)	0.010(5)*	0.19(3)

TABLE 6 (cont'd). FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (U_{eq}, Å^2) OF EXTRA-FRAMEWORK ATOMS AND THEIR SITE-OCCUPANCY FACTORS FOR VARIOUS CANCRINITE-GROUP MINERALS

Sample	Atom	*x*	*y*	*z*	U_{eq}	s.o.f.
kovd15/1		0.0	0.0	0.889(3)	0.038(6)*	0.169(11)
kovd5		0.0	0.0	0.9054(15)	0.0223(18)	0.252(6)
kir2343		0.0	0.0	0.9089(7)	0.0146(11)*	0.251(5)
tz3/1		0.0	0.0	0.899(4)	0.059(12)	0.365(18)
tz5/1	C(2)	0.0	0.0	0.936(3)	0.029(5)*	0.272(10)
11/1		0.0	0.0	0.9029(8)	0.0198(17)*	0.247(4)
mmf28962		0.0	0.0	0.944(3)	0.011(3)*	0.185(12)
mmf62633/2		0.0	0.0	0.912(2)	0.038(6)	0.373(14)
ggm44331		0.0	0.0	0.935(3)	0.012(5)*	0.216(15)
kovd15/1		0.0344(19)	0.1142(17)	0.889(3)	0.080(7)*	0.169(11)
kovd5		0.0576(4)	0.1179(4)	0.9054(15)	0.0317(14)	0.252(6)
kir2343		0.0580(4)	0.1178(4)	0.9089(7)	0.0225(9)*	0.251(5)
tz3/1		0.059(2)	0.1194(9)	0.899(4)	0.056(6)	0.365(18)
tz5/1	OC(2)	0.0522(16)	0.1168(13)	0.936(3)	0.067(5)*	0.272(10)
11/1		0.0577(5)	0.1185(4)	0.9029(8)	0.0262(12)*	0.247(4)
mmf28962		0.0575(7)	0.1165(6)	0.944(3)	0.026(3)*	0.185(12)
mmf62633/2		0.0590(7)	0.1185(7)	0.912(2)	0.044(3)	0.373(14)
ggm44331		0.0603(12)	0.1155(12)	0.935(3)	0.034(5)*	0.216(15)
kovd15/1		0.0	0.0	0.516(3)	0.024(5)*	0.097(8)
kovd5		-	-	-	-	-
kir2343		-	-	-	-	-
tz3/1		-	-	-	-	-
tz5/1	C(3)	-	-	-	-	-
11/1		0.0	0.0	0.581(4)	0.007(3)*	0.092(10)
mmf28962		0.0000	0.0000	0.626(3)	0.024(3)*	0.225(16)
mmf62633/2		-	-	-	-	-
ggm44331		0.0	0.0	0.611(8)	0.023(6)*	0.21(3)
kovd15/1		0.1005(10)	0.0051(10)	0.516(3)	0.034(5)*	0.097(8)
kovd5		-	-	-	-	-
kir2343		-	-	-	-	-
tz3/1		-	-	-	-	-
tz5/1	OC(3)	-	-	-	-	-
11/1		0.0566(12)	0.1145(9)	0.581(4)	0.016(3)*	0.092(10)
mmf28962		0.0572(6)	0.1172(6)	0.626(3)	0.024(2)*	0.225(16)
mmf62633/2		-	-	-	-	-
ggm44331		0.0541(15)	0.1138(15)	0.611(8)	0.034(5)*	0.21(3)
kovd15/1		-	-	-	-	-
kovd5		0.0	0.0	0.758(4)	0.010(3)	0.15(2)
kir2343		0.0	0.0	0.7583(11)	0.0111(11)*	0.196(5)
tz3/1		-	-	-	-	-
tz5/1	C(4)	0.0	0.0	0.762(4)	0.016(5)	0.160(14)
11/1		0.0	0.0	0.7581(15)	0.0108(16)*	0.172(7)
mmf28962		0.0	0.0	0.844(4)	0.006(3)*	0.150(11)
mmf62633/2		-	-	-	-	-
ggm44331		0.0	0.0	0.810(6)	0.018(6)*	0.234(19)
kovd15/1		-	-	-	-	-
kovd5		0.0570(8)	0.1171(8)	0.758(4)	0.024(4)	0.15(2)
kir2343		0.0580(3)	0.1188(3)	0.7583(11)	0.0175(10)*	0.196(5)
tz3/1		-	-	-	-	-
tz5/1	OC(4)	0.0589(13)	0.1170(12)	0.762(4)	0.024(4)*	0.160(14)
11/1		0.0567(5)	0.1186(4)	0.7581(15)	0.0176(14)*	0.172(7)
mmf28962		0.0587(9)	0.1192(9)	0.844(4)	0.025(3)*	0.150(11)
mmf62633/2		-	-	-	-	-
ggm44331		0.060(2)	0.123(2)	0.810(6)	0.071(7)*	0.234(19)

