

## LABUNTSOVITE: SOLID SOLUTIONS AND FEATURES OF THE CRYSTAL STRUCTURE

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### ABSTRACT

Our study of solid solution in labuntsovite and related monoclinic minerals is based on chemical and electron-microprobe data for 44 samples (19 published and 25 new). The crystal structures of three samples with distinct compositions, recently refined, are here compared with the published structural data. Correlations between the composition and infrared spectral parameters for labuntsovite and labuntsovite-type minerals were determined. The general formula of minerals with labuntsovite structure ( $Z = 1$ ) is  $A_1A_2A_3A_{3-2x}[M_2(H_2O)_{2x}][M_1(O,OH)_8][Si_4O_{12}]_4 \cdot nH_2O$ , where  $0 < x < 2$ ,  $A_1 = Na, Ca, \square$ ;  $A_2 = K, Na, H_3O, \square$ ,  $A_3 = K, Ba, Sr, H_3O, \square$ ,  $M_1 = Ti, Nb$ ;  $M_2 = Mn^{2+}, Fe^{2+}, Mg, Zn, \square$ , usually,  $n \approx 8$ . Correlations are observed among some components (large cations such as K, Ba, etc.,  $R^{2+}$  octahedrally coordinated cations, total number of octahedral cations). The  $A_3$  and  $M_2$  positions are linked and occupied according to alternative mechanisms, e.g.,  $A_3 [(2K)] + M_2 [\square] \leftrightarrow A_3 [2H_2O] + M_2 [Mn, Fe, Mg]$ . Four subgroups of monoclinic labuntsovite-type minerals are distinguished. 1) There are those with the labuntsovite structure and a predominance of vacancies in the  $M_2$  octahedra; more than 50% of the  $A_3$  sites are occupied by large cations. 2) There are minerals with the labuntsovite structure having a predominance of Fe, Mg, Mn, or Zn in the  $M_2$  positions (linking octahedra) and a predominance of  $H_2O$  in the  $A_3$  position; their formula is:  $Na_4K_4(K, Ba \dots)_{4-2x} [R^{2+}_x(H_2O)_{2x}] [Ti_8(O, OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ , where  $1 < x < 2$ , and  $R = Mn, Fe, Mg, Zn$ . 3) There are minerals with vacant  $M_2$  positions and more than three positions of extra-framework cations (vuoriyarvite and its analogues). An extensive solid-solution involving Ti and Nb, Na and K is typical for these phases. 4) Finally, there are minerals with the kuzmenkoite structure, which show a predominance of Mn, Fe, Mg, or Zn in the  $M_2$  positions, and two positions of extra-framework cations. A low content of Na is typical for minerals of this subgroup. Their formula ( $Z = 1$ ) is:  $K_4 \square_4 [(Mn, Fe \dots)_2(H_2O)_4] [(Ti, Nb)_8(OH, O)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

*Keywords:* labuntsovite, chemical composition, solid solution, crystal structure.

### SOMMAIRE

Notre étude de l'étendue des solutions solides dans les minéraux monocliniques du groupe de la labuntsovite est fondée sur les données de microsonde électronique et les données chimiques (voie humide) pour 44 échantillons, dont 25 sont nouvelles. Les détails de la structure de trois échantillons ayant une composition distincte, récemment acquis, sont évalués en comparaison des données structurales déjà publiées. Nous avons déterminé les corrélations entre les compositions et les paramètres des spectres dans l'infra-rouge de la labuntsovite et les minéraux de ce groupe. La formule générale des minéraux adoptant cette structure ( $Z = 1$ ) serait  $A_1A_2A_3A_{3-2x} [M_2(H_2O)_{2x}] [M_1(O,OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$  [ $0 < x < 2$ ,  $A_1 = Na, Ca, \square$ ;  $A_2 = K, Na, H_3O, \square$ ,  $A_3 = K, Ba, Sr, H_3O, \square$ ,  $M_1 = Ti, Nb$ ;  $M_2 = Mn^{2+}, Fe^{2+}, Mg, Zn, \square$ , et, en général,  $n \approx 8$ ]. Nous observons des corrélations parmi certains des composants (cations de taille importante, comme K, Ba, etc., cations  $R^{2+}$  à coordination octaédrique, nombre total de tels cations). Les positions  $A_3$  et  $M_2$  sont liées et remplies selon une série de mécanismes alternatifs, par exemple,  $A_3 [(2K)] + M_2$

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[□]  $\delta$  A3 [2H<sub>2</sub>O] + M2 [Mn,Fe,Mg]. On distingue quatre sous-groupes de minéraux monocliniques du groupe de la labuntsovite. 1) Il y a ceux qui adoptent la structure de la labuntsovite et qui montrent une prédominance de lacunes dans le site M2 à coordination octaédrique; plus de 50% des sites A3 sont remplis par des cations de taille importante. 2) Il y a ceux qui adoptent la structure de la labuntsovite avec une prédominance de Fe, Mg, Mn, ou Zn dans les sites M2 (octaèdres assurant les liens) et de H<sub>2</sub>O dans la position A3; leur formule serait Na<sub>4</sub>K<sub>4</sub>(K,Ba...)\_{4-2x} [R^{2+}\_x(H<sub>2</sub>O)\_{2x}] [Ti<sub>8</sub>(O,OH)<sub>8</sub>] [Si<sub>4</sub>O<sub>12</sub>]<sub>4</sub>•nH<sub>2</sub>O, dans laquelle 1 < x < 2, et R = Mn, Fe, Mg, Zn. 3) Il y a ensuite les minéraux ayant des lacunes dans les sites M2 et plus de trois positions de cations en dehors de la trame (vuoriyarvite et ses analogues). Une solution solide étendue impliquant Ti et Nb, Na et K est typique de ces phases. 4) Enfin, il y a les minéraux adoptant la structure de la kuzmenkoïte, qui montrent une prédominance de Mn, Fe, Mg, ou Zn dans les sites M2, et deux positions externes à la trame. Une faible teneur en Na est typique de ces minéraux, dont la formule (Z = 1) serait: K<sub>4</sub>□<sub>4</sub> [(Mn,Fe...)\_{2}(H<sub>2</sub>O)<sub>4</sub>] [(Ti,Nb)<sub>8</sub>(OH,O)<sub>8</sub>] [Si<sub>4</sub>O<sub>12</sub>]<sub>4</sub>•nH<sub>2</sub>O.

*Mots-clés:* labuntsovite, composition chimique, solution solide, structure cristalline.

