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RARE-METAL «ZEOLITES» OF THE HILAIRITE GROUP

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The hilairite group includes hilairite, calciohilairite, komkovite, sazykinaite-(Y) and pyatenkoite-(Y). Their unique structural type is based on a mixed framework of screwed chains (Si_3O_9) and isolated M-octahedra (M = Zr, Ti, Y+Ln); large cations (Na, Ca, Ba, and subordinated K, Sr) and water molecules settle down in extensive zeolite-like cages and channels. Some features of chemical composition and properties of hilairite-group minerals are easily explained if to consider them as specific rare-metal «zeolites». Hilairite-group minerals occur in hydrothermalites of the Khibiny-Lovozero alkaline complex, Kola Peninsula. This paper gives a review of publications on the hilairite group, describes new finds in Khibiny and Lovozero massifs, gives 29 chemical analyses of these minerals, including 17 analyses made by the authors. The isomorphous series hilairite — calciohilairite was established in material from Lovozero, as well as Ba-K- and Sr-containing varieties of calciohilairite. The first finds of hilairite and pyatenkoite-(Y) in Khibiny are described. The comparative analysis of IR spectra of all group members is given for the first time. Crystal chemistry, properties and genesis of hilairite-like minerals are discussed in view of their zeolite-like structure.

4 tables, 2 figures and 27 references.

Introduction

Hilairite crystallochemical group unites five minerals — trigonal (rhombohedral — *R32*) rare-metal silicates with a unique structural motive: hilairite, calciohilairite, komkovite, sazykinaite-(Y) and pyatenkoite-(Y) (Table 1). Infinite screwed chains (Si_3O_9) extended along the main axis make the basis of their structure. Si-tetrahedra are jointed by pendent apices with M-octahedra, forming a mixed framework $\{M(Si_3O_9)\}$, where dominant M-cations in different cases are Zr, Ti, and (Y+Ln). A step of (Si_3O_9) chain along the axis *c* is three Si-tetrahedra; M-octahedra, each of which is connected to three silica-oxygen chains, repeat with the same period. The structure contains large cages and channels, where extra-framework alkaline and alkaline-earth cations (Na, Ca, Ba, and subordinated K and Sr) and water molecules settle down. The structure of hilairite-group minerals includes two nonequivalent octahedric positions of M. In hilairite, calciohilairite and komkovite, Zr sharply prevails in both M-positions, in sazykinaite-(Y) one of them (M1) is selectively occupied with atoms of Y or Ln (with corresponding increase of M-O distance), whereas the second (M2) remains occupied by zirconium; pyatenkoite-(Y) is an isostructural analogue of sazykinaite-(Y), where Zr is replaced by Ti (Ilyushin *et al.*, 1981; Sokolova *et al.*, 1991; Rastsvetaeva and Khomyakov, 1992, 1996; Pushcharovsky *et al.*, 2002).

Hilairite-group minerals are rather rare minerals of hydrothermal rocks related to diverse alkaline complexes: nepheline syenite, alkaline granite, and carbonatite. Despite of being rare, these minerals are very interesting in crystallochemical and genetic relation due to the original structural motif, wide variability of composition at preservation of the motif, unusual type of cation ordering (rare-earth members of the group) and a number of other specific features, which are easy to explain if to consider hilairite-like phases in view of their strongly pronounced zeolite-like structure.

The greatest variety of hilairite-group representatives is observed in hydrothermal rocks of the well-known Khibiny-Lovozero alkaline complex on the Kola Peninsula. All members of the group, except for komkovite, are present here, the number of their finds comes to a dozen; in some cases these minerals are the main concentrators of zirconium, yttrium and heavy lantanides in late paragenesis. This paper is devoted to the description of hilairite-group minerals from new occurrences in Lovozero and Khibiny massifs, and also to the discussion of some interesting mineralogical and crystallochemical features of the entire group.