Ow: oxygen atoms belonging to H_2O molecules, OC: oxygen atoms belonging to CO_3 groups. *: U_{iso}.

TABLE 7. INTERATOMIC DISTANCES (MINIMUM, MAXIMUM, AVERAGED, Å) IN TETRAHEDRA FOR VARIOUS CANCRINITE-GROUP MINERALS

Sample	Si,Al	Si-O_{min}	Si-O_{max}	Si-O_{av}	(Al,Si)-O_{min}	(Al,Si)-O_{max}	(Al,Si)-O_{av}
kovd15/1	$Si_{6.7}Al_{5.3}$	1.6088(11)	1.6202(11)	1.615	1.7200(11)	1.7372(11)	1.727
kovd5	$Si_{6.65}Al_{5.35}$	1.6116(7)	1.6208(7)	1.6159	1.7173(7)	1.7386(7)	1.7271
kir2343	$Si_{6.6}Al_{5.4}$	1.6116(7)	1.6205(8)	1.6165	1.7180(7)	1.7356(8)	1.7265
tz3/1	$Si_{6.3}Al_{5.7}$	1.601(5)	1.629(4)	1.615	1.724(5)	1.740(4)	1.734
tz5/1	$Si_{6.5}Al_{5.5}$	1.604(2)	1.622(2)	1.613	1.715(2)	1.738(2)	1.728
11/1	$Si_{6.45}Al_{5.55}$	1.6103(9)	1.6195(8)	1.614	1.7213(10)	1.7447(8)	1.732
mmf28962	$Si_{6.2}Al_{5.8}$	1.6048(9)	1.6230(10)	1.615	1.7200(10)	1.7468(11)	1.734
mmf62633/2	$Si_{6.2}Al_{5.8}$	1.6019(18)	1.621(2)	1.613	1.7195(19)	1.753(2)	1.737
ggm44331	$Si_{6.4}Al_{5.6}$	1.6092(17)	1.6203(19)	1.615	1.7189(17)	1.751(2)	1.735

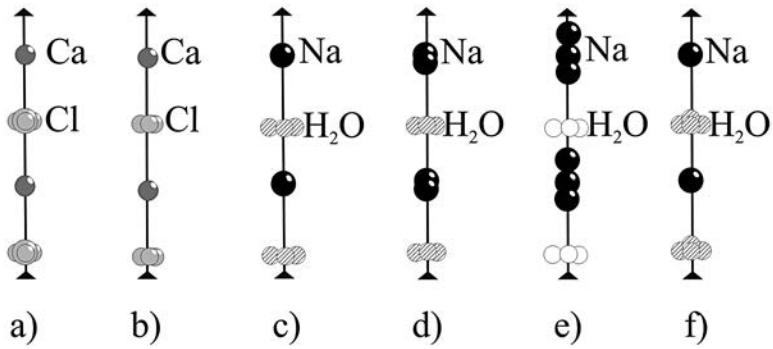

FIG. 6. Contents of the narrow channel in cancrinite-group minerals with an *AB*-type framework: a: balliranoite, b: davyne, c–e: different varieties of cancrinite, f: cancrisilite. Sources: a: Chukanov *et al.* (2010), b: Bonaccorsi *et al.* (1990), e: Chukanov *et al.* (2009b), others: this work (samples: c: kovd15/1, d: mmf28962, f: u1631).