## INTRODUCTION

Labuntsovite has been considered a very rare mineral. Recently, however, labuntsovite and related minerals have been found in various pegmatites and hydrothermal deposits of alkaline, and especially apgaitic composition, as well as carbonatites (Chukanov *et al.* 1999, Golovina *et al.* 1998, Horváth *et al.* 1998, Konev *et al.* 1996, Mandarinov & Anderson 1989, Petersen *et al.* 1996, Rastsvetaeva *et al.* 1994, 1996, 1997a, 1998, Subbotin *et al.* 1998).

Labuntsovite was first discovered by A.N. Labuntsov in 1925 at the Yum'egor Pass, Khibina alkaline massif, Kola Peninsula, and briefly described under the name "titanium elpidite", as its crystal morphology resembles that of elpidite, but chemically it exhibits a predominance of Ti over Zr (Labuntsov 1926). In 1949, the mineral was found by E.I. Semenov in several localities of the neighboring Lovozero alkaline massif, and named labuntsovite (Semenov & Burova 1955). These authors mentioned the principal compositional difference between this mineral and elpidite, and proposed for labuntsovite the following formula: (K,Na,Ba,Ca,Mn)(Ti,Nb) [Si<sub>2</sub>(O,OH)<sub>7</sub>] • 0.6H<sub>2</sub>O.

The orthorhombic symmetry of labuntsovite was deduced from goniometric data (Semenov & Burova 1955). Subsequently, it was established that in contrast to nenadkevichite, labuntsovite is monoclinic (Kuz'menko & Kazakova 1955, Semenov 1959) but both of them have close stoichiometry and similar X-ray-diffraction patterns. The existence of an isomorphous series between labuntsovite and nenadkevichite has been proposed (Semenov 1959), but a structural difference between these two minerals was inferred from the compositional data (Bulakh & Evdokimov 1973). The solution of crystal structures of labuntsovite (Golovastikov 1973) and nenadkevichite (Perrault *et al.* 1973) has shown that nenadkevichite is orthorhombic (space group *Pbam*), but labuntsovite is monoclinic. The change in symmetry results from different configuration of the titano- or niobosilicate framework, composition and distribution of alkaline and alkaline-earth cations.

Wet-chemical and electron-probe analyses show a wide variation of chemical composition for labuntsovite (Bulakh & Evdokimov 1973, Konev *et al.* 1996, Organova *et al.* 1976, Subbotin *et al.* 1998). Hence, such terms as "potassian labuntsovite", "niobolabuntsovite", "monoclinic nenadkevichite", "titanium nenadkevichite", *etc.* may be found in the literature (Organova *et al.* 1976, Kostyleva-Labuntsova *et al.* 1978). It has been established that the structural features of monoclinic labuntsovite-type minerals are different depending on their composition (Golovina *et al.* 1998, Organova *et al.* 1976, 1981, Rastsvetaeva *et al.* 1994, 1996, 1997a, 1998), but the correlation between composition and crystal structure has not been discussed. Consequently, the incorrect formula (K,Ba,Na)(Ti,Nb)(Si,Al)<sub>2</sub>(O,OH)<sub>7</sub>•H<sub>2</sub>O is commonly used for labuntsovite in mineralogical practice. This formula reflects neither real compositions nor correct structural features of labuntsovite.

We have compiled the published data on the composition and crystal chemistry of monoclinic labuntsovite-type phases and examined a representative collection of these minerals (25 samples) from alkaline massifs of Kola Peninsula (Khibina, Lovozero, Kovdor, and Turii Mys) and Siberia (Murun). Their compositional characteristics are given in Table 1. The examined samples are briefly described in the Appendix.

## EXPERIMENTAL METHODS

The parameters of the monoclinic unit-cells have been refined with an ENRAF-NONIUS CAD-4F diffractometer (monochromatized MoK $\alpha$  diffraction,  $\lambda$  0.71073 Å). The software package AREN (Andrianov 1987) was used in all the calculations. The structure was determined by direct methods on the basis of the centrosymmetric space-group *Fmmm*. A refinement of the phases of structure amplitudes enabled us to locate all the atoms that form the octahedral and tetrahedral components of the framework. At the final stage, all positions, including those of H<sub>2</sub>O, alkaline and large alkaline-earth atoms, were refined. The details of the experiment and methods used to refine the structure for