Occurrence

Hilairite $Na_2ZrSi_3O_9{\cdot}3H_2O$ is the most widespread member of the group. It was discovered by G.Chao at al. (1974) in hydrothermal rocks related to nepheline syenites and alkali-rich pegmatites of agpaitic Mont Saint-Hilaire complex in Quebec, Canada. It associates here with gaidonnayite, elpidite, natrolite, microcline, analcite, albite, aegirine, rutile, zircon, fluorite, calcite, sulfides (Chao *et al.*, 1974; Horvath and Gault, 1990; Horvath and Pfenninger-Horvath, 2000). Hilairite, in association with aegirine, natrolite, serandite, sphalerite, cordylite and zakharovite, also occurs in miarolitic cages of agpaitic nepheline syenite, which makes part of the nearby Saint Amable sill (Horvath *et al.*, 1998). This mineral in late pegmatite paragenesis is related to alkaline and nepheline syenites of Southern Norway: with pyrophanite, astrophyllite, catapleiite, analcite, boehmite, etc. in Bratthagen near Larvik and in Langesundsfjord — on islands Siktesце (with albite, gaidonnayite, zircon) and Vesle Arце (with aegirine and zircon) (Raade, Mladeck, 1977; Raade *et al.*, 1980; Andersen *et al.*, 1996). Hilairite in Vuoriyarvi alkaline-ultrabasic complex in Northern Karelia was described in cavities in dolomite carbonatites in association with carbonate-apatite and pyrite (Voloshin *et al.*, 1989). Hilairite enriched with calcium settles between grains of albite, potassic feldspar, quartz, aenigmatite, and narsarsukite in alkaline granite of the southern part of Strange Lake complex (Quebec-Labrador, Canada). However, the data on chemistry of the mineral are absent because of small quantity of substance (Birkett *et al.*, 1992). Hilairite was also found in alkaline complex Poзos de Caldas in Brazil (Horvath *et al.*, 1998). In the majority of listed cases, this mineral occurs in cavities, where forms light (colorless, white, pink, cream, light brown) subisometric crystals up to 4 mm with faces {11-20} and {01-12}, sometimes also {-1-120} (class of symmetry

Table 1. **Comparative characteristics of hilairite-group minerals**

Mineral	**Hilairite**	**Calciohilairite**	**Komkovite**	**Sazykinaite-(Y)**	**Pyatenkoite-(Y)**
Idealized formula	$Na_2ZrSi_3O_9 \cdot 3H_2O$	$CaZrSi_3O_9 \cdot 3H_2O$	$BaZrSi_3O_9 \cdot 3H_2O$	$Na_5YZrSi_6O_{18} \cdot 6H_2O$	$Na_5YTiSi_6O_{18} \cdot 6H_2O$
Symmetry	Trigonal, *R*32	Trigonal, *R*32	Trigonal, *R*32	Trigonal, *R*32	Trigonal, *R*32
Unit cell parameters					
a, Å	10.556	10.498	10.52	10.825	10.696
c, Å	15.855	7.975	15.72	15.809	15.728
V, Å^3	1532	761	1507	1604	1558
Z	6	3	6	3	3
Framework density (number of framework atoms in 1000 Å^3)	15.7	15.8	15.9	15.0	15.4
Refractive indices					
n_e	1.596	1.619	1.644	1.578	1.607
n_o	1.609	1.622	1.671	1.585	1.612
$D_{meas.}$, g/cm^3	2.72	2.68	3.31	2.67	2.68
$D_{calc.}$, g/cm^3	2.74	2.74	3.31	2.74	2.70
References	Chao *et al.*, 1974; Ilyushin *et al.*, 1981	Boggs, 1988; Pushcharovsky *et al.*, 2002	Voloshin *et al.*, 1990; Sokolova *et al.*, 1991	Khomyakov *et al.*, 1993; Rastsvetaeva and Khomyakov, 1992	Khomyakov *et al.*, 1996; Rastsvetaeva and Khomyakov, 1996

32), frequently twinned. Fine-grained masses are also present.

In the territory of the USSR, hilairite for the first time was described by A.P.Khomyakov and N.M.Chernitsova (1980) on the material of three finds in the Lovozero massif. In samples from underground workings in the Alluaiv Mountain, hilairite has been met as yellowish and brownish transparent rhombohedral crystals 0.5-1 mm in size, closely associating with neighborite in small cavities of pegmatoid ultra-alkaline rocks, which veined and streaky bodies occur in poikilitic cancrisilite-sodalite-nepheline syenite. Major minerals in these rocks are potassic feldspar, nepheline, sodalite, cancrisilite, aegirine, alkaline amphibole; typical minor and accessory minerals are analcite, natrolite, ussingite, lorenzenite, lamprophyllite, eudialyte, parakeldyshite, apatite, ilmenite, gaidonnayite, steenstrupine, loparite, sulfides, etc. This paragenesis includes villiaumite, kogarkoite, sidorenkite, thermonatrite. Hilairite in another association was found in borehole core from the same Alluaiv Mountain: here its pink crystals up to 1 mm occur on walls of cavities in albite rock associating with elpidite, siderite and hisingerite-like phase. At last, in a sheet-like pegmatite on the Karnasurt Mountain, hilairite was found as pink opal-like grains up to 1 cm in dense fine-grained albite rock with serandite and sphalerite. In all three cases the mineral is determined in X-ray powder patterns and by optical properties (Khomyakov and Chernitsova, 1980), the chemical composition was not studied. G.D.Ilyushin *et al.* (1981) studied the crystal structure of hilairite in a single crystal from the Alluaiv Mountain for the first time and described its structural type, which has appeared to be a new one.

