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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 cancrinitie 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<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>), anions (CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) and H<sub>2</sub>O, with special emphasis on oxalate and phosphate anions. The idealized formula of cancrinite has been refined: Na<sub>7</sub>Ca[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>1,5</sub>•2H<sub>2</sub>O. 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 une 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<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>), anions (CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) et H<sub>2</sub>O, avec emphase particulière portée sur les anions oxalate et phosphate. La formule idéale de la cancrinite a été affinée: Na<sub>7</sub>Ca[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>1.5</sub>•2H<sub>2</sub>O. 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, 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<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>), anions (species-defining: CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, S<sup>2-</sup>,  $C_2O_4^{2-}$ ,  $PO_4^{3-}$ ) 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 extraframework 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 extraframework components. In particular, we recently discovered in these minerals two earlier unknown extraframework 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  $\varepsilon$  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 12.55-12.85Å, 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







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

Mineral	Space group	<i>a</i> , Å	<i>c</i> , Å	Ζ	S	implified formula		References
					framework ı	narrow channel	wide channel	
					Cancrinite subg	roup		
Cancrisilite	P6₃mc	12.57-12.60	5.10-5.11	1	$Si_{6.7\text{-}7.6}\text{Al}_{5.3\text{-}4.4}\text{O}_{24}$	$Na_2(H_2O)_2$	Na <sub>5</sub> (CO <sub>3</sub> ) <sub>1-1.4</sub> (H <sub>2</sub> O) <sub>1-0</sub>	Khomyakov <i>et al.</i> (1991a,b), this work
Cancrinite	<i>P</i> 6 <sub>3</sub> *	12.61-12.67	5.11-5.18	1	$Si_{6.0-6.8}AI_{6.0-5.2}O_{24}$	Na <sub>1.6-2</sub> (H <sub>2</sub> O) <sub>0-2</sub>	(Na <sub>5.8-4</sub> Ca <sub>0.2-2</sub> ) (CO <sub>3</sub> ) <sub>1.4-1.6</sub>	Grundy & Hassan (1982), Ballirano & Maras (2004), Hassan <i>et. al.</i> (2006), Chukanov <i>et al.</i> (2009b), this work
Vishnevite	<i>P</i> 6 <sub>3</sub>	12.62-12.83	5.14-5.27	1	$Si_{6.0-6.4}AI_{6.0-5.6}O_{24}$	$Na_2(H_2O)_2$	(Na <sub>6-3</sub> K <sub>0-3</sub> Ca <sub>0-0.9</sub> ) (SO <sub>4</sub> ) <sub>0.6-1.3</sub>	Hassan & Grundy 1984, Pushcharovskii <i>et al.</i> (1989) Della Ventura <i>et al.</i> (2007) this work
Hydroxycancrinite	P3	12.74	5.18	1	$\mathrm{Si}_{6}\mathrm{Al}_{6}\mathrm{O}_{24}$	$Na_2(H_2O)_2$	Na <sub>6</sub> (OH) <sub>2</sub> **	Nadezhina <i>et al.</i> (1991), Khomyakov <i>et al.</i> (1992)
Depmeierite	<i>P</i> 6 <sub>3</sub>	12.73	5.18	1	$\mathrm{Si}_{6}\mathrm{Al}_{6}\mathrm{O}_{24}$	$Na_2(H_2O)_2$	Na <sub>6</sub> (PO <sub>4</sub> ) <sub>0.67</sub>	Pekov <i>et al.</i> (2010)
Kyanoxalite	<i>P</i> 6 <sub>3</sub>	12.74	5.21	1	$Si_{6-7}Al_{6-5}O_{24}$	$Na_2(H_2O)_2$	(H <sub>2</sub> O) Na <sub>5</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>0.5-1</sub> (H <sub>2</sub> O) <sub>3-2</sub>	Chukanov <i>et al.</i> (2009a), this work
					Davyne serie	s		
Davyne	P6 <sub>3</sub> /m or P6 <sub>3</sub>	12.70-12.85	5.33-5.37	1	$\mathrm{Si}_{6}\mathrm{Al}_{6}\mathrm{O}_{24}$	$Ca_2Cl_2$	(Na,K,Ca) <sub>6</sub> (SO <sub>4</sub> ) <sub>0.5-1</sub> Cl <sub>1-0</sub>	Bonaccorsi <i>et al.</i> (1990), Hassan & Grundy (1990), Ballirano <i>et al.</i> (1996, 1998). Rozenberg <i>et al.</i> (2009), this work
Balliranoite	<i>P</i> 6 <sub>3</sub>	12.695	5.325	1	$\mathrm{Si}_{6}\mathrm{Al}_{6}\mathrm{O}_{24}$	$Ca_2Cl_2$	Na <sub>6</sub> (CO <sub>3</sub> )**	Chukanov et al. (2010)
					Others			
Quadridavyne Microsommite Pitiglianoite	P6 <sub>3</sub> P6 <sub>3</sub> /m P6 <sub>3</sub>	25.77 22.14 22.12	5.37 5.35 5.22	4 3 3	Si <sub>6</sub> Al <sub>6</sub> O <sub>24</sub> Si <sub>6</sub> Al <sub>6</sub> O <sub>24</sub> Si <sub>6</sub> Al <sub>6</sub> O <sub>24</sub>	$Ca_2Cl_2$ $Ca_2Cl_2$ $Na_2(H_2O)_2$	Na <sub>6</sub> Cl <sub>2</sub> ** Na <sub>4</sub> K <sub>2</sub> (SO <sub>4</sub> )** Na <sub>4</sub> K <sub>2</sub> (SO <sub>4</sub> )**	Bonaccorsi <i>et al.</i> (1994), Bonaccorsi <i>et al.</i> (2001) Merlino <i>et al.</i> (1991)

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

\* Note that for a variety intermediate between cancrinite and hydroxycancrinite, space group P3 was reported (Rastsvetaeva *et al.* 2007); \*\* end-member formula.