TABLE 1. PROPORTION OF CATIONS IN LABUNTSOVITE AND RELATED MINERALS

	Na	K	Ba	Sr	Mg	Mn	Fe	Ti	Nb	Si	Al	Other components	Ref.
1	4.04	5.48	1.06	-	0.49	0.04	0.09	7.96	-	15.93	0.07		1
2	4.10	4.72	0.15	-	0.64	0.05	0.50	7.88	-	15.98	0.02		1
3	4.37	3.69	1.14	-	1.01	-	0.06	7.69	-	16	-		2
4	3.94	5.30	0.97	-	0.16	0.04	0.57	8.05	0.03	16	-		2
5	3.88	3.32	1.49	-	-	0.12	0.53	7.78	0.04	15.81	0.19		3
6	3.76	3.85	1.29	0.01	0.87	0.03	0.30	7.88	0.06	16	-	Zr <sub>0.02</sub> Zn <sub>0.01</sub>	3
7	3.71	3.75	1.78	-	-	0.38	0.30	8.00	0.07	15.84	0.16	Ca <sub>0.20</sub>	4
8	4.35	3.73	2.08	-	0.24	0.56	0.13	7.97	0.08	16	-		3
9	4.11	3.40	1.53	-	-	0.29	0.68	8.00	0.11	15.81	0.19	Ca <sub>0.34</sub>	4
10	3.50	3.55	1.56	-	0.58	0.08	0.50	7.80	0.14	16	-	Zr <sub>0.02</sub>	3
11	4.04	3.61	1.56	-	-	0.10	0.73	8.06	0.15	15.86	0.14		4
12	4.38	3.77	1.59	-	0.47	0.14	0.33	8.00	0.15	15.81	0.19		4
13	2.80	3.56	1.49	-	0.04	0.60	0.59	7.47	0.20	15.99	0.01	Zr <sub>0.01</sub> Zn <sub>0.01</sub>	3
14	4.16	3.97	1.99	0.03	0.40	0.09	0.47	7.64	0.21	16	-		3
15	4.45	4.64	1.59	-	1.08	0.07	0.81	7.96	0.21	16	-	Ca <sub>0.05</sub>	4
16	4.43	5.11	0.28	-	0.12	0.74	0.41	7.69	0.22	16	-		2
17	2.44	3.62	1.35	-	0.25	0.76	0.42	7.49	0.25	15.41	0.59	Ca <sub>0.51</sub>	5
18	2.40	3.59	1.34	-	0.24	0.78	0.45	7.46	0.25	15.40	0.60	Ca <sub>0.49</sub>	4
19	4.88	3.78	1.24	-	0.10	0.75	0.20	7.42	0.31	16	-		2
20	4.20	4.59	1.51	-	0.15	-	0.88	7.72	0.36	16	-		3
21	4.28	3.97	1.45	0.08	0.21	0.61	0.22	7.85	0.38	15.98	0.02	Zr <sub>0.02</sub> Zn <sub>0.04</sub>	3
22	3.99	3.99	1.31	-	0.59	0.04	0.59	7.63	0.38	16	-	Zr <sub>0.02</sub> Zn <sub>0.03</sub>	3
23	3.21	4.30	0.97	-	0.85	-	0.43	7.51	0.47	16	-	Zr <sub>0.05</sub>	3
24	4.08	4.87	1.36	-	0.24	-	0.64	7.63	0.58	16	-		3
25	4.59	3.86	1.58	-	0.21	0.66	0.36	6.84	0.61	15.64	0.36	Zr <sub>0.31</sub> Ca <sub>0.20</sub>	4
26	3.52	4.55	1.25	-	0.22	-	0.70	7.38	0.69	16	-		3
27	0.46	3.43	0.17	-	0.17	1.26	0.36	7.11	0.81	16	-		6
28	4.52	6.37	0.39	-	0.08	0.23	0.19	7.08	0.85	16	-		2
29	4.42	4.14	0.56	-	0.23	1.26	0.21	6.83	0.87	16	-		3
30	3.83	6.11	0.13	0.07	0.03	0.18	0.03	7.33	0.92	15.98	0.02		3
31	1.65	4.61	0.12	0.01	0.03	0.84	0.15	6.84	1.40	16	-	Zr <sub>0.02</sub> Zn <sub>0.01</sub>	3
32	2.76	3.97	0.10	-	0.07	1.46	0.22	6.48	1.62	16	-		3
33	3.13	4.57	0.16	0.01	0.18	0.47	0.16	6.19	1.66	16	-	Zr <sub>0.03</sub> Zn <sub>0.05</sub>	3
34	4.06	3.85	1.54	0.01	0.01	0.61	0.21	6.28	1.77	16	-		3
35	4.29	5.45	0.69	-	0.06	0.43	0.18	5.99	1.84	16	-	Zr <sub>0.14</sub>	3
36	3.32	4.86	1.03	0.01	0.01	0.22	0.03	6.11	1.98	16	-		3
37	4.20	6.78	0.01	-	0.02	0.40	0.03	5.31	2.34	15.94	0.06	Ca <sub>0.02</sub>	3
38	4.13	7.64	-	-	-	-	-	5.56	2.45	16	-		7
39	1.49	1.33	0.28	0.81	-	-	-	5.49	2.61	16	-	Zn <sub>1.37</sub>	3
40	2.82	4.90	0.84	0.02	0.02	0.37	0.70	4.69	3.47	16	-	Zr <sub>0.02</sub> Zr <sub>0.03</sub> Ca <sub>0.01</sub>	3
41	3	1.5	-	-	-	-	-	3.8	4.2	16	-	Ca <sub>1.5</sub>	2
42	1.37	2.70	0.51	0.10	-	1.87	-	3.16	4.96	15.85	0.15		3
43	3.28	3.76	0.16	-	-	-	-	0.88	7.28	15.84	0.16	Ca <sub>0.48</sub>	8
44	2.36	4.04	0.56	-	-	-	-	0.28	7.36	16	-		9

Note: the samples are arranged in order of increasing Nb content. Atomic proportions are expressed in atoms per formula unit calculated on the basis of Si + Al = 16. References: 1 Konev *et al.* (1996), 2 Organova *et al.* (1976), 3 this work, 4 Evdokimov (1982), 5 Golovastikov (1973), 6 Chukanov *et al.* (in press), 7 Rastsvetaeva *et al.* (1996), 8 Petersen *et al.* (1996), 9 Subbotin *et al.* (1997).

microtwinning specimens (#8–10 in Table 2) are described elsewhere (Rastsvetaeva *et al.* 1994, 1996, 1997a, 1998, Golovina *et al.* 1998).

The electron-microprobe analyses were performed using a CAMEBAX analyzer equipped with a Link AN 10000 spectrometer, and a diameter of the electron beam ranging from 2 to 4  $\mu\text{m}$  and a current of 1.2 nA. The standards used are: albite (for Na and Al), orthoclase (for K), wollastonite (for Si and Ca), synthetic SrSO<sub>4</sub> (for Sr), synthetic BaSO<sub>4</sub> (for Ba), MgO (for Mg), pure Fe, Mn, Zn, Ti, Nb, and Zr.

The IR spectra of the specimens, prepared as pellets with KBr, were recorded using a Specord 75 IR spectrophotometer with resolution  $\leq 3 \text{ cm}^{-1}$  in the region 400–2000  $\text{cm}^{-1}$ , and  $\leq 8 \text{ cm}^{-1}$  in the region 2000–3700

$\text{cm}^{-1}$ . The wavenumber standards used are NH<sub>3</sub> and polystyrene.

#### STRUCTURAL FEATURES OF MONOCLINIC LABUNTSOVITE-TYPE MINERALS

Orthorhombic phases are not described in this work. All known orthorhombic minerals with a labuntsovite-like structure are members of only one isomorphous series between nenadkevichite, Na<sub>3-x</sub>(Nb,Ti)<sub>2</sub>[Si<sub>4</sub>O<sub>12</sub>](OH)<sub>2</sub>·nH<sub>2</sub>O, and korobitsynite, recently approved by the CNMMN, IMA (no. 98–019) as a new mineral species having the composition Na<sub>3-x</sub>(Ti,Nb)<sub>2</sub>[Si<sub>4</sub>O<sub>12</sub>](OH,O)<sub>2</sub>·nH<sub>2</sub>O (Pekov *et al.* 1999). The crystal structure of both minerals is known (Perrault *et al.* 1973,