Davyne-series minerals contain the $[\cdots Ca\cdots Cl\cdots]^{\infty}$ chains in the narrow channel. Calcium atoms are located on the three-fold axis, whereas Cl atoms occupy the sites on the axis or can be shifted away from it (Figs. 6a, b; Bonaccorsi *et al.* 1990, Hassan & Grundy 1990, Ballirano *et al.* 1996, 1998, Rozenberg *et al.* 2009, Chukanov *et al.* 2010).

The wide channel in CGM with an *AB*-type framework hosts the most diverse constituents: cations (Na^+, K^+, Ca^{2+}), anions (CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-, $C_2O_4^{2-}$, PO_4^{3-}) and, in some cases, additional H_2O molecules. The anions are located on the axis of the channel, cations are situated between these anions and walls of the channel (Figs. 1, 7); the H_2O molecules (if they are present) can occupy sites both on the axis and near it. The increase of the *a* parameter of the unit cell in pitiglianoite, microsommite and quadridavyne (Table 1) is caused by the distribution of components in the wide channel (Merlino *et al.* 1991, Bonaccorsi *et al.* 1994, 2001).

In some cases, cations in the wide channel occupy a single site [*A*], *e.g.* in depmeierite (Pekov *et al.* 2010) and in some varieties of cancrinite (samples tz3/1 and tz5/1: Table 6) and vishnevite [Hassan & Grundy (1984): Figures 7b, e–g, k, l]. However, for the majority of samples, splitting of this site into two subsites [*A*] (closer to the axis of the channel) and [*A'*] is typical (Table 6, Figs. 1, 7a, c–d, h–j). In Table 6, compositions of these subsites are given as mixed Na + Ca in proportions obtained from electron-microprobe data: it seems impossible to determine the ratio correctly because both subsites have significant vacancies. If a mineral contains much K as the largest extra-framework cation, then this is mainly concentrated in the [*A'*] sites (*e.g.*, vishnevite: Pushcharovskii *et al.* 1989, Della Ventura *et al.* 2007). The maximum possible amount of cations in the wide channel is 6 *apfu*; their real content is, from structural data, not less than 5 *apfu*.

Anions in the wide channel of CGM with an *AB*-type framework display different geometries (Fig. 7): triangular (CO_3^{2-}), tetrahedral (SO_4^{2-}, PO_4^{3-}), dumbbell-like