Constituent Ca		Canci	ncrisilite		Cancrinite			Vishr	nevite		Depmeierite		Kyanoxalite*			
	o.d (21 ar range	l. nal.) av.	l.d. (10 anal.) range av.		o.d. (243 anal.) range av.		l. (35 a range	d. anal.) av.	o. (30 a range	d. inal.) av.	l.c (13 a range	d. inal.) av.	0. (2 a range	d. nal.) av.	o.d. (16 anal.) range av.	
Na₂O wt.%	14.7 -	22.1	20.9 -	21.9	13.7 -	19.7	9.8 -	18.4	10.1 -	17.1	12.4 -	17.6	19.6 -	21.3	12.3 -	18.6
K <sub>2</sub> O	23.3 0.0 -	-	22.7 0.0 -	-	23.7	-	23.6	0.6	22.7 0.0 -	6.6	20.8	4.4	23.0 0.3 -	0.4	23.7 0.0 -	1.2
CaO	0.5	0.3	0.4 0.0 -	0.3	0.9 -	5.3	1.0	5.6	0.0 -	1.3	0.0 -	1.4	0.5 b.d.l.	-	0.0 -	0.4
SrO	1.2 0.0 -	0.15	0.8		10.1 0.0 -	0.1	11.7 0.0 -	0.8	4.8 0.0 -	-	3.9		b.d.l	-	1.2 0.0 -	-
MgO	1.2 b.d.l.	-	0.0 -	-	1.7 0.0 -	-	2.1	0.4	1.2 b.d.l.	-	0.0 -		b.d.l.	-	0.6 b.d.l.	
$Fe_2O_3$	0.0 -	-	0.1 -	-	0.4 0.0 -	-	0.5 0.0 -	0.3	0.0 -	-	0.3 0.0 -	0.4	b.d.l.	-	0.0 -	-
$AI_2O_3$	0.4 22.8 - 1	24.7	0.5 22.3 -	23.9	1.1 26.2 -	28.8	0.8 24.6 -	28.4	0.7 25.5 -	28.1	1.8 27.3 -	29.1	29.1 -	29.2	0.4 26.0 -	27.3
SiO <sub>2</sub>	26.0 40.7 - 4	43.2	27.2 40.4 -	43.2	31.9 32.8 -	37.6	30.0 33.6 -	36.3	29.8 32.1 -	34.4	30.8 33.4 -	35.2	29.4 36.5 -	36.9	28.8 37.0 -	40.0
$P_2O_5$	45.9 0.0 -	-	46.0		45.5 0.0 -	-	40.3 0.0 -	-	38.6 0.0 -	-	37.2		37.5 3.3 -	3.5	43.2 0.0 -	0.3
SO3	0.6 0.0 - 1.2	0.1	0.0 - 0.4	0.1	0.5 0.0 - 2.7	0.4	0.2 0.0 - 4.7	0.6	0.4 4.8 - 8.9	6.9	4.4 - 7.0	6.1	3.8 0.0 - 0.2	0.1	2.2 0.0 - 1.7	0.7
CI	b.d.l.	-	0.0 -	-	0.0 -	-	0.0 -	0.1	0.0 -	0.1	0.0 -	0.2			0.0 -	0.1
F	b.d.l.	-	0.1		b.d.l.	-	0.0 -	-	b.d.l.	-	0.4	-	b.d.l.	-	b.d.l.	-
CO <sub>2</sub>	4.3	4.3	4.0 -	4.4	3.4 -	4.0	3.2 -	5.9		·	0.0 -	1.2	1	1	3.2§	3.2 <sup>§</sup>
$H_2O$	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	- 6.09	5.93 - 6 46	- 6.14	5.78 - 6 23	6.03	6.19	- 6.21	6.50 6.96	- 6.65
AI	4.34 -	4.84	4.36	4.76	5.15 -	5.70	5.23	- 5.87	5.54 ·	- 5.86	5.73 ·	5.92	5.77	- 5.79	5.00 ·	- 5.35
Fe	0.00 -	-	0.01		0.00 -	-	0.00	- 0	0.00		0.00 -	0.05	b.d.l.	-	0.00	
Na	6.21 -	7.09	6.68	7.11	4.18 -	6.40	3.32	- 6.12	3.60 -	5.74	4.32 -	5.86	6.32	- 6.95	4.18	5.97
к	7.48 0.00 -	-	7.35 0.00		7.32 0.00 -	-	7.83 0.00	- 0.13	7.54 0.00 ·	1.65	7.71 0.15 -	0.99	7.58 0.07	- 0.09	7.41 0.00 ·	- 0.25
Ca	0.11 0.00 -	0.05	0.08 0.00 ·	- 0.05	0.23 0.16 -	0.97	0.38 0.24	- 1.03	3.33 0.00 ·	- 0.16	2.93 0.00 -	0.28	0.12 b.d.l.	-	0.43 0.00 ·	- 0.06
Sr	0.23 0.00 -	0.01	0.13		1.83 0.00 -	0.01	2.18 0.00		0.88 0.00 ·	- 0.01	0.70		b.d.l.	-	0.21 0.00 ·	
Mg	0.12 b.d.l.	-			0.22 0.00 -		0.22 0.00	- 0	0.12 b.d.l.	-	0.00 -		b.d.l.	-	0.05 b.d.l.	-
Σe.f.c.		7.15		7.16	0.11	7.38	0.13	7.32		7.56	0.08	7.13		7.04		6.28
PO4	0.00 -	-			0.00 -		0.00		0.00 ·				0.47	- 0.49	0.00 -	- 0.05
SO4	0.09 0.00 -	0.01	0.00	0.01	0.07 0.00 -	0.1	0.02 0.00	- 0.12	0.07 0.64 ·	- 0.92	0.56 -	0.79	0.53 0.00	- 0.00	0.30 0.00 -	- 0.09
CI	0.15 b.d.l.	-	0.04 0.00 ·		0.36 0.00 -		0.61 0.00	- 0.00	1.15 0.00 ·	- 0.00	1.31 0.00 -	0.04	0.02 b.d.l.	-	0.21 0.00 ·	- 0.02
F	b.d.l.	-	0.03		0.37 b.d.l.	-	0.16 0.00		0.29 b.d.l.	-	0.12		b.d.l.	-	0.31 b.d.l.	-
CO <sub>3</sub>	1.05	1.05	0.91	- 1.01	1.16 -	1.26	0.26 0.76	- 1.37			0.00 -	0.27	0.22	0.22	0.46 <sup>§</sup>	0.46§
- OH**	0.2	0.2	1.10 0.02	- 0.16	1.37 0.00 -	0.10	1.80 0.00	- 0.12			0.50		0.02	0.02	0.01	0.01
H,O	2.55	2.55	0.30 2.79	- 2.99	0.31 2.30 -	2.61	0.20	- 2.35			1.41 -	3.33	3.35	3.35	4.74	4.74
Al/Si	0.57 -	0.68	3.20 0.57 0.80	- 0.66	3.01 0.75 - 1.01	0.91	5.17 0.79 1.04	- 0.97	0.86	- 0.95	4.77 0.93 - 1.04	0.99	0.93	- 0.93	0.73	- 0.80