TABLE 2. CRYSTAL-STRUCTURE CHARACTERISTICS OF LABUNTSOVITE AND RELATED MONOCLINIC MINERALS

#	§	Mineral	a, Å	b, Å	c, Å	β, °	A3 <sub>total</sub>	M2	M1	Ref.
1	17	Labuntsovite	14.18	13.70	7.74	117.0	(K,Ba) <sub>2</sub> (OH) <sub>2</sub>	□ <sub>1,0</sub> (Ti,Nb) <sub>1,0</sub>	Ti <sub>8</sub>	1
2	19	Labuntsovite	14.24	13.77	7.78	116.8	(Ba,K) <sub>2,4</sub> (H <sub>2</sub> O,OH) <sub>1,6</sub>	□ <sub>1,2</sub> Ti <sub>0,4</sub> Nb <sub>0,3</sub> Mg <sub>0,1</sub>	Ti <sub>8</sub>	2
3	16	Labuntsovite	14.29	13.85	7.78	116.8	(H <sub>2</sub> O,OH,K) <sub>4</sub>	Mn <sub>0,7</sub> Fe <sub>0,4</sub> Nb <sub>0,22</sub> □ <sub>0,68</sub>	Ti <sub>8</sub>	2
4	8	"Ba-labuntsovite"	14.22	13.75	7.77	116.7	Ba <sub>2,2</sub> (H <sub>2</sub> O) <sub>1,8</sub>	□ <sub>1,1</sub> Mn <sub>0,9</sub>	Ti <sub>8</sub>	3, 4
5	16	K-rich labuntsovite	14.33	13.83	7.79	117.1	K <sub>2,6</sub> Ba <sub>0,8</sub> (H <sub>2</sub> O) <sub>0,6</sub>	□ <sub>1,7</sub> Mn <sub>0,15</sub> Fe <sub>0,1</sub> Mg <sub>0,05</sub>	Ti <sub>7,2</sub> Nb <sub>0,8</sub>	5, 4
6	37	K-rich labuntsovite	14.42	13.91	7.80	116.9	K <sub>3,2</sub> (H <sub>2</sub> O) <sub>0,8</sub>	□ <sub>1,6</sub> Mn <sub>0,4</sub>	Ti <sub>4,4</sub> Nb <sub>1,6</sub>	5, 4
7	27	Kuzmenkoite	14.37	13.91	7.81	117.1	K <sub>0,6</sub> (H <sub>2</sub> O) <sub>3,4</sub>	Mn <sub>1,3</sub> Fe <sub>0,2</sub> Mg <sub>0,2</sub> □ <sub>0,3</sub>	Ti <sub>7,0</sub> Nb <sub>1,0</sub>	6, 7
8	38	"K,Ti-nenadkevichite"	14.39	13.90	7.83	117.6	K <sub>4</sub>	□ <sub>2</sub>	Ti <sub>5,6</sub> Nb <sub>2,4</sub>	8
9	41	"Ti-nenadkevichite"	14.75	14.37	8.01	117.4	(Na,Ca,K, Sr,□) <sub>4</sub> ?	□ <sub>2</sub>	Nb <sub>4,2</sub> Ti <sub>3,8</sub>	9
10	44	Vuoriyarvite	14.69	14.16	7.86	117.9	(K,Na,□) <sub>4</sub>	□ <sub>2</sub>	Nb <sub>4,4</sub> Ti <sub>3,6</sub>	10, 11

The unit-cell parameters for the samples 1–3, 7 are given in a consistent orientation corresponding to space group *C2/m* (for vuoriyarvite, *Cm*), *Z* = 1. The Sr content of sample 7 has been determined recently, during its re-examination. Samples 2 and 3 have been described as "labuntsovite-I" and "labuntsovite-II", respectively, by Organova *et al.* (1981). A3<sub>total</sub> includes A3 cations and H<sub>2</sub>O molecules in the complex M2(H<sub>2</sub>O)<sub>2</sub> (the distance between the A3 position and the position of these H<sub>2</sub>O molecules is ~0.3 Å). In earlier works (Golovastikov *et al.* 1973, Organova *et al.* 1976), the existence of the complex [M2(OH)<sub>2</sub>]<sup>2+</sup> had been proposed. The positions A1 and A2 are occupied with Na and K, respectively. References: 1 Golovastikov *et al.* (1973), 2 Organova *et al.* (1981), 3 Rastsvetaeva *et al.* (1997), 4 this work, 5 Rastsvetaeva *et al.* (1998), 6 Golovina *et al.* (1998) 7 Chukanov *et al.* (in press), 8 Rastsvetaeva *et al.* (1996), 9 Organova *et al.* (1976), 10 Rastsvetaeva *et al.* (1994), 11 Subbotin *et al.* (1998). # Sample number, § sample number in Table 1.

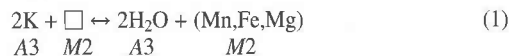
Rastsvetaeva *et al.* 1997b); it contains zeolite-like cavities of only one type. Their small size excludes any significant occupancy by large cations like K, Ba, and Sr for minerals of this series.

On the other hand, monoclinic members differ in crystal-structure features. The summarized structural data (Golovastikov 1973, Organova *et al.* 1976, 1981, Rastsvetaeva *et al.* 1996, 1997a, 1998) give the following general formula for labuntsovite and isostructural monoclinic minerals (*Z* = 1): A<sub>1</sub>4A<sub>2</sub>4A<sub>3</sub>4–2<sub>x</sub> [M<sub>2</sub><sub>x</sub>(H<sub>2</sub>O)<sub>2x</sub>] [M<sub>1</sub>8(O,OH)<sub>8</sub>] [Si<sub>4</sub>O<sub>12</sub>]<sub>4</sub>•nH<sub>2</sub>O (usually, *n* ≈ 8), where *x* varies from 0 to 2; A<sub>1</sub> = Na, Ca, □; A<sub>2</sub> = K, Na, H<sub>3</sub>O, □; A<sub>3</sub> = K, Ba, Sr, H<sub>3</sub>O, □; M<sub>1</sub> = Ti, Nb; M<sub>2</sub> = Mn<sup>2+</sup>, Fe<sup>2+</sup>, Mg, Zn, □. Molecules of H<sub>2</sub>O [(H<sub>2</sub>O)<sub>2x</sub>] may compensate for the cation deficiency at the A<sub>3</sub> site if K, Ba, Sr or H<sub>3</sub>O are absent in this position. The crystal structure of these minerals is built of columns of M<sub>1</sub> octahedra linked by four-membered rings [Si<sub>4</sub>O<sub>12</sub>] and, in addition, by M<sub>2</sub> octahedra. Atoms of alkaline and alkaline-earth elements and H<sub>2</sub>O molecules occupy numerous cavities in this framework, creating a structural resemblance with zeolites (Organova *et al.* 1976).

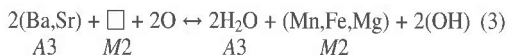
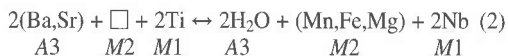
Some of structurally investigated monoclinic labuntsovite-type minerals are characterized by the presence of additional cation-bearing octahedra linking the columns of Ti(Nb) octahedra into bands or layers (Golovastikov 1973, Organova *et al.* 1976, 1981, Rastsvetaeva *et al.* 1997a, 1998, Golovina *et al.* 1998),

whereas so-called "monoclinic nenadkevichite" (Organova *et al.* 1976, Rastsvetaeva *et al.* 1994, 1996) does not contain additional cation octahedra. In the last case, the absence of linking M<sub>2</sub> octahedra promotes the occupancy of two neighboring A<sub>3</sub> positions by large cations (K, Ba or Sr), thus stabilizing the monoclinic structure of the mineral. In the presence of linking octahedra, these positions contain H<sub>2</sub>O.