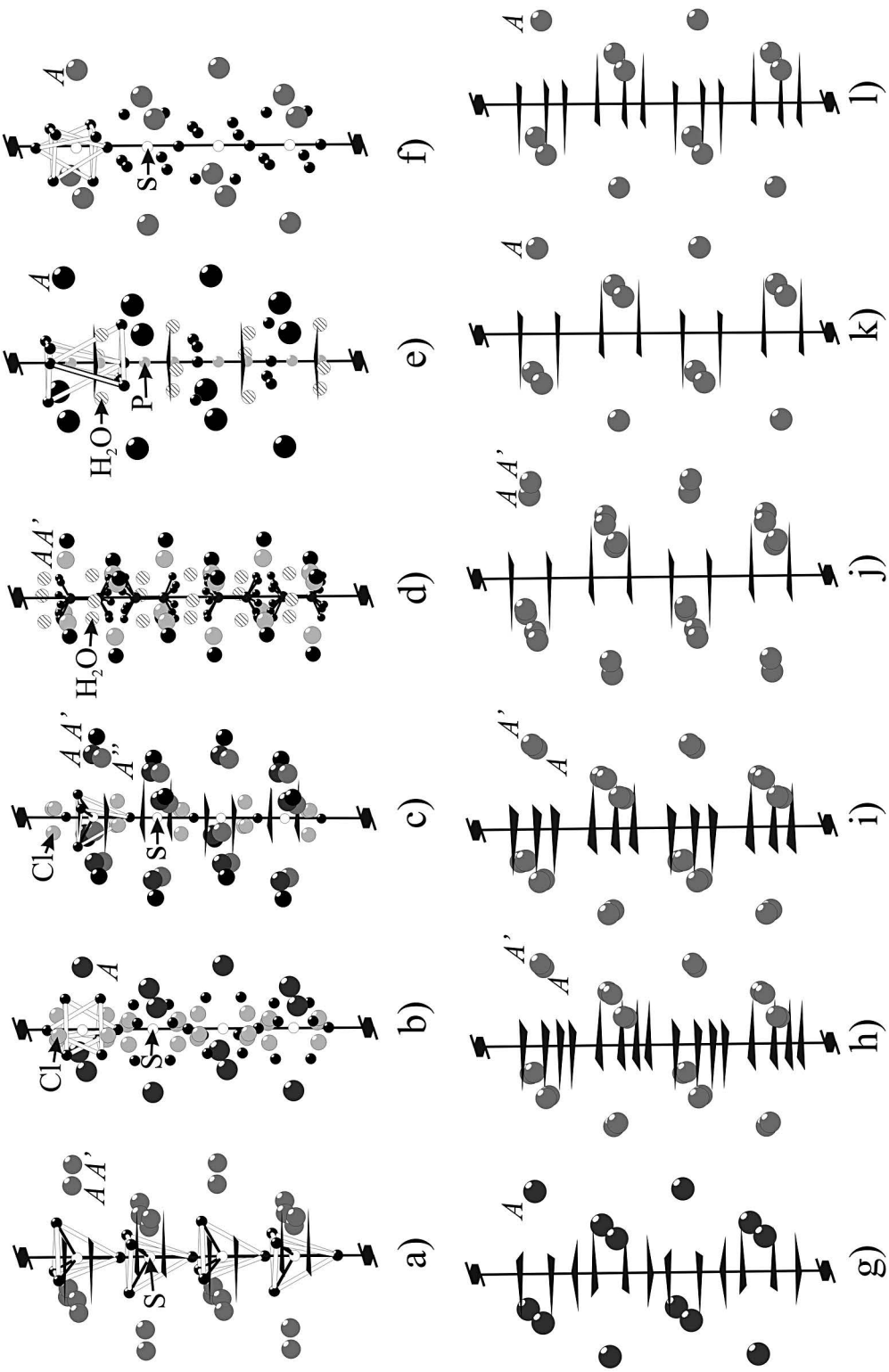

FIG. 7. Contents of the wide channel in cancrinite-group minerals with an *AB*-type framework: a,c: balliranoite, b: davyne, d: kyanoxalite, e: depmeierite, f: vishnevite, g–l: different varieties of cancrinite. Sources: a: Chukanov *et al.* (2010), b: Bonaccorsi *et al.* (1990), c: Ballirano *et al.* (1998), d: Chukanov *et al.* (2009a), e: Pekov *et al.* (2010), f: Hassan & Grundy (1984), others: this work (samples g: kovd15/1, h: 11/1, i: kovd5, j: mmf62633/2, k: tz3/1, l: tz5/1).

($C_2O_4^{2-}$), linear (OH^-), or "point" (Cl^-). Flat-triangular groups CO_3^{2-} or "point" anions Cl^- can be present in one unit cell (or, more exactly, in the corresponding fragment of the wide channel) in an amount not more than 2 *pfu*. For larger (elongate along *z*) anions, such as SO_4^{2-}, PO_4^{3-} or $C_2O_4^{2-}$, they seem rather unlikely to be present in an amount exceeding one per unit cell (= *pfu*). However, they can be combined with CO_3^{2-} or Cl^-, as it is typical for davyne-series members (Ballirano *et al.* 1996, Rozenberg *et al.* 2009, Chukanov *et al.* 2010), and in this case, the general amount of anions in the wide channel can also reach 2 *pfu*. The anion sites in the wide channel of CGM with an *AB*-type framework, unlike the cation sites, are significantly vacant in many cases.