We have discovered hilairite in the Khibiny massif, where it was not known before. Known collector A.S.Podlesnyi collected samples with hilairite in an underground working of the Kirovskiy apatite mine (level +252 m) in the Kukisvumchorr Mountain. The pegmatite where it was found out has received the name of «Hilairitovoye» after the find of fine specimens with hilairite. This is a lens more than 10 m in the extent and more than 1 m thick in ijolite-urtite near the contact with apatite-nepheline rock. We have determined 50 (!) mineral kinds, including more than 20 rare-metal minerals, from the « Hilairitovoye» body. The main components of pegmatite are microcline, nepheline, and aegirine; titanite, pectolite, natrolite, eudialyte, rinkite, astrophyllite, apatite, fluorite, dawsonite, and sulfides are abundant. The richest hydrothermal mineralization is developed in small cavities in «pillows» of microcline. Walls of these cavities are covered with crystals of albite, calcite, quartz, ankerite, apatite and associated various rare-metal minerals – alkaline silicates of zirconium (hilairite, elpidite, catapleiite, gaidonnayite), beryllium (epididymite, eudidymite), niobium and titanium (nenadkevichite, vuoriyarvite-K, tsepinite-K, labuntsovite-Mg), carbonates of strontium, barium and rare-earth elements (strontianite, donnayite-(Y), mckelviyte-(Y), ancylite-(Ce), synchysite-(Ce), kukharenkoite-(La), carbocernaite, burbankite). Anatase, barite, gobbinsite, celadonite, muscovite, hisingerite, thorite, hematite, etc. are also discovered here in late associations. Hilairite forms fine crystals up to 6 mm in the greatest dimension and have been made out by faces of rhombohedron {01-12} and trigonal prisms {11-20} and {-1-120}. The ratio of areas of these faces defines the habit and shape of crystals: most frequently there are isometric pseudo-rhombic dodecahedric individuals, sometimes extended along axis *c*, and rare rhombohedra almost without prism faces (Fig. 1b-e). Faces of hilairite crystals are usually smooth, brilliant, less often covered with complex figures of growth. Crystals are opaque, saturated with microinclusions, giving them different shades of brown color, from dark-chocolate to light-coffee. Clusters of hilairite crystals are frequent here, they even form brushes.

One more find of hilairite we made in the Lovozero massif. This mineral, represented by a high-calcium variety, composes core of some crystals of calciohilairite in cavities of albitized porphyraceous lujavrites on the Flora Mountain (Pekov, 2000). This occurrence is characterized in more detail below.

Calciohilairite $CaZrSi_3O_9{\cdot}3H_2O$ was described as a new mineral from miarolitic cavities in boulders of alkaline granites of the Golden Horn batholith on the slope of Liberty Bell Mountain in the northern part of Cascade Range, Washington, USA. It was discovered as white and bluish crystals (up to 2 mm), formed by faces {11-20}, {-1-120} and {01-12} in association with microcline, quartz, albite, chlorite, fluorite, bastnaesite, zircon, malachite (Boggs, 1988). Calciohilairite was found in the latest paragenesis in cavities of nepheline syenite in Saint Amable as several beige and white prismatic-rhombohedral crystals 0.5 – 0.9 mm in size. In one case it grows on natrolite together with nenadkevichite, rhodochrosite, polylithionite, fluorite, aegirine and pyrite, in another it associates with astrophyllite, aegirine, eudialyte, microcline, manganneptunite, natrolite and birnessite pseudomorphs after serandite. The composition of mineral from Saint Amable, in the data of electron microprobe sounding is: $(Ca_{0.99}K_{0.01})_{\Sigma 1.00}(Zr_{0.96}Ti_{0.02}Mn_{0.01})_{\Sigma 0.99}(Si_{3.00}Al_{0.01})_{\Sigma 3.01}O_{8.98}\cdot 3H_2O$ (Horvath *et al.*, 1998). At Mont Saint-Hilaire, calciohilairite was noted as aggregates to 1 mm in association with quartz in cavities in alkaline hornfels (Horvath and Pfenninger-Horvath, 2000).