The structural characteristics of six samples of labuntsovite, one sample of kuzmenkoite (recently approved by the CNMMN, IMA, no. 98–058) (see below), and three samples of "monoclinic analogues of nenadkevichite" are given in Table 2. The samples of labuntsovite (#1–6 in Table 2) are characterized by an identical structure and wide variations in the occupancies of the A<sub>3</sub> and M<sub>2</sub> sites. Isomorphous substitutions in "monoclinic nenadkevichite" (#8–10 in Table 2), including the recently discovered mineral vuoriyarvite (see below), affect mainly the M<sub>1</sub> sites (Ti–Nb), and A-sites (Na–K). In labuntsovite and kuzmenkoite (#7 in Table 2), smaller R<sup>2+</sup> cations (Mg, Mn, Fe) tend to occupy the M<sub>2</sub> sites (linking octahedra). The A<sub>3</sub> and M<sub>2</sub> positions are related and occupied according to the following mechanism:



In the case of alkaline-earth cations the following mechanisms are possible:



These schemes of substitution are made possible because a distance between the A3 and M2 positions is short, and the simultaneous presence of large cations (K, Ba, Sr) at the A3 site, and  $R^{2+}$  cations at the M2 site is impossible.

In earlier works (Golovastikov 1973, Organova *et al.* 1976), the presence of Ti and Nb atoms in the M2 position has been supposed. Under this assumption, the presence of OH groups in the A3 position is possible from the viewpoint of local charge-balance. Recent data (Rastsvetaeva *et al.* 1997a, 1998, Golovina *et al.* 1998) show that the M2 position is occupied only with  $R^{2+}$  cations (Fe, Mn, Mg) forming the complexes  $[R(\text{H}_2\text{O})_2]^{2+}$ . Minerals with above-mentioned structure are widely distributed.

Two new monoclinic labuntsovite-type mineral species, vuoriyarvite and kuzmenkoite, were described recently. These minerals differ from labuntsovite in the configuration of the framework, the number of extra-framework cation sites, and the nature of their occupancy. Vuoriyarvite,  $(\text{K,Na})_2(\text{Nb,Ti})_2\text{Si}_4\text{O}_{12}(\text{O,OH})_2 \cdot 4\text{H}_2\text{O}$ , space group *Cm*, is characterized by the absence of linking M2 octahedra; this mineral is virtually devoid of Mg, Mn, Fe, and Zn. The structure of vuoriyarvite contains four sites occupied by K, three occupied by Na, and five sites occupied with  $\text{H}_2\text{O}$  molecules; the degree of occupancy of all these sites varies from 1/4 to 3/4 (Rastsvetaeva *et al.* 1994, Subbotin *et al.* 1998).

Kuzmenkoite,  $\text{K}_2(\text{Mn,Fe}) (\text{Ti,Nb})_4 [\text{Si}_4\text{O}_{12}]_2(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ , space group *C2/m*, is a Na-free or Na-poor mineral with only two extra-framework cation sites. The A1 position (occupied with Na in labuntsovite) is absent in kuzmenkoite. This absence seems to be a result of significant distortion of the framework (in comparison with that of labuntsovite) (Golovina *et al.* 1998, Chukanov *et al.*, 1999).

#### COMPOSITIONAL VARIATION AND SOLID SOLUTION

Formulae of 44 samples of monoclinic labuntsovite-type minerals were calculated from results of wet-chemical and electron-microprobe analyses on the basis of 16 tetrahedrally coordinated cations (Si + Al). For each of 25 samples studied in this work, average compositions were calculated from results of 7–10 electron microprobe analyses. The data presented in Tables 1 and 2 demonstrate that:

1. The total number of octahedrally coordinated cations  $\Sigma^{[\text{VI}]}R = \text{Ti, Nb, Zr, Mn, Fe, Mg, Zn}$  per unit cell ( $Z = 1$ , *i.e.*, Si + Al = 16) ranges from 8 to 10. Among these cations, the total amount of high-field-strength elements Ti, Nb and Zr per formula unit (*apfu*) is 8.

Hence, the number of cations in excess of 8 *apfu* octahedral cations is practically identical to amount of Mn, Mg, Fe, Zn (Fig. 1). These cations (effective ionic radii about 0.7–0.8 Å) exhibit a strong tendency to occupy the M2 sites (linking octahedra).

2. The number of octahedrally coordinated cations  $\Sigma^{[\text{VI}]}R = 8 + x$  decreases with increasing content of alkaline and large alkaline-earth (Ba, Sr) cations. However, most of the actual compositions are displaced to the left (Fig. 2) relative to the theoretical line calculated from the substitution schemes (1–3). This displacement may result from the distribution of excess (>4 *apfu*) Na atoms in A2 (more likely) or in A3 sites. Another possible explanation is the presence of vacancies at the A2 and A3 positions or possible partial occupancy of these sites by  $\text{H}_3\text{O}^+$  ions. The presence of hydronium ions in labuntsovite has been inferred from infrared (IR) spectroscopy data by Arkhipenko *et al.* (1977). The IR spectra of some specimens of  $R^{2+}$ -enriched labuntsovite also contain a weak narrow band of stretching vibrations of non-hydrogen-bonded OH-groups, which absorb in the region 3620–3640  $\text{cm}^{-1}$ . The frequency 3620  $\text{cm}^{-1}$  is characteristic for Mn- and Fe-rich varieties of labuntsovite, whereas a band at 3640  $\text{cm}^{-1}$  is observed in IR spectra of Mg-enriched labuntsovite. A minor (OH) content may be present at the A3 site, related with M2 cations.

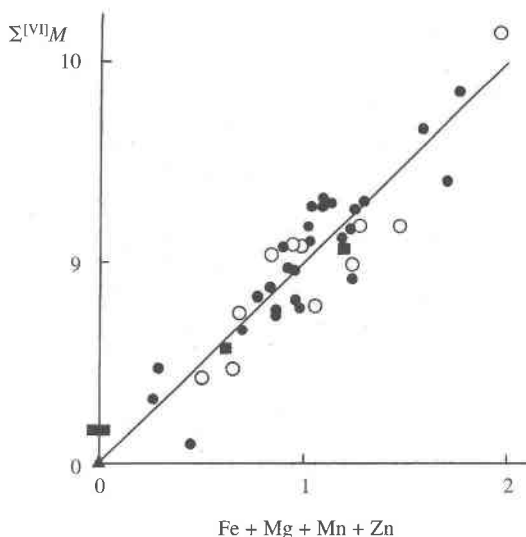


FIG. 1. The correlation between the total number of octahedrally coordinated cations (*apfu*) and the number of low-field-strength octahedrally coordinated cations (Mn, Mg, Fe, Zn) for monoclinic labuntsovite-type minerals: ●: present work, ○: Organova *et al.* (1976), ■: Konev *et al.* (1996), ▲: Rastsvetaeva *et al.* (1996), ???: Petersen *et al.* (1996).