Various anions can be ordered in the wide channel or substitute one for another. The first case is illustrated by the separation of SO_4^{2-} and CO_3^{2-} in balliranoite [Chukanov *et al.* (2010): Fig. 7a]. Depmeierite, with two independent phosphorus sites (Pekov *et al.* 2010), offers another example: the P(1) site is occupied by P and C together, whereas P(2) contains P atoms only (Fig. 7e).

Only one (Kozu & Takane 1933) or two positions of CO_3 groups were earlier reported for cancrinite and cancrisilite (Grundy & Hassan 1982, Khomyakov *et al.* 1991a, Ballirano & Maras 2004, Hassan *et al.* 2006). Our data show that the number of positions of CO_3 groups in the wide channel of carbonate members of the cancrinite subgroup varies from two to four (Table 6, Figs. 7a, g–l). The character of distribution of CO_3 groups and the number of their positions strongly influences the IR spectrum of cancrinite (Chukanov *et al.* 2011).

From our structural data, it can be seen that cancrinite is characterized by a relatively stable content of carbonate anions: $(CO_3)_{1.4–1.7}$ *pfu* (Tables 3, 6). The data published by other authors correspond to the same range: $(CO_3)_{1.5}$ (Grundy & Hassan 1982), $(CO_3)_{1.425}$ (Ballirano & Maras 2004), $(CO_3)_{1.44–1.52}$ (Hassan *et al.* 2006). The only exceptions are the varieties of cancrinite transitional to hydroxycancrinite (Rastsvetaeva *et al.* 2007) and to kyanoxalite (Rozenberg *et al.* 2009, our data: kovd5: Table 3) with the substitutions $2(OH)^- \rightarrow CO_3^{2-}$ and $C_2O_4^{2-} \rightarrow CO_3^{2-}$, respectively, that cause a decrease in the CO_3 content to 1.0–0.9 *pfu*.

In the kyanoxalite structure, the dumbbell–like groups C_2O_4 statistically occupy two positions. Twelve (6 + 6) maxima of electron density instead of four (2 + 2) were found for O atoms belonging to each C_2O_4 group (Fig. 7d). This situation is probably caused by the location of the oxalate group in three preferred orientations (Chukanov *et al.* 2009a).

In kyanoxalite and depmeierite, in addition to cations and anions, the wide channel hosts also H_2O molecules: 3 and 1 *pfu*, respectively (Chukanov *et al.* 2009a, Pekov *et al.* 2010). The presence of 1 H_2O *pfu* in the wide channel was also reported for the original cancrisilite with 1.2 CO_3 *pfu* (Khomyakov *et al.* 1991a, 1991b). In our cancrisilite sample (u1631 with 1.4 CO_3 *pfu*), no H_2O was found in the wide channel (Tables 3–4). In general, the H_2O content in the wide channel of CGM with an *AB*-type framework shows a negative correlation with the total amount of extra-framework anions located there.

Discussion

The chemical and structural data for cancrinite reviewed above show that the commonly quoted idealized formula $Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_2{\cdot}nH_2O$ does not correspond to the overwhelming majority of compositions as far as the Na:Ca ratio and the CO_3 content are concerned. Using all these data, we report here a refined definition of the idealized formula of cancrinite.