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

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;  $\Sigma e.f.c.$ : sum of extra-framework cations; \*: including intermediate members of the cancrinite–kyanoxalite series with significant content of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (as documented with IR spectroscopy data); <sup>§</sup> : C<sub>2</sub>O<sub>3</sub>/C<sub>2</sub>O<sub>4</sub> instead of CO<sub>2</sub>/CO<sub>3</sub>; \*\*: calculated from charge balance.

	Hydroxy- cancrinite	Э	Dav	/yne	e Balli- Pitiglia ranoite noite		glia- bite	ilia- Micro ite somm		ro- Quadri- nite davyne		
	l.d. (1 anal.)	o. (16 a range	d. inal.) av	ا 23 a range .	d. anal.) av.	o.d. (1 anal.)	l. ) (3 a range	.d. inal.) av.	(8 a range	d. nal.) av.	l. (10 a range	d. mal.) av.
Na <sub>2</sub> O wt	.% 23.4	11.3 -	13.6	8.0 -	13.5	13.1	15.4 -	17.1	8.5 -	10.3	10.9 -	11.7
K <sub>2</sub> O	0.4	0.3 -	5.1	0.3 -	2.7	3.1	6.8 -	8.4	4.3 -	7.6	3.4 -	6.0
CaO	0.9	9.1 0.9 -	10.3	8.0 0.6 -	11.9	12.7	9.4 0.0 -	-	11.5 10.1 -	11.5	8.0 9.0-	9.9
SrO		0.0 -	0.2	0.0 -	-	b.d.l.	0.1		14.7		11.5	
MgO	0.2	1.2 0.0 -	-	0.2	-	b.d.l.						
$\rm Fe_2O_3$		0.0 -	-	0.2		b.d.l.						
$Al_2O_3$	31.1	0.9 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 -	33.4	31.4 -	32.2	32.4	33.9 -	35.5	30.7 -	32.0	32.6 -	32.9
$SO_3$		3.3 -	4.6	0.4 -	5.2	2	5.6 -	6.9	1.7 -	4.7	0.0 -	0.5
C1		6.7 7.9 -	6.9	8.8 5.2 -	7.7	7.4	7.6		7.2 6.2 -	7.4	1.1 10.4 -	10.9
F		6.4 b.d.l.	-	11.5 0.0 -	0.2	b.d.l.			9.1		12.1 0.0 -	0.2
$\begin{array}{c} CO_2 \\ H_2 O \end{array}$	1.6 5.4			0.5		3.2 0.2					0.0	
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	5.94	5.88	6.01	5.98	5.70	- 5.85	5.97 ·	6.27	5.89	5.98
Fe	0.02	0.00 · 0.12		0.20		b.d.l.	5.95		0.57		0.03	
Na	7.46	4.07	4.75	2.92	4.89	4.70	5.57	- 5.72	2.90	3.57	3.77	4.16
К	0.10	0.00 -	· 1.2	0.07 -	0.63	0.73	1.40	- 1.88	0.94	1.73	0.78	1.40
Са	0.16	2.19 0.15 ·	2.02	1.90 1.90 -	2.37	2.53	2.16 0.00 ·		2.62 2.01 ·	2.20	1.90 1.74 ·	1.94
Sr		2.46 0.00 ·	0.02	2.77		b.d.l.	0.02		2.72		2.22	
Mg		0.13				b.d.l.						
Σe.f.c.	7.72	0.32	7.99		7.89	7.96		7.60		7.5		7.5
$SO_4$		0.47	0.63	0.05	0.74	0.27	0.68	- 0.91	0.23	0.64	0.01	- 0.06
CI		0.97	2.13	1.64 -	2.44	2.34	1.00		1.91	2.26	3.18	3.39
F		2.23 b.d.l.	-	3.57 0.00 · 0.29	0.11	b.d.l.			2.75		3.76 0.00 · 0.33	0.14
CO₃ OH H₂O	0.36 1.23 2.35			5.25		0.82 0.00 0.12					0.00	
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