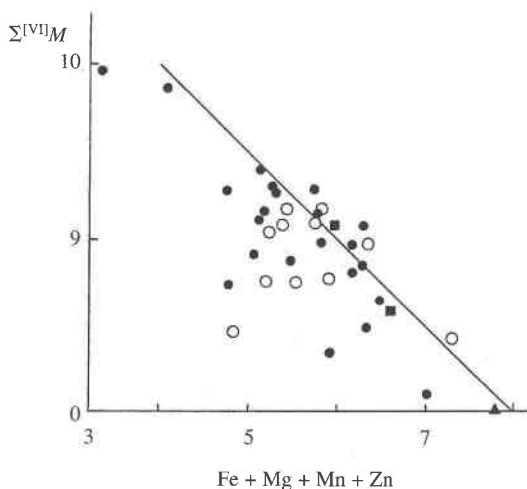


FIG. 2. The correlation between the total number of octahedrally coordinated cations (*apfu*) and the number of "large cations" (K, Ba, Sr, Na<sup>(2)</sup>) for monoclinic labuntsovite-type minerals: ●: present work, ○: Organova *et al.* (1976), ■: Konev *et al.* (1996), ▲: Rastsvetaeva *et al.* (1996). Na<sup>(2)</sup> is the number of Na atoms in excess of 4 *apfu*.

3. The K content varies from 2.7 to 8.0 *apfu*. If the K content is  $\leq 4$  *apfu*, K atoms mainly occupy the A2 site. The K atoms in excess of 4 *apfu*, together with the majority of Ba, occupy the A3 position (Rastsvetaeva *et al.* 1997a, 1998), which is confirmed by IR data. In IR spectra of K-poor labuntsovite ( $K \leq 4$  *apfu*), the band of

asymmetrical Si–O–Si stretching vibrations near 1050  $\text{cm}^{-1}$  is absent (Fig. 3). The increase in K content from 4 to 8 *apfu* leads to activation of this band (Fig. 4). This finding is explained by the occupancy of the A3 position by Ba and the excess in K over 4 *apfu*.

4. The Na content in labuntsovite is usually close to 4 *apfu*. An excess in Na (denoted as Na<sup>(2)</sup> on Fig. 2), can be distributed between the A2 and A3 positions.

The above-described data suggest that several phases can exist with the structure of labuntsovite. These differ in site occupancies in the crystal structure. In this work, we do not discuss the nomenclature status of these phases (mineral species, varieties, *etc.*), but consider four subgroups of monoclinic labuntsovite-type minerals.

Subgroup 1. Minerals with the labuntsovite structure (space group *C2/m*) characterized by three A positions, and a predominance of vacancies in the M2 octahedra; more than 50% of A3 positions are occupied by large cations (K, Ba, Sr, H<sub>3</sub>O).  $R^{2+} = \text{Mn, Mg, Fe, and Zn}$ , and  $x < 1$  for all formulae.

1.1. A mineral with a predominance of K<sup>+</sup> in the A3 position (Rastsvetaeva *et al.* 1996, 1998; #28, 37, 38 in Table 1; #5, 6, 8 in Table 2):  $\text{Na}_4\text{K}_4\text{K}_{4-2x}[\text{R}^{2+}_x(\text{H}_2\text{O})_{2x}][\text{Ti}_8(\text{O,OH})_8][\text{Si}_4\text{O}_{12}]_4 \cdot n\text{H}_2\text{O}$ .

1.2. A mineral with a predominance of Ba<sup>2+</sup> in the A3 position (Rastsvetaeva *et al.* 1997a; #4 in Table 1; see Fig. 5):  $\text{Na}_4\text{K}_4\text{Ba}_{4-2x}[\text{R}^{2+}_x(\text{H}_2\text{O})_{2x}][\text{Ti}_8(\text{O,OH})_8][\text{Si}_4\text{O}_{12}]_4 \cdot n\text{H}_2\text{O}$ .

1.3. A mineral with a predominance of (H<sub>3</sub>O)<sup>+</sup> in the A3 position; it is not known to occur in nature with certainty, but labuntsovite from the Trona mine, Wyoming (Organova *et al.* 1976, Milton *et al.* 1958; #3 in Table 1), may represent such a phase:  $\text{Na}_4\text{K}_4(\text{H}_3\text{O})_{4-2x}[\text{R}^{2+}_x(\text{H}_2\text{O})_{2x}][\text{Ti}_8(\text{O,OH})_8][\text{Si}_4\text{O}_{12}]_4 \cdot n\text{H}_2\text{O}$ .

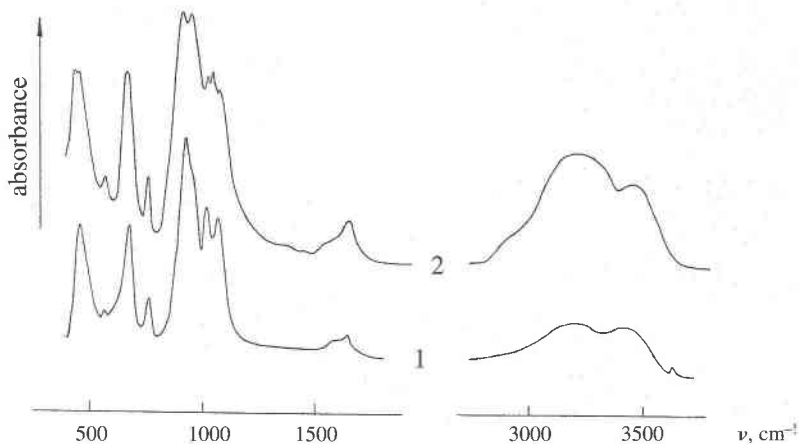


FIG. 3. IR spectra of potassium-poor (curve 1, corresponds to #8 in Table 1) and potassium-rich (curve 2, corresponds to #30 in Table 1) labuntsovite-type minerals.