A wide compositional range (Figs. 2–3) caused by a complicated system of coupled heterovalent substitutions, first $Na^+ \leftrightarrow Ca^{2+}$, $Si^{4+} \leftrightarrow Al^{3+}$ and $CO_3^{2-} \leftrightarrow (\square,H_2O)^0$, prevents the presentation of the idealized formula of cancrinite using a single end-member. Figure 2 and Tables 2–3 show that the mineral species called cancrinite occupies the compositional field limited by three formal end-members with the following formulae (with whole-number coefficients): $Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_2{\bullet}nH_2O$ – $Na_7[Al_5Si_7O_{24}](CO_3){\bullet}nH_2O$ – $Na_8[Al_6Si_6O_{24}](CO_3){\bullet}nH_2O$. In its generalized form, the cancrinite formula could be presented as follows: $(Na_{8-x-y}Ca_x\square_y)[Al_{6-z}Si_{6+z}O_{24}](CO_3)_{1-2}{\cdot}nH_2O$, where $x = 0–2$, $y = 0–1$, $z = 0–1$, and $n = 0–3$, or, taking into account the distribution of extra-framework components in the narrow and the wide channels: $[Al_{6-z}Si_{6+z}O_{24}][Na_2(H_2O)_{0-2}][(Na_{6-x-y}Ca_x\square_y)(CO_3)_{1-2}(H_2O)_{1-0}]$.

The average of the $Ca_{0.3–1.7}$ range corresponds to 1.0 *apfu* Ca. This is also close to the averaged Ca content for all 278 analytical datasets involved in Table 2. Chemical data for cancrinite show that the CO_3 content rarely exceeds 1.5 *pfu*. Independently obtained from the results of all known structural studies, the data show that the amount of CO_3 groups in cancrinite varies from 1.4 to 1.7 *pfu*. Thus, the most adequate idealized formula for cancrinite seems a "middle-member" formula corresponding to the midpoint, in terms of extra-framework components, of the above-discussed compositional field: $Na_7Ca[Al_6Si_6O_{24}](CO_3)_{1.5}{\bullet}2H_2O$.

The transition from the Al,Si-ordered framework to the Al,Si-disordered one in the series of carbonate members of the cancrinite subgroup (*i.e.*, the transition from cancrinite to cancrisilite) probably occurs over a threshold value of the Si:Al ratio. Our IR data (Chukanov *et al.* 2011) show that cancrinite and cancrisilite are dimorphs in the compositional range $Al_{5.15–5.3}Si_{6.7–6.85}$ (Fig. 2). From structural data, contents of Na and CO_3 in cancrisilite are 7.4 and 1.4 *pfu* (Table 3), respectively, which exceeds the "ideal" values: 7 and 1. It is a sign that the mineral species cancrisilite is in fact a solid-solution series, like

cancrinite. In terms of extra-framework components, this series can be presented as follows: $Na_7[Al_5Si_7O_{24}](CO_3)\bullet 2–3H_2O – Na_8[Al_5Si_7O_{24}](CO_3)_{1.5}\bullet 2H_2O$.

Figure 3 shows two chemical varieties of vishnevite: one is K-rich (the most common in nature) and the other, K-poor. They do not form a continuous series: the K-rich variety contains not less than 0.9 *apfu* K, whereas the K-poor one, not more than 0.3 *apfu* K. Only the latter has an affinity to Ca and shows a tendency to form a solid-solution series (non-continuous in part of extra-framework anions: see above) with cancrinite. This phenomenon is obviously caused by crystal-chemical reasons. In the Vishnevye Mountains, we have found a paragenesis of cancrinite and vishnevite with different compositions of extra-framework cations: cancrinite contains 4.3–6.8 wt.% CaO (=0.8–1.2 *apfu* Ca) and is K-depleted (0.0–0.4% K_2O = 0–0.12 *apfu* K), whereas vishnevite is K-rich (8.1–8.7% K_2O = 1.8–2.1 *apfu* K) and Ca-poor (0.5–0.9% CaO = 0.1–0.2 *apfu* Ca). Such compositions of the cation–anion pairs occluded in the wide channel seem caused by relative sizes of their components: K^+ larger than Ca^{2+} is combined with SO_4^{2-} larger than CO_3^{2-}.