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

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;  $\Sigma e.f.c.$ : 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), Vuorivarvi (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<sub>2</sub>O-poor variety of cancrinite). III. Alkalirich 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<sub>2</sub>O-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  $\times$ 16 mm<sup>2</sup>). Both CO<sub>2</sub> and H<sub>2</sub>O were determined by selective sorption from gaseous products obtained by heating the mineral at 1080°C in oxygen; for CO<sub>2</sub>, we used the askarite sorbent (an asbestiform matter saturated with NaOH), and for H<sub>2</sub>O, we used Mg(ClO<sub>4</sub>)<sub>2</sub>. 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 electronprobe 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, cancrinitesubgroup 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<sub>6.0</sub>Al<sub>6.0</sub> to Si<sub>7.6</sub>Al<sub>4.4</sub>. Other CGM (Olysych 2010) typically show only insignificant deviations from the stoichiometric ratio Si<sub>6.0</sub>Al<sub>6.0</sub> (Si<sub>6.1</sub>Al<sub>5.9</sub> – Si<sub>5.9</sub>Al<sub>6.1</sub>). An increase of the Si:Al ratio is typical in the CO<sub>3</sub>-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<sub>4</sub>) 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<sub>4</sub>. 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  $0.37 \ apfu = 1.2 \text{ wt.}\%$  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<sub>4</sub> *pfu* (in literature, analyses with SO<sub>4</sub> 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<sub>4</sub> as an impurity anion: for them, no more than 0.36 SO<sub>4</sub> *pfu* is typical. These fields are separate; thus, the cancrinite–vishnevite solid-solution series is probably not continuous as far as the CO<sub>3</sub>:SO<sub>4</sub> 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" cancrinitesubgroup 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<sub>2.90</sub>K<sub>2.02</sub>Ca<sub>2.04</sub> (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	Space	e a, Å	<i>V</i> , Å <sup>3</sup>	DM 0	h,k,l	Reflections	R1(F)	Structur	al formula
Locality	group	° uniqu (/ >		unique/used [ $l > 2\sigma(l)$ ]	/ GoF	framework	narrow channel wide channel		
u1631* Lovozero	P6₃mc	12.584(2) 5.101(1)	699.5(2)	1** 3.24- 48.41	-24/24, -24/26, -9/8	21816 / 2118 / 1865 ( <i>R</i> <sub>et</sub> = 0.0300)	0.0216 / 0.0469 / 1.063	$Si_{7.4}Al_{4.6}O_{24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>5.4</sub> (CO <sub>3</sub> ) <sub>1.4</sub>
kir2343* Khibiny	<i>P</i> 6 <sub>3</sub>	12.607(2) 5.111(1)	703.5(2)	1** 3.23- 40.49	-23/23, -23/23, -9/6	20213 / 2630 / 2484 ( $R = 0.0207$ )	0.0224 / 0.0557 / 1.089	$Si_{\!6.6}Al_{\!5.4}O_{\!24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>5.5</sub> Ca <sub>0.4</sub> (CO <sub>3</sub> ) <sub>1.5</sub>
11/1* Khibiny	<i>P</i> 6 <sub>3</sub>	12.618(2) 5.116(1)	705.4(2)	1** 1.86- 40.57	-23/23,-23/23, -9/9	(N <sub>int</sub> 0.0207) 20257 / 3004 / 2814 (P. = 0.0241)	0.0242 / 0.0524 / 1.083	$\rm{Si}_{6.45}\rm{Al}_{5.55}\rm{O}_{24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>5.45</sub> Ca <sub>0.55</sub> (CO <sub>3</sub> ) <sub>1.5</sub>
kovd15/1* Kovdor	<i>P</i> 6 <sub>3</sub>	12.683(2) 5.190(1)	723.0(2)	1** 4.34- 36.93	-21/13, -20/21, -7/8	$(R_{int} = 0.0241)$ 18032 / 2402 / 2193 $(R_{int} = 0.0244)$	0.0276 / 0.0796 / 1.130	$Si_{6.7}Al_{5.3}O_{24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>4.8</sub> K <sub>0.3</sub> (CO <sub>3</sub> ) <sub>0.9</sub> ***
kovd5* Kovdor	<i>P</i> 6 <sub>3</sub>	12.606(2) 5.118(1)	704.3(2)	1** 3.23- 45.84	-23/25, -23/24, -9/9	$(R_{int} = 0.0211)$ 21598 / 3682 / 3042 ( $R = 0.0272$ )	0.0280 / 0.0630 / 1.057	$Si_{\!_{6.65}}AI_{\!_{5.35}}O_{\!_{24}}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>5.8</sub> Ca <sub>0.2</sub> (CO <sub>3</sub> ) <sub>1.4</sub>
ggm 44331* Vishnevve	P6 <sub>3</sub> Mtns	12.627(2) 5.136(1)	709.2(2)	2** 3.23- 32.64	-18/18, -18/19, -7/7	$(R_{int} = 0.0212)$ 22106 / 1675 / 1387 ( $R_{int} = 0.0651$ )	0.0413 / 0.0866 / 1.008	$\rm{Si}_{6.4}\rm{Al}_{5.6}\rm{O}_{24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>5.0</sub> Ca <sub>1.0</sub> (CO <sub>3</sub> ) <sub>1.7</sub>
tz3/1* Tamazegh	<i>P</i> 6 <sub>3</sub> t	12.625(2) 5.122(1)	707.0(2)	1** 1.86- 40.71	-23/18, -17/20, -9/9	$(R_{int} = 0.0001)$ 17259 / 2513 / 1284 ( $R_{int} = 0.0904$ )	0.0565 / 0.1093 / 1.012	$Si_{6.3}Al_{5.7}O_{24}$	Na <sub>1.7</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>4.3</sub> Ca <sub>1.2</sub> (CO <sub>3</sub> ) <sub>1.5</sub>
tz5/1* Tamazegh	<i>Р</i> 6 <sub>3</sub> t	12.618(2) 5.144(1)	709.3(2)	1** 1.86- 40.57	-23/23, -23/23, -9/7	$(N_{int} = 0.0304)$ 20143 / 2866 / 1699 ( $P_{int} = 0.1193$ )	0.0472 / 0.1035 / 1.016	$Si_{6.5}Al_{5.5}O_{24}$	Na <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>4.6</sub> Ca <sub>0.9</sub> (CO <sub>3</sub> ) <sub>1.4</sub>
mmf 62633/2* Dakbuupur	<i>P</i> 6 <sub>3</sub>	12.613(1) 5.124(1)	706.0(2)	2** 3.23- 34.85	-20/20, -20/20, -8/8	$(N_{int} = 0.1130)$ 26160 / 2006 / 1666 ( $P_{int} = 0.0710$ )	0.0483 / 0.1149 / 1.029	$Si_{6.2}Al_{5.8}O_{24}$	Na <sub>1.6</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>4.2</sub> Ca <sub>1.6</sub> (CO <sub>3</sub> ) <sub>1.6</sub>
mmf 28962* Ilmeny Mtn	<i>Р</i> 6 <sub>3</sub> s	12.617(2) 5.129(1)	707.1(2)	2** 3.23- 34.91	-20/20, -19/20, -8/8	$(R_{int} = 0.0710)$ 26734 / 2000 / 1750 $(R_{int} = 0.0439)$	0.0273 / 0.0628 / 0.965	$\rm{Si}_{6.2}\rm{Al}_{5.8}\rm{O}_{24}$	Na <sub>1.8</sub> (H <sub>2</sub> O) <sub>2</sub> Na <sub>4.7</sub> Ca <sub>1.2</sub> (CO <sub>3</sub> ) <sub>1.5</sub>