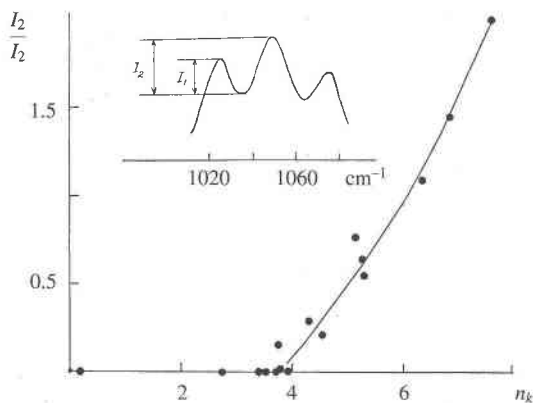


FIG. 4. The dependence of relative intensity of asymmetric Si-O-Si stretching vibrations in IR spectra of labuntsovite on potassium content.

Subgroup 2. Labuntsovite proper, characterized by three  $A$  positions, with a predominance of  $R^{2+}$  cations in the  $M2$  position (linking octahedra) and a predominance of  $H_2O$  in the  $A3$  position (space group  $C2/m$ ). Its general formula is:  $Na_4K_4(K,Ba,\dots)_{4-2x} [R^{2+}_x(H_2O)_{2x}] [Ti_8(O,OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ , where  $1 < x < 2$  and  $R^{2+} = Mn, Fe, Mg, Zn$ . In accordance with isomorphous substitutions at  $M2$ , the following members can be distinguished:

2.1. Mn-dominant member,  $R = Mn$  (probably #32 in Table 1).

2.2. Mg-dominant analogue of 2.1,  $R = Mg$  (probably #23 in Table 1).

2.3. Zn-dominant analogue of 2.1,  $R = Zn$  (probably #39 in Table 1).

2.4. Fe-dominant analogue of 2.1,  $R = Fe$  (probably #20 in Table 1).

The formula of a hypothetical end-member with a fully occupied  $M2$  position is  $Na_4K_4\Box_4 [R^{2+}_2(H_2O)_4] [Ti_8(O,OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ . The composition of natural labuntsovite ranges between this formula and that of an end-member with an empty  $M2$  position.

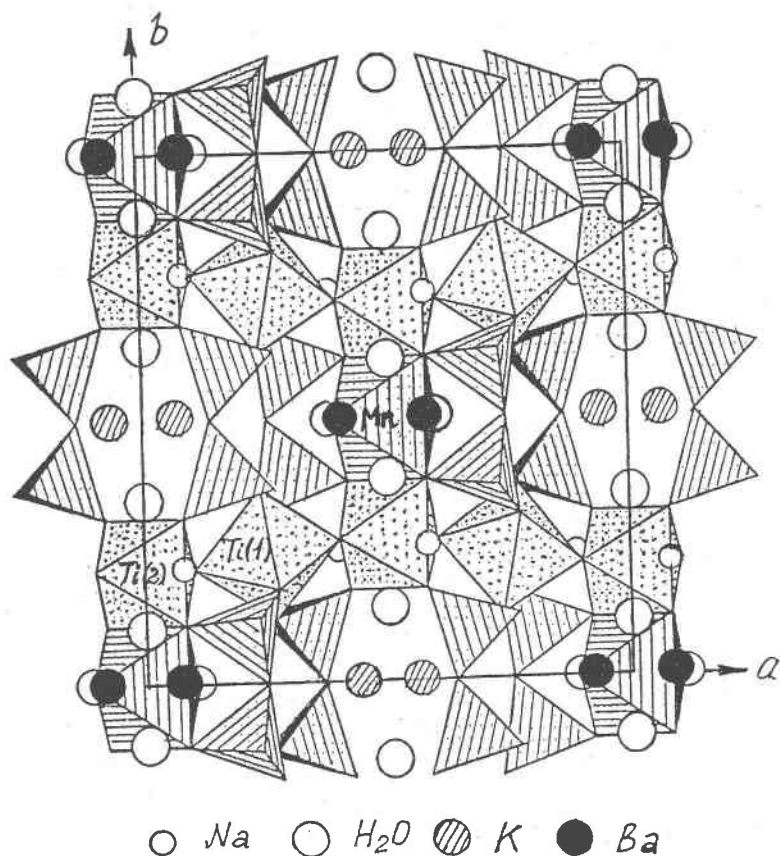


FIG. 5. The crystal structure of "Ba-labuntsovite", an analogue of labuntsovite with a high degree of order between potassium and barium (#8 in Table 1 and #4 in Table 2).

Subgroup 3. Minerals with vacant  $M2$  positions and more than three  $A$  positions (space group  $Cm$  or  $C2/m$ ). These show a chain motif of octahedra, and broad isomorphism involving Ti and Nb, Na and K. Such minerals were described as "monoclinic nenadkevichite" or "monoclinic analogues of nenadkevichite". It seems that the latter name is more correct since nenadkevichite is an orthorhombic mineral with an essentially different structure. Monoclinic analogues of nenadkevichite exhibit a strong tendency to microtwinning resulting from vacancies at the  $M2$  site (Organova *et al.* 1976, Rastsvetaeva *et al.* 1994).

### 3.1. Nb-dominant phases:

3.1.1. Vuoriyarvite,  $Cm$  (Rastsvetaeva *et al.* 1994, Subbotin *et al.* 1998; #44 in Table 1, #10 in Table 2):  $(K, Na, \square)_{12} [(Nb, Ti)_8(O, OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

3.1.2. An analogue of vuoriyarvite with  $Na > K$ ,  $C2/m$  (Organova *et al.* 1976; #41 in Table 1, #9 in Table 2):  $(Na, Sr, K, Ca, \square)_{12} [(Nb, Ti)_8(O, OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

A high content of Sr has been recently determined in this specimen. It is possible that  $Sr^{2+}$  can stabilize a monoclinic structure similar to other large cations:  $Ba^{2+}$ ,  $K^+$ ,  $H_3O^+$ .

### 3.2. Ti-dominant phases:

3.2.1. Ti-dominant analogue of phase 3.1.2. (not studied in detail; the approximate composition is  $Na_{3.6}Sr_{1.4}Ba_{0.8}Ca_{0.2}K_{0.1}Ti_{5.0}Nb_{3.0}(O, OH)_8 [Si_4O_{12}]_4 \cdot nH_2O$ ). The general formula is:  $(Na, Sr, K, Ca, \square)_{12} [(Ti, Nb)_8(O, OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

Subgroup 4. Minerals with the kuzmenkoite structure, with a distorted framework, two  $A$  positions and a predominance of  $R^{2+}$  cations in the  $M2$  position (space group  $C2/m$ ).