The compositional field of minerals with Cl in the narrow channel, namely members of the davyne series, quadridavyne and microsommite, is quite different in Figure 4 from the field of cancrinite-subgroup members. This is an important argument for the assumption that in the narrow channel, the substitution $Cl^- \rightarrow H_2O^0$ (and, correspondingly, $Ca^{2+} \rightarrow Na^+$, for a charge-balance reason) does not occur. It accentuates the crystal-chemical individuality of the cancrinite subgroup.

At the same time, the continuous field (Fig. 4) between davyne-series minerals, quadridavyne and microsommite, as well as the distinct negative correlation between Cl and S contents for the samples with Cl > 2 *apfu*, show the continuity of substitutions between extra-framework anions, especially Cl^- and SO_4^{2-}, in the wide channel. Existence of the continuous solid-solution series between davyne and balliranoite (Balliranо *et al*. 1998, Chukanov *et al*. 2010) confirms the involvement of CO_3^{2-} in these substitutions.

The distinction of the cancrinite subgroup based on crystal-chemical criteria, namely the *AB*-type framework, the smallest type of unit cell and the presence of Na in the narrow channel (Pekov *et al*. 2010), has, as it turns out, also a significant geological (genetic) importance: all six members of this subgroup (Table 1) occur in alkaline intrusive complexes, being formed in the postmagmatic derivatives of various rocks. In some cases, they are rock-forming minerals (cancrinite, vishnevite, kyanoxalite). These minerals are unknown in other geological formations, except rare finds of cancrinite in alkaline volcanic complexes. At the same time, all other CGM are typical of other formations, especially alkaline effusive rocks and lazurite-bearing metasomatic rocks, but unknown in alkaline intrusive complexes. The only exception is carbobystrite, $Na_8[Al_6Si_6O_{24}](CO_3)\bullet 4H_2O$, with an *ABAC*-type framework, an extremely rare mineral, found as a single 3-mm grain in a hyperagpaitic pegmatite in Khibiny (Khomyakov *et al*. 2010).

The CGM with significant, typically species-defining amounts of C-bearing extra-framework anions are concentrated in alkaline intrusive complexes. On the other hand, S- and Cl-rich members of the group strongly prevail in other formations where C-rich CGM are rare.

Cancrinite-subgroup members are sensitive indicators of CO_2 activity at postmagmatic stages of evolution of alkaline intrusive complexes. This can be clearly illustrated by comparison of the composition of these minerals from the Khibiny and Lovozero complexes (Fig. 8), which are neighbors but geochemically and petrologically different (Kogarko *et al*. 1995). In Khibiny, the carbonate members of the cancrinite subgroup are widespread, whereas its other members are represented only by late K-rich vishnevite found in very small amount. On the contrary, at Lovozero the carbonate members of the subgroup are uncommon and mainly represented by cancrisilite, whereas vishnevite and kyanoxalite are rock-forming minerals. Hydroxycancrinite and depmeierite are known only at Lovozero. At the same time, cancrinite, the most common member of the group in the overwhelming majority of other alkaline intrusive complexes of the world, is rare at Lovozero and represented by its unusual Ca-poor and oxalate-rich variety. This difference is obviously caused by quite different redox conditions at the postmagmatic stages: significantly oxidizing at Khibiny and reducing at Lovozero (Chukanov *et al*. 2009a).

Thus, cancrinite-subgroup minerals in derivatives of alkaline intrusive complexes show a strong affinity to CO_3^{2-}: members of the subgroup with other extra-framework anions in the wide channel (SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}, OH^-) can form only under low activity of CO_2. Formation of hydroxycancrinite seems possible only in a system where the medium is depleted in all above-listed anions; the rarity of this mineral is probably caused by the necessity "to compete" with sodium aluminosilicates without additional anions (albite, nepheline, zeolites, *etc*.) that have a broad field of thermodynamic stability.