The fourth in the world and the first in Russia find of calciohilairite was made by one of authors on the Flora Mountain in the northern endocontact of the Lovozero massif (Pekov, 2000). This is probably richest of all known occurrences of this mineral; calciohilairite here is the main Zr concentrator in hydrothermal rocks. It gives isometric, frequently split crystals to 0.5 mm formed by faces of rhombohedron {01-12} and prisms {11-20} and {-1-120} (Fig. 1c). Aggregates of split individuals, sometimes spherical, up to 1 mm in diameter, are usual here. Fresh crystals are transparent, of light brown (coffee) color. The altered varieties are turbid to completely opaque, milky-white or have color of ivory. Calciohilairite grows on walls of cavities in albitized porphyraceous murmanite-eudialyte and lorenzenite-eudialyte lujavrites near the contact with a pegmatite vein. It associates with aegirine, natrolite, lorenzenite, epididymite, carbonate-fluorapatite, pyrite, and especially close – with minerals of labuntsovite-group: kuzmenkoite-Mn, labuntsovite-Mn, organovaite-Mn, vuoriyarvite-K. Core of some calciohilairite crystals correspond by composition to high-calcium or high-potassium varieties of hilairite.

Other variety of enriched with barium calciohilairite is found in cavities in a hydrothermally altered zone of a large pegmatite in the Lepkhe-Nel'm Mountain in the same Lovozero massif. This body has an irregular form and occurs in feldspathoid poikilitic syenite. Marginal parts of pegmatite are mainly composed of potassic feldspar, aegirine, nepheline, eudialyte, magnesio-arfvedsonite, lamprophyllite, lorenzenite; the core has experienced an intensive hydrothermal alteration and contains, in addition to relics of the listed minerals, abundant halloysite and natrolite. Once abundant mineral of pectolite-serandite series is totally replaced with water oxides of Mn. Hydrothermal mineralization is also intensive in the intermediate zone of pegmatite, where fluorapatite, carbonate-apatite, tainiolite, polylithionite, neptunite, catapleiite, kupletskite, barytolamprophyllite, tundrite-(Ce), vinogradovite, Nb-titanite, minerals of labuntsovite group (tsepinite-Na, tsepinite-K, paratsepinite-Ba, kuzmenkoite-Zn, alsakharovite-Zn), harmotome, and Ba-containing calciohilairite develop in cavities. The last forms single translucent white rhombohedral crystals (Fig. 1a) to 0.5 mm together with natrolite growing on microcline, aegirine, and lorenzenite.

Komkovite $BaZrSi_3O_9\cdot 3H_2O$ is only known in carbonatites of the Vuoriyarvi alkaline-ultrabasic massif in the Northern Karelia. It was described from the borehole core, in dolomite streaks cross-cutting metasomatically altered pyroxenite. Its brown rhombohedral crystals to 5 mm grow on dolomite in cavities of streaks together with phlogopite, strontianite, barite, georgechaoite, and pyrite (Voloshin *et al.*, 1990).

Sazykinaite-(Y) $Na_5(Y,HREE)ZrSi_6O_{18}\cdot 3H_2O$ was discovered in hydrothermally altered ultra alkaline pegmatite, occurring on urtite/apatite-nepheline contact in the Koashva Mountain in the Khibiny massif. It forms yellowish-greenish rhombohedra up to 2 mm across, formed by faces {01-12}, closely associating with lemmleinite-K in cavities in essentially aegirinic zone of pegmatite containing also natrolite, potassic feldspar, pectolite, alkaline amphibole, lomonosovite, sphalerite, etc. (Khomyakov *et al.*, 1993).

Recently sazykinaite-(Y) was also found in Saint-Hilaire, in cavities in essentially sodalite hyper alkaline rock as crystals formed by faces of rhombohedron {01-12} with a narrow band of prism {11-20}, in association with ussingite, serandite, mangan-neptunite, lintisite, erdite and vuonnemite (Horvath, Pfenninger-Horvath, 2000).