### 4.1. Ti-dominant phases:

4.1.1. Kuzmenkoite (Golovina *et al.* 1998, Chukanov *et al.* 1999, #27 in Table 1, #7 in Table 2). The general formula ( $Z = 1$ ) is:  $K_4\square_4 [(Mn, Fe)_2(H_2O)_4] [(Ti, Nb)_8(OH, O)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

### 4.2. Nb-dominant phases:

4.2.1. An analog of kuzmenkoite with  $Nb > Ti$  (probably #42 in Table 1). The general formula ( $Z = 1$ ) is:  $(K, Ba, Na)_4\square_4 [(Mn, Zn, Fe, Mg)_2(H_2O)_4] [(Nb, Ti)_8(OH, O)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

This scheme shows some possible principles of classification for monoclinic labuntsovite-type minerals. It is possible that it will be extended with new finds (for example Nb-, Sr- and Ca-dominant analogues of labuntsovite).

As a conclusion, it is interesting to consider the formula of labuntsovite

$(K, Ba, Na, Ca)_8(Ti, Nb)_9(O, OH)_{10}[Si_4O_{12}]_4 \cdot nH_2O$  ( $n \approx 7$ ) proposed by Golovastikov (1973). If the formula is correct, Ti, Nb, and  $R^{2+}$  cations are distributed over all octahedrally coordinated  $M1$  and  $M2$  sites, and the mineral can be considered as a cation-disordered Ti-dominant (for  $M2$  position) species,  $Na_4K_4K_{4-2x}[Ti_1(H_2O)_{2x}][Ti_8(O, OH)_8][Si_4O_{12}]_4 \cdot nH_2O$ . But on the basis of the above- described structural features of

labuntsovite-type minerals, a disordered distribution of octahedrally coordinated cations leading to the predominance of high valence and high-field-strength cations (Ti, Nb) in the  $M2$  positions is unlikely.

## ACKNOWLEDGEMENTS

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## APPENDIX. BRIEF DESCRIPTION OF SAMPLES EXAMINED

The numbers below correspond to numbers in Table 1.

#1, #25. Turii Mys. Brick-red short-prismatic crystals up to 2 mm in cavities of fenitized sandstone; coexists with aegirine, albite, calcite.

#4. Murun. Orange prismatic grains up to 2 mm in pegmatitic rock; coexists with feldspar, aegirine, nepheline, titanite, sulfides.

#6. Khibina, Kirovskii mine. Red prismatic crystals up to 3 mm in cavities of natrolite veinlet in nepheline syenite; coexists with lamprophyllite, aegirine.

#8. Khibina, Kirovskii mine. Orange long-prismatic crystals up to 2 cm in length in cavities of pegmatite veinlet in nepheline syenite; coexists with calcite, stromianite, aegirine, microcline.

#13. Khibina, Kirovskii mine. Orange prismatic crystals up to 0.5 mm in cavities of feldspar pegmatoid veinlet in nepheline syenite; coexists with aegirine.

#20. Khibina, Niorkpakhk Mountain. Red spherulites up to 5 mm in diameter consist of columnar crystals in albite–natrolite pegmatite.

#21. Khibina, Kirovskii mine. Orange long-prismatic crystals up to 1 mm in cavities of microcline-rich pegmatite vein in nepheline syenite; coexists with calcite, aegirine, apatite, sphalerite, molybdenite.

#22. Khibina, Kirovskii mine (drillcore). Orange-red prismatic crystals up to 3 mm form subparallel intergrowths with #21 in cavity of feldspar veinlet in nepheline syenite.

#23. Kovdor. Orange prismatic crystals up to 4 mm in cavities of dolomite carbonatite vein; coexists with dolomite, calcite, catapleite, pyrite, anatase.

#24. Khibina, Niorkpakhk Mountain. Spherulites up to 5 mm in diameter consist of zonally colored (from colorless to brownish red) columnar crystals in albite–natrolite pegmatitic body.

#26. Khibina, Niorkpakhk Mountain. Radial aggregate consists of orange-red columnar crystals up to 2 cm in length in cavities of pegmatitic vein; coexists with feldspar, aegirine, hemimorphite, and Fe–Mn hydrous silicates, among others.

#27. (Kuzmenkoite) Lovozero, Flora Mountain. Yellowish prismatic crystals up to 1 mm in cavities of hydrothermally altered murmanite lujavrite; coexists with natrolite, labuntsovite, calciohilairite, carbonate–fluorapatite.

#29. Khibina, Koashva Mountain. Brick-red isometric crystals up to 3 mm in cavities of albite–aegirine pegmatitic rock.

#30. Khibina, Koashva Mountain (drillcore). Light orange irregular grains up to 1 mm in pectolite–microcline veinlet in urtite.

#31. Khibina, Suoluav Mountain. Brownish prismatic crystals up to 1 mm in cavities of pegmatitic veinlet; coexists with microcline, aegirine, and mangan-neptunite, among others.

#32. Lovozero, Flora Mountain. Yellowish orange prismatic crystals up to 2 mm in cavities of albitized murmanite lujavrite; coexists with microcline, lorenzenite, aegirine, natrolite, apatite.

#33. Khibina, Koashva Mountain. Light-orange thick-tabular crystals up to 1 mm replacing lomonosovite in pegmatite lens in urtite; coexists with murmanite, aegirine, arfvedsonite, microcline, sodalite, lamprophyllite, rinkite.

#34. Khibina, Hackmann Valley. Orange isometric crystals up to 4 mm in microcline–natrolite vein in gneiss-like rischorrite; coexists with aegirine, catapleite, apatite, and barylite, among others.

#35. Khibina, Koashva Mountain. Honey-colored short-prismatic crystals up to 0.2 mm in cavities of pegmatite in urtite; coexists with aegirine, lamprophyllite, barytolamprophyllite.

#36. Khibina, Kirovskii mine. Zonally colored (from colorless to orange) prismatic crystals up to 2 mm in cavities of pegmatite in nepheline syenite; with microcline, lamprophyllite, mangan-neptunite, vinogradovite, apophyllite, calcite.

#37. Khibina, Koashva Mountain. Pale lilac short-prismatic crystals up to 1 mm in cavities of hydrothermally altered hyperagpaitic pegmatite in contact zone between urtite and apatite–nepheline rock; coexists with aegirine, natrolite, pectolite, lomonosovite, sitinakite, belovite-(Ce).

#39. Lovozero, Lepkhe–Nelm Mountain. White flattened prismatic crystals up to 1 cm in cavities of pegmatite lens in nosean syenite; coexists with lamprophyllite, eudialyte, aegirine, microcline, natrolite, apatite, taeniolite, vinogradovite, and titanite, among others.

#40. Khibina, Kirovskii mine (drillcore). Yellowish brown flattened prismatic crystals up to 5 mm form subparallel intergrowths with #19 in cavity of feldspar veinlet in nepheline syenite.

#42. Lovozero, Karnasurt Mountain. Pale pink grains up to 0.1 mm in pseudomorph after vuonnemite in border zone of pegmatite in lujavrite; coexists with nenadkevichite, natrolite, microcline, aegirine, and steenstrupine-(Ce), among others.