\* u1631  $w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.0489P]$ ; P = ([max of (0 or  $F_o^2$ )] + 2 $F_c^2$ )/3. \* kir2343  $w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 0.1701P]$ ; P = ([max of (0 or  $F_o^2$ )] + 2 $F_c^2$ )/3. \* kovd15/1  $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.01826P]$ ; P = ([max of (0 or  $F_o^2$ )] + 2 $F_c^2$ )/3. \* kovd15/1  $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.1826P]$ ; P = ([max of (0 or  $F_o^2$ )] + 2 $F_c^2$ )/3. \* kovd5  $w = 1/[\sigma^2(F_o^2) + (0.0310P)^2 + 0.0316P]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* gm44331  $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.007]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* tz5/1  $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.007]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* tz5/1  $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.007]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* tz5/1  $w = 1/[\sigma^2(F_c^2) + (0.0434P)^2 + 0.007]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* tz5/1  $w = 1/[\sigma^2(F_c^2) + (0.0434P)^2 + 0.0714P)^2 + 0.007]$ ; P = ([max of (0 or  $F_c^2$ )] + 2 $F_c^2$ )/3. \* tz5/1  $w = 1/[\sigma^2(F_c^2) + (0.0434P)^2 + 0.0714P)^2 + 0.0714P)^2 + 0.00714P)^2 + 0.$ 

from Lovozero, where depmeierite, a new member of this subgroup with  $PO_4^{3-}$  as species-defining extraframework 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<sub>3</sub> 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<sub>5.5</sub>Si<sub>6.5</sub>–Al<sub>6.0</sub>Si<sub>6.0</sub>, 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–hydroxy-cancrinite 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<sub>7.63</sub>Al<sub>4.37</sub> to Si<sub>6.66</sub>Al<sub>5.34</sub>. 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<sub>5.78</sub>Al<sub>6.22</sub> to Si<sub>6.46</sub>Al<sub>5.54</sub>, 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  $(U_{\rm eq},\, {\rm \AA}^2)$  OF ATOMS AND SITE-OCCUPANCY FACTORS FOR CANCRISILITE§