One of authors (I.V.P.) has found that sazykinaite-(Y) is rather common in the pegmatitic complex of the Koashva Mountain in Khibiny, formed by a series of morphologically and structurally similar bodies located strictly on the contact of urtite with a large deposit of apatite-nepheline rock. In addition to pegmatite, in which sazykinaite-(Y) was described for the first time by A.P.Khomyakov *et al.* (1993), this mineral was found in three bodies where it is not only the unique phase of Y and HREE, but also one of basic carriers of Zr in hydrothermal paragenesis (Pekov, 1998). Sazykinaite-(Y) only occur in cavities and most frequently – in dissolution hollows in eudialyte as doubtless source of Zr, Y, and HREE. Rhombohedral crystals of sazykinaite-(Y) (Fig. 1a) usually do not exceed 1 – 2 mm, but occasionally up to 5 – 6 mm. They are very frequently split, have a blocky-mosaic structure. Other simple forms, except for {01-12}, were not revealed in the materal from Khibiny. It has light yellow, pale-brown or greenish color, sometimes almost colorless, and transparent. Sometimes sazykinaite-(Y) associates with other alkaline Zr-silicates – catapleiite, umbite, kostylevite, wadeite – but almost never in direct contact with them. Sazykinaite-(Y) associates with aegirine, natrolite, microcline, pectolite, lamprophyllite, magnesiumastrophyllite, sphalerite, sometimes lemmleinite-K, sitinakite, nacaphite, sodalite, lomonosovite, etc. Its association with minerals of light lantanides, practically deprived of Y and HREE (vitusite-(Ce), belovite-(Ce), petersenite-(Ce), remondite-(La), rinkite, potassic rhabdophane-(Ce), etc is characteristic. In some pegmatites it is possible to see sazykinaite-(Y) in the neighbourhood with «salt» minerals – villiaumite, Na-carbonates, soda-phosphate, in others they are completely leached.

Pyatenkoite-(Y) $Na_5(Y,HREE)TiSi_6O_{18}\cdot 3H_2O$, a titanium analogue of sazykinaite-(Y), was described as a new mineral from hydrothermal rocks of the Alluaiv Mountain in the Lovozero massif. Its colorless rhombohedral crystals formed by faces {01-12} and up to 0.5 mm, grow on walls of cavities and cracks in lomonosovite, associating with albite, natrolite, gonnardite, aegirine, neptunite and fluorite (Khomyakov *et al.*, 1996). No other finds of this mineral are known till now.

We have discovered pyatenkoite-(Y) in the Kukisvumchorr Mountain in the Khibiny massif. It is determined in sample #447 from A.S.Podlesny collection. This sample is a fragment of prospecting well core, drilled in an underground working at level +252 m in the Kirovskii mine. Pyatenkoite-(Y) forms light gray with greasy luster translucent crystals up to 1.5 mm, quite often split, made out by rhombohedron faces {01-12}, with a band of prism faces {11-20} and {-1-120} (Fig. 1b). These crystals and their aggregates on walls of cavities occur in the axial zone of a pegmatite streak composed of white to colorless microcline with small amount of black needle-like aegirine. To walls, the streak is enriched with aegirine; nepheline and rinkite appear in it. In cavities, film and spheroidal grains of brown and black solid bitumen are observed together with pyatenkoite-(Y).

Chemical Composition

The chemical (cation) composition of minerals (Tables 2 and 3) was determined by electron microprobe using the Camebax SX 50 instrument at the Department of Mineralogy of the Lomonosov Moscow State University. In order to prevent destruction of samples, the analysis was carried out by a rastered beam from an area of 10 x 10 microns at accelerating voltage 15 kV and beam current 20 nA. The standards were: albite (Na), orthoclase (K, Al, Si), andradite (Ca, Fe), $SrSO_4$ (Sr), $BaSO_4$ (Ba), amphibole (Mg), $MnTiO_3$ (Mn, Ti), ZnO (Zn), phosphates of individual REE like $(REE)PO_4$ (REE = Y and lantanides), ThO_2 (Th), Zr (Zr), Hf (Hf), Nb (Nb).

The basic features of composition of investigated minerals are given below.

Ratio $Si/\Sigma M \approx 3$ was observed in all samples, which, undoubtedly, is related to precisely separated «building» functions of the cations forming a mixed framework.

Among M-cations, Zr dominates in hilairite, calciohilairite and sazykinaite-(Y), while Hf, Ti

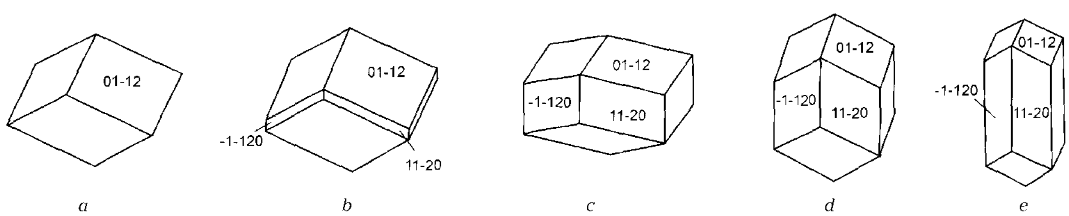

Fig. 1. *Crystals of hilairite-group minerals from the Khibiny, Lovozero alkaline complex, Kola Peninsula*

a – sazykinaite-(Y) from the Koashva Mountain, Khibiny, pyatenkoite-(Y) from the Alluaiv Mountain, Lovozero, and calciohilairite from the Lepkhe Nel'm Mountain, Lovozero;
b – pyatenkoite-(Y) from the Kukisvumchorr Mountain, Khibiny;
c – calciohilairite from the Flora Mountain, Lovozero;
d–e – hilairite from the Kukisvumchorr Mountain, Khibiny