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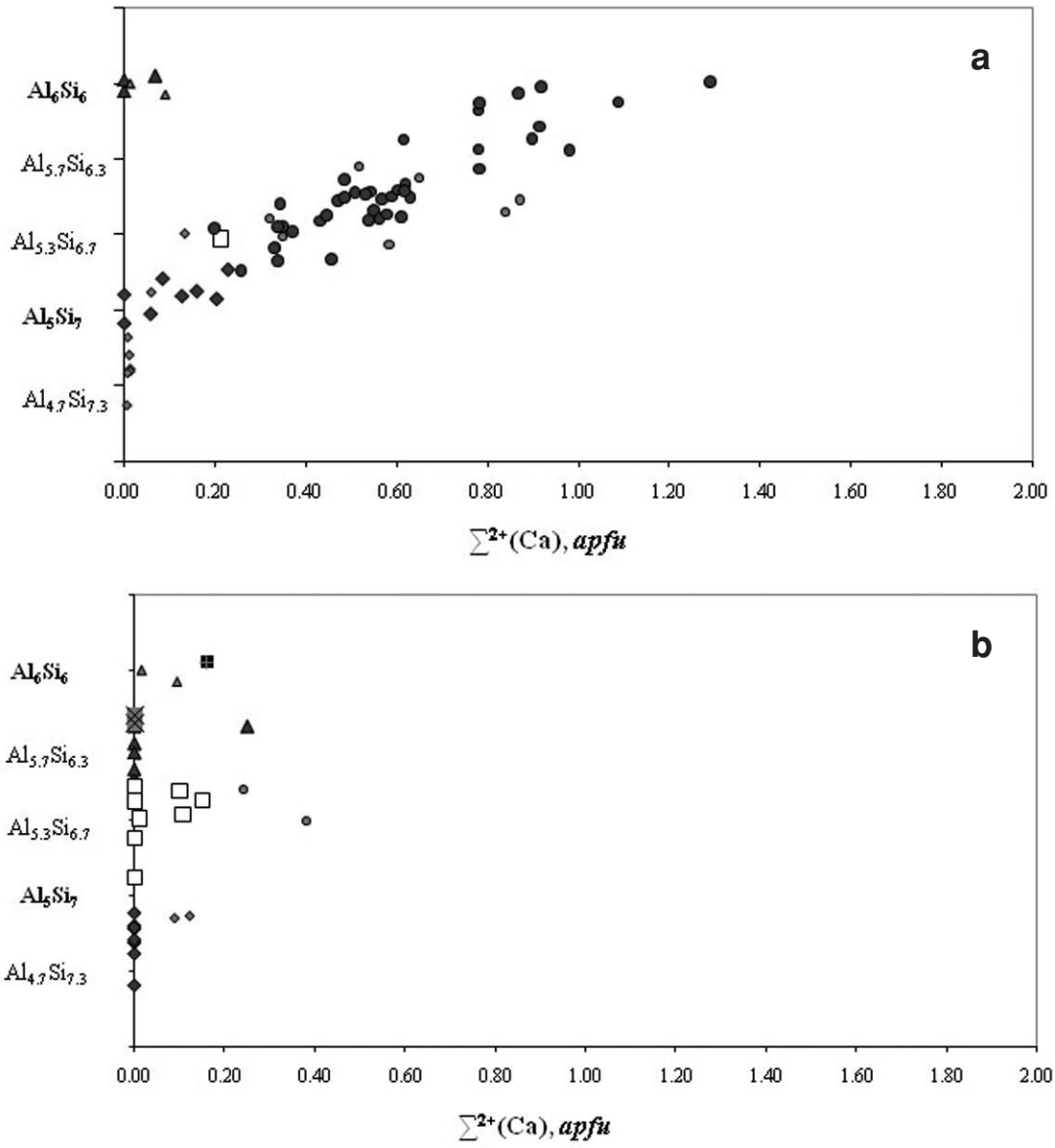

FIG. 8. Chemical features of cancrinite-subgroup minerals from Khibiny (a) and Lovozero (b) alkaline complexes, Kola Peninsula, Russia. Legend: see Figure 2.

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