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

Ow: oxygen atoms belonging to H<sub>2</sub>O molecules, OC: oxygen atoms belonging to CO<sub>3</sub> groups. \*:  $U_{\rm go}$ . Interatomic distances (Si,Al)–O in tetrahedra vary from 1.6581(6) to 1.6698(6) Å; the averaged value is 1.6632 Å. <sup>§</sup> Sample u1631.

Sample	Atom*	x	У	Z	$U_{\rm eq}$
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 <sub>0.89</sub> Si <sub>0.11</sub>	0.07606(3)	0.41389(3)	0.75067(12)	0.00924(7)
kovd5	Al <sub>0.89</sub> Si <sub>0.11</sub>	0.07557(2)	0.412385(19)	0.75065(7)	0.00764(4)
kir2343	Al <sub>0.90</sub> Si <sub>0.10</sub>	0.07563(2)	0.41234(2)	0.75076(9)	0.00719(4)
tz3/1	Al <sub>0.94</sub> Si <sub>0.06</sub>	0.07537(14)	0.41230(13)	0.7511(7)	0.0088(3)
tz5/1	Al <sub>0.92</sub> Si <sub>0.08</sub>	0.07534(7)	0.41255(6)	0.7509(3)	0.00886(12)
11/1	Al <sub>0.93</sub> Si <sub>0.07</sub>	0.07525(3)	0.41236(2)	0.75094(10)	0.00723(5)
mmf28962	Al <sub>0.97</sub> Si <sub>0.03</sub>	0.07506(3)	0.41250(3)	0.75085(10)	0.00954(8)
mmf62633/2	Al <sub>0.97</sub> Si <sub>0.03</sub>	0.07504(6)	0.41252(6)	0.7511(2)	0.00991(15)
ggm44331	Al <sub>0.94</sub> Si <sub>0.06</sub>	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)
125/1		0.20368(18)	0.40528(18)	0.0629(4)	0.0159(3)
11/1 mmf28062		0.20317(8)	0.40479(7)	0.05897(10)	0.01388(12)
mmf62633/2		0.20306(9)	0.40495(10)	0.6582(4)	0.0166(2) 0.0156(4)
aam//331		0.20203(17)	0.40420(19)	0.0002(4)	0.0130(4) 0.0172(4)
kovd15/1	O(2)	0.20301(10)	0.40430(17)	0.0003(4)	0.0172(4)
kovd5	0(2)	0.11582(7)	0.56377(6)	0.72443(19)	0.0200(2)
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	<b>A</b> (1)	0.02867(17)	0.34943(18)	0.0600(4)	0.0168(4)
KOVO15/1	0(4)	0.32153(11)	0.36118(11)	0.0386(2)	0.0191(2)
KOVOD		0.31010(0)	0.36021(7)	0.04513(13)	0.01569(12)
KII∠343 +→2/1		0.3101/(/)	0.30021(8)	0.04001(10)	0.01547(12)
123/1		0.3141(5)	0.3576(2)	0.0443(7) 0.0422(4)	0.0177(10) 0.0178(4)
11/1		0.31531(19)	0.3570(2)	0.0422(4)	0.01/0(4)
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)
aam44331		0.31430(17)	0.35775(18)	0.0427(4)	0.0177(4)

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

Values of the AI:Si ratio in AI-dominant sites are given on the basis of electron-microprobe data, taking into account the (AI,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<sub>6.05</sub>(Al,Fe)<sub>5.95</sub>–Si<sub>6.96</sub>(Al,Fe)<sub>5.04</sub>. 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,Sidisordered 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  $P6_{3}mc$ . 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,Sidisorder, 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<sup>+</sup> and H<sub>2</sub>O. The H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O-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<sub>2</sub>O-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<sub>2</sub>O site and, thus, appearance of an additional degree of freedom for Na along the **c** axis.