Table 2. **Chemical composition of hilairite, calciohilairite and komkovite**

	1	2	3	4	5	6	7	8	9	10	11
					wt. %						
Na_2O	14.77	–	–	13.43	14.32	0.20	0.22	0.24	0.13	0.20	0.00
K_2O	–	–	–	0.52	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	0.13
CaO	–	13.56	–	0.20	n.c.	11.25	10.74	10.70	11.62	11.41	0.08
BaO	–	–	30.02	n.c.	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	28.19
CuO	–	–	–	n.c.	n.c.	0.19	0.77	1.12	0.42	0.74	n.c.
FeO	–	–	–	0.03	n.c.	0.03	0.70	0.03	0.12	0.09	0.33
Al_2O_3	–	–	–	0.03	n.c.	2.61	2.59	1.06	0.05	0.28	n.c.
SiO_2	42.97	43.58	35.28	42.08	44.12	38.81	39.03	39.74	41.16	41.37	34.44
TiO_2	–	–	–	0.04	0.00	0.09	0.09	0.04	0.04	0.02	0.00
ZrO_2	29.37	29.79	24.12	29.72	30.43	31.64	32.37	33.37	33.58	32.02	24.94
HfO_2	–	–	–	n.c.	0.21	n.c.	n.c.	n.c.	n.c.	n.c.	0.46
H_2O	12.89	13.07	10.58	13.54	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10.70
Total	100.00	100.00	100.00	99.62	89.08	84.82	86.51	86.32	87.12	86.13	99.27
	Formula units, calculation for 9 oxygen atoms										
Na	2.00	–	–	1.85	1.89	0.03	0.03	0.03	0.02	0.03	–
K	–	–	–	0.05	–	–	–	–	–	–	0.01
Ca	–	1.00	–	0.02	–	0.86	0.81	0.82	0.87	0.86	0.01
Ba	–	–	1.00	–	–	–	–	–	–	–	0.95
Cu	–	–	–	–	–	0.01	0.04	0.06	0.02	0.04	–
Fe	–	–	–	–	–	–	0.04	–	0.01	0.01	0.02
Σefc	**2.00**	**1.00**	**1.00**	**1.92**	**1.89**	**0.90**	**0.92**	**0.91**	**0.92**	**0.94**	**0.99**
Al	–	–	–	–	–	0.22	0.22	0.09	–	0.02	–
Si	3.00	3.00	3.00	2.99	3.01	2.78	2.76	2.83	2.89	2.92	2.95
Zr	1.00	1.00	1.00	1.03	1.01	1.11	1.12	1.16	1.15	1.10	1.04
Hf	–	–	–	–	–	–	–	–	–	–	0.01
H_2O	3.00	3.00	3.00	3.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.08

Notes:
1 – calculated composition of $Na_2ZrSi_3O_9 \cdot 3H_2O$;
2 – calculated composition of $CaZrSi_3O_9 \cdot 3H_2O$;
3 – calculated composition of $BaZrSi_3O_9 \cdot 3H_2O$;
4 – hilairite: Mont Saint-Hilaire, Quebec (Chao *et al.*, 1974),
– the total also includes (wt. %): MgO 0.01, MnO 0.02;
5 – hilairite: Vuoriyarvi, North Karelia (Voloshin *et al.*, 1989);
6 – 10 – calciohilairite: Golden Horn, Washington (Boggs, 1988);
11 – komkovite, Vuoriyarvi (Voloshin *et al.*, 1990).
Σefc – total of extra-framework cations;
n.d. – not detected;
n.c. – not cited in the original paper.