Sample	Atom x y		У	z	$U_{\rm eq}$	s.o.f.				
Narrow channel										
kovd15/1 kovd5 kir2343 tz3/1 tz5/1 11/1 mmf28962 mmf62633/2 ggm44331	Na Na Na Na Na Na Na Na	0.6667 0.6667 0.6667 0.6667 0.6667 0.6667 0.6667 0.6667 0.6667	0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333 0.3333	0.1270(4) 0.1315(3) 0.1308(3) 0.1353(9) 0.1311(7) 0.1323(3) 0.124(2) 0.187(7) 0.1380(10) 0.1345(6)	0.0346(4) 0.0299(2) 0.0370(13) 0.0422(6) 0.0288(2) 0.0343(19) 0.026(7) 0.0382(12) 0.0374(6)	1.00 1.00 0.845(11) 1.00 0.705(8) 0.18 0.815(12) 1.00				
kovd15/1 kovd5 kir2343 tz3/1 tz5/1 11/1 mmf62633/2 ggm44331	Ow	0.6980(8) 0.6873(6) 0.6143(5) 0.695(6) 0.697(3) 0.6157(4) 0.6849(16) 0.691(3) 0.686(3)	0.3874(7) 0.3015(6) 0.3129(7) 0.3756(13) 0.378(2) 0.3146(9) 0.3068(15) 0.3741(10) 0.303(2)	0.6897(12) 0.6848(8) 0.6849(10) 0.684(2) 0.6905(18) 0.6852(8) 0.6857(13) 0.679(3) 0.679(3)	0.0582(17) 0.0562(11) 0.0570(13) 0.061(8) 0.073(8) 0.0534(12) 0.066(2) 0.061(4) 0.064(3)	0.33				
Wide channel										
kovd15/1 kovd5 kir2343 tz3/1 tz5/1 11/1 mmf28962 mmf62633/2 ggm44331	A A A A A A A A A A A A A A A A	$\begin{array}{c} 0.13129(11)\\ 0.1249(3)\\ 0.1194(4)\\ 0.1236(3)\\ 0.1195(5)\\ 0.1230(3)\\ 0.12555(11)\\ 0.1255(11)\\ 0.12248(5)\\ 0.1190(8)\\ 0.12273(18)\\ 0.1320(10)\\ 0.12252(11)\\ 0.14224(16)\\ 0.1223(5)\\ 0.1269(8)\\ \end{array}$	0.26535(15) 0.2525(2) 0.2418(4) 0.2504(3) 0.2410(4) 0.24943(11) 0.2525(4) 0.24170(19) 0.24770(19) 0.24770(19) 0.24759(9) 0.2866(14) 0.2866(14) 0.28601(8)	0.2863(2) 0.2972(7) 0.2672(12) 0.2992(8) 0.2677(13) 0.2994(5) 0.2996(8) 0.2996(8) 0.276(2) 0.2913(5) 0.2998(17) 0.2959(3) 0.288(4) 0.2867(16) 0.301(2)	0.0522(5) 0.0254(4) 0.0279(10) 0.0230(4) 0.0259(10) 0.0269(4) 0.0209(5) 0.0263(10) 0.0263(4) 0.0223(4) 0.0222(3) 0.0222(3) 0.02241(12) 0.040(2)	$\begin{array}{l} Na_{0.81}K_{0.05}\\ Na_{0.62}Ca_{0.02}\\ Na_{0.35}Ca_{0.01}\\ Na_{0.57}Ca_{0.06}\\ Na_{0.37}Ca_{0.02}\\ Na_{0.57}Ca_{0.02}\\ Na_{0.57}Ca_{0.02}\\ Na_{0.55}Ca_{0.05}\\ Na_{0.55}Ca_{0.05}\\ Na_{0.55}Ca_{0.06}\\ Na_{0.45}Ca_{0.04}\\ Na_{0.64}Ca_{0.16}\\ Na_{0.15}Ca_{0.02}\\ Na_{0.06}Ca_{0.02}\\ Na_{0.04}Ca_{0.10}\\ Na_{0.34}Ca_{0.10}\\ Na_{0.35}Ca_{0.07}\\ \end{array}$				
kovd15/1 kovd5 kir2343 tz3/1 tz5/1 11/1 mmf28962 mmf62633/2 ggm44331	C(1)	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	0.679(2) 0.644(4) 0.6399(8) 0.669(3) 0.644(2) 0.660(2) 0.715(4) 0.6751(18) 0.692(5)	0.039(5)* 0.036(4) 0.0215(13)* 0.040(6) 0.019(4)* 0.0177(17)* 0.021(3)* 0.044(5) 0.016(7)*	0.171(10) 0.32(2) 0.289(6) 0.402(18) 0.289(13) 0.225(11) 0.211(14) 0.211(14) 0.432(14) 0.19(3)				
kovd15/1 kovd5 kir2343 tz3/1 tz5/1 11/1 mmf28962 mmf62633/2 ggm44331	OC(1)	0.0540(13) 0.0575(6) 0.0579(3) 0.0559(19) 0.0577(5) 0.0577(5) 0.0575(6) 0.0578(6) 0.0574(12)	0.1141(12) 0.1180(6) 0.1182(3) 0.1178(9) 0.1178(8) 0.1187(4) 0.1202(5) 0.1186(6) 0.1194(12)	0.679(2) 0.644(4) 0.6399(8) 0.669(3) 0.644(2) 0.660(2) 0.715(4) 0.6751(18) 0.692(5)	0.055(5)* 0.043(3) 0.0233(9)* 0.046(5) 0.024(3)* 0.0163(13)* 0.022(2)* 0.046(4) 0.010(5)*	0.171(10) 0.32(2) 0.289(6) 0.402(18) 0.289(13) 0.225(11) 0.211(14) 0.432(14) 0.19(3)				

TABLE 6. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS ( $U_{\rm eq}$ , Å<sup>2</sup>) OF EXTRA-FRAMEWORK ATOMS AND THEIR SITE-OCCUPANCY FACTORS FOR VARIOUS CANCRINITE-GROUP MINERALS

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

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

Ow: oxygen atoms belonging to H<sub>2</sub>O molecules, OC: oxygen atoms belonging to CO<sub>3</sub> groups. \*: U<sub>iso</sub>.