Table 2 **– continued (new analyses)**

	12	13	14	15	16	17	18	19	20	21	22
					wt. %						
Na_2O	13.04	2.33	1.02	0.57	0.07	0.00	0.28	0.10	0.00	0.00	0.31
K_2O	0.66	3.08	3.13	3.02	3.00	1.58	2.09	2.03	1.43	0.43	0.46
CaO	0.05	4.09	4.97	5.19	5.65	6.19	6.96	7.54	9.38	11.47	6.89
SrO	0.00	0.00	0.00	0.00	0.43	0.54	0.67	1.34	1.24	0.62	0.00
BaO	0.40	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.15
MnO	0.52	0.49	0.35	0.41	0.42	0.14	0.25	0.29	0.13	0.01	0.31
FeO	0.53	0.05	0.00	0.00	0.04	0.05	0.03	0.00	0.05	0.08	0.07
ZnO	0.00	0.00	0.03	0.61	0.19	0.09	0.18	0.00	0.14	0.00	0.00
Al_2O_3	0.06	0.00	0.00	0.00	0.00	0.03	0.02	0.05	0.03	0.05	1.36
SiO_2	42.66	43.43	44.58	43.94	44.99	47.40	44.90	41.94	42.64	41.82	43.70
TiO_2	0.00	0.46	0.58	0.71	0.98	1.07	0.81	0.87	0.92	0.55	0.33
ZrO_2	28.92	27.41	28.27	28.76	30.41	29.89	29.23	29.51	29.17	29.57	26.46
HfO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.63	0.00	0.79	0.00
Nb_2O_5	0.74	3.34	3.11	2.39	1.08	2.26	1.76	1.41	1.30	1.34	0.00
Total	87.58	84.87	86.04	85.60	87.26	89.24	87.47	85.69	86.43	86.73	86.04
	Formula units, calculation for 9 oxygen atoms										
Na	1.77	0.32	0.14	0.08	0.01	–	0.04	0.01	–	–	0.04
K	0.06	0.28	0.28	0.27	0.26	0.13	0.18	0.18	0.13	0.04	0.04
Ca	–	0.31	0.37	0.39	0.42	0.44	0.51	0.57	0.70	0.86	0.52
Sr	–	–	–	–	0.02	0.02	0.03	0.06	0.05	0.03	–
Ba	0.01	0.01	–	–	–	–	–	–	–	–	0.17
Mn	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.02	0.01	–	0.02
Fe	0.03	–	–	–	–	–	–	–	–	–	
Zn	–	–	–	0.03	0.01	–	0.01	–	0.01	–	–
Σefc	**1.99**	**0.95**	**0.81**	**0.79**	**0.74**	**0.60**	**0.78**	**0.84**	**0.90**	**0.93**	**0.79**
Al	–	–	–	–	–	–	–	–	–	–	0.11
Si	2.99	3.07	3.09	3.08	3.09	3.13	3.07	2.98	2.98	2.93	3.10
Ti	–	0.02	0.03	0.04	0.05	0.05	0.04	0.05	0.05	0.03	0.02
Zr	0.99	0.95	0.96	0.98	1.02	0.96	0.98	1.02	1.00	1.01	0.92
Hf	–	–	–	–	–	–	0.01	0.01	–	0.02	–
Nb	0.02	0.11	0.10	0.08	0.03	0.07	0.05	0.05	0.04	0.04	–

Notes:
12 – hilairite: the Kukisvumchorr Mountain, Khibiny;
13 – hilairite: the Flora Mountain, Lovozero (the core of calciohilairite crystal);
14 – 21 - calciohilairite: the Flora Mountain;
22 – calciohilairite: the Lepkhe Nel'm Mountain, Lovozero.
In all analyses the contents of Mg, REE, Cl are below detection the limits by the electron microprobe;
Σefc – the sum of extra-framework cations.

Table 3. **Chemical composition of sazykinaite-(Y) and pyatenkoite-(Y)**

	1	2	3	4	5	6	7	8	9	10	11	12
						wt. %						
Na_2O	18.02	18.98	15.18	15.45	14.47	14.07	15.20	13.80	12.54	17.25	17.16	16.02
K_2O	–	–	3.05	2.49	2.55	4.06	1.82	4.19	2.12	0.14	0.13	0.13
Y_2O_3	13.13	13.83	8.74	9.31	9.30	8.30	8.15	5.57	11.41	6.64	11.60	10.05
La_2O_3	–	–	0.00	0.01	0.01	0.05	0.02	0.15	0.00	0.10	0.00	0.00
Ce_2O_3	–	–	0.17	0.25	0.66	0.23	0.12	2.65	0.30	0.34	0.00	0.00
Pr_2O_3	–	–	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00
Nd_2O_3	–	–	0.25	0.06	0.63	0.24	0.17	2.16	0.24	0.60	0.00	0.00
Sm_2O_3	–	–	0.38	0.48	0.95	0.63	0.24	0.79	0.32	1.14	0.00	0.32
Eu_2O_3	–	–	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00
Gd_2O_3	–	–	1.03	0.95	1.22	0.78	0.79	0.91	0.83	1.78	0.00	0.28
Tb_2O_3	–	–	0.21	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00
Dy_2O_3	–	–	1.26	1.21	1.14	0.98	1.17	0.95	1.19	2.39	0.67	0.76
Ho_2O_3	–	–	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.24	0.00	0.00
Er_2O_3	–	–	0.79	0.98	0.68	0.67	0.60	0.62	0.88	0.94	1.31	0.93
Tm_2O_3	–	–	0.16	0.00	0.00	0.00	0.00	0.00	0.15	0.08	0.00	0.00
Yb_2O_3	–	–	0.60	0.57	0.47	0.66	0.42	0.48	0.72	0.14	1.07	0.71
Lu_2O_3	–	–	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00
ThO_2	–	–	0.74	1.07	1.03	0.68	1.08	0.00	0.36	0.36	0.00	1.33
SiO_2	41.94	44.16	40.51	41.64	41.34	40.45	41.01	43.41	41.35	42.96	44.04	43.89
TiO_2	–	9.79	1.36	1.04	1.40	0.10	0.33	0.40	0.67	8.16	9.64	9.55
ZrO_2	14.33	–	10.24	9.32	9.30	13.92	13.99	13.60	9.99	0.38	0.00	0.00
Nb_2O_5	–	–	1.30	1.34	1.02	0.00	0.36	0.00	1.25	2.68	0.11	2.39
H_2O	12.58	13.24	12.6	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Total	100.00	100.00	98.81	86.17	86.17	85.82	85.83	90.16	84.78	87.26	85.73	86.36
						Formula units, calculation for 18 oxygen atoms						
Na	5.00	5.00	4.38	4.44	4.15	4.08	4.35	3.83	3.65	4.70	4.60	4.28
K	–	–	0.58	0.47	0.48	0.78	0.34	0.76	0.41	0.03	0.02	0.02
Y	1.00	1.00	0.69	0.73	0.73	0.66	0.64	0.42	0.91	0.50	0.85	0.74
La	–	–	–	–	–	–	–	0.01	–	0.005	–	–
Ce	–	–	0.01	0.01	0.04	0.01	0.005	0.14	0.02	0.02	–	–
Pr	–	–	–	–	–	–	–	0.01	–	–	–	–
Nd	–	–	0.01	–	0.04	0.01	0.01	0.11	0.01	0.03	–	–
Sm	–	–	0.02	0.03	0.05	0.04	0.03	0.04	0.02	0.06		0.02
Eu	–	–	0.01	–	–	–	–	–	–	0.03	–	–
Gd	–	–	0.05	0.06	0.06	0.04	0.04	0.04	0.04	0.08	–	0.01
Tb	–	–	0.01	–	–	–	–	–	–	0.02	–	–
Dy	–	–	0.06	0.06	0.06	0.05	0.06	0.04	0.06	0.11	0.03	0.03
Ho	–	–	–	–	–	–	–	–	0.01	0.01	–	–
Er	–	–	0.04	0.04	0.03	0.03	0.03	0.03	0.04	0.04	0.06	0.04
Tm	–	–	0.01	–	–	–	–	–	0.01	0.005	–	–
Yb	–	–	0.03	0.03	0.02	0.03	0.02	0.02	0.03	0.01	0.05	0.03
Th	–	–	0.03	0.04	0.04	0.03	0.04	–	0.01	0.01	–	0.04
Si	6.00	6.00	6.03	6.15	6.12	6.06	6.06	6.21	6.20	6.03	6.09	6.05
Ti	–	1.00	0.15	0.12	0.15	0.01	0.04	0.04	0.08	0.86	1.00	0.99
Zr	1.00	–	0.74	0.68	0.67	1.02	1.01	0.95	0.73	0.03	–	–
Nb	–	–	0.09	0.09	0.07	–	0.02	–	0.08	0.17	0.01	0.15
H_2O	6.00	6.00	6.25	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

Notes:

1 – calculated composition of $Na_5YZrSi_6O_{18}\cdot6H_2O$;
2 – calculated composition of $Na_5YTiSi_6O_{18}\cdot6H_2O$;
3 – 9 – sazykinaite-(Y) from the Koashva Mountain, Khibiny:
3 – Khomyakov *et al.*, 1993;
4 – 7 – Pekov, 1998 (4 and 5 – zonal crystal: 4 – core, 5 – marginal zone);
8 – 9 – Yakovenchuk *et al.*, 1999 (the total also includes, wt. %: analysis 8 – FeO 0.26; analysis 9 – CaO 0.07, SrO 0.08);
10 – pyatenkoite-(Y) the Alluaiv Mountain, Lovozero (Khomyakov *et al.*, 1996);
11 – 12 – pyatenkoite-(Y) from the Kukisvumchorr Mountain, Khibiny;
n.d. – water content was not detected