Sample	Si,Al	Si-O <sub>min</sub>	Si-O <sub>max</sub>	Si-O <sub>av</sub>	(Al,Si)-O <sub>min</sub>	(AI,Si)-O <sub>max</sub>	(Al,Si)-O <sub>av</sub>
kovd15/1	Si <sub>67</sub> Al <sub>53</sub>	1.6088(11)	1.6202(11)	1.615	1.7200(11)	1.7372(11)	1.727
kovd5	Si6 65 Al 5 35	1.6116(7)	1.6208(7)	1.6159	1.7173(7)	1.7386(7)	1.7271
kir2343	Si <sub>6.6</sub> Al <sub>5.4</sub>	1.6116(7)	1.6205(8)	1.6165	1.7180(7)	1.7356(8)	1.7265
tz3/1	Si <sub>6 3</sub> Al <sub>5 7</sub>	1.601(5)	1.629(4)	1.615	1.724(5)	1.740(4)	1.734
tz5/1	Si <sub>6 5</sub> Al <sub>5 5</sub>	1.604(2)	1.622(2)	1.613	1.715(2)	1.738(2)	1.728
11/1	Si6 45 AI5 55	1.6103(9)	1.6195(8)	1.614	1.7213(10)	1.7447(8)	1.732
mmf28962	Si <sub>6 2</sub> Al <sub>5 8</sub>	1.6048(9)	1.6230(10)	1.615	1.7200(10)	1.7468(11)	1.734
mmf62633/2	Si <sub>6 2</sub> Al <sub>5 8</sub>	1.6019(18)	1.621(2)	1.613	1.7195(19)	1.753(2)	1.737
ggm44331	Si <sub>6.4</sub> Al <sub>5.6</sub>	1.6092(17)	1.6203(19)	1.615	1.7189(17)	1.751(2)	1.735

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



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<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>), anions (CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) and, in some cases, additional H<sub>2</sub>O 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<sub>2</sub>O 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 depreierite (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





 $(C_2O_4^{2-})$ , linear (OH<sup>-</sup>), or "point" (Cl<sup>-</sup>). Flat-triangular groups  $CO_3^{2-}$  or "point" anions Cl<sup>-</sup> 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<sup>-</sup>, 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub>O molecules: 3 and 1 *pfu*, respectively (Chukanov *et al.* 2009a, Pekov *et al.* 2010). The presence of 1 H<sub>2</sub>O *pfu* in the wide channel was also reported for the original cancrisilite with  $1.2 \text{ CO}_3 pfu$  (Khomyakov *et al.* 1991a,

1991b). In our cancrisilite sample (u1631 with  $1.4 \text{ CO}_3$  *pfu*), no H<sub>2</sub>O was found in the wide channel (Tables 3–4). In general, the H<sub>2</sub>O 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<sub>6</sub>Ca<sub>2</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O does not correspond to the overwhelming majority of compositions as far as the Na:Ca ratio and the CO<sub>3</sub> 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<sup>+</sup>  $\leftrightarrow$  Ca<sup>2+</sup>, Si<sup>4+</sup>  $\leftrightarrow$  Al<sup>3+</sup> and CO<sub>3</sub><sup>2-</sup>  $\leftrightarrow$  $(\Box, H_2O)^0$ , 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):  $Na_6Ca_2[Al_6Si_6O_{24}](CO_3)_2 \cdot nH_2O - Na_7[Al_5Si_7O_{24}]$  $(CO_3) \bullet nH_2O - Na_8[Al_6Si_6O_{24}](CO_3) \bullet nH_2O$ . In its generalized form, the cancrinite formula could be presented as follows:  $(Na_{8-x-y}Ca_x \Box_y)[Al_{6-z}Si_{6+z}O_{24}]$  $(CO_3)_{1-2}$ ·*n*H<sub>2</sub>O, where x = 0-2, y = 0-1, z = 0-1, and *n* = 0-3, or, taking into account the distribution of extraframework components in the narrow and the wide channels:  $[Al_{6-7}Si_{6+7}O_{24}][Na_2(H_2O)_{0-2}][(Na_{6-x-v}Ca_x \Box_v)]$  $(CO_3)_{1-2}(H_2O)_{1-0}].$ 

The average of the Ca<sub>0.3-1.7</sub> 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<sub>3</sub> content rarely exceeds 1.5 *pfu*. Independently obtained from the results of all known structural studies, the data show that the amount of CO<sub>3</sub> 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<sub>7</sub>Ca[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>1.5</sub>•2H<sub>2</sub>O.

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<sub>3</sub> 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<sub>3</sub>)•2–3H<sub>2</sub>O –  $Na_8[Al_5Si_7O_{24}]$ (CO<sub>3</sub>)<sub>1.5</sub>•2H<sub>2</sub>O.

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 extraframework 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<sup>+</sup> larger than Ca<sup>2+</sup> 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<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, in the wide channel. Existence of the continuous solid-solution series between davyne and balliranoite (Ballirano *et al.* 1998, Chukanov *et al.* 2010) confirms the involvement of CO<sub>3</sub><sup>2-</sup> 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,  $Na_8[Al_6Si_6O_{24}](CO_3) \cdot 4H_2O$ , 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 speciesdefining 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<sub>2</sub> 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 extraframework 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 abovelisted 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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