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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 ( $\text{Si}_3\text{O}_9$ ) and isolated M-octahedra ( $M = \text{Zr, Ti, Y} + \text{Ln}$ ); 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 ( $\text{Si}_3\text{O}_9$ ) 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  $\{M(\text{Si}_3\text{O}_9)\}$ , where dominant M-cations in different cases are Zr, Ti, and (Y + Ln). A step of ( $\text{Si}_3\text{O}_9$ ) 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 lanthanides 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**  $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  is the most widespread member of the group. It was discovered by G. Chao *et al.* (1974) in hydrothermal rocks related to nepheline syenites and alkali-rich pegmatites of agpaite 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 agpaite 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 Langesundsford – on islands Siktesø (with albite, gaidonnayite, zircon) and Vesle Arøe (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 Pozos 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	$\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$	$\text{CaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$	$\text{BaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$	$\text{Na}_5\text{YZrSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$	$\text{Na}_5\text{YTiSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$
Symmetry	Trigonal, <i>R</i> 32	Trigonal, <i>R</i> 32	Trigonal, <i>R</i> 32	Trigonal, <i>R</i> 32	Trigonal, <i>R</i> 32
Unit cell parameters					
<i>a</i> , Å	10.556	10.498	10.52	10.825	10.696
<i>c</i> , Å	15.855	7.975	15.72	15.809	15.728
<i>V</i> , Å <sup>3</sup>	1532	761	1507	1604	1558
<i>Z</i>	6	3	6	3	3
Framework density (number of framework atoms in 1000 Å <sup>3</sup> )					
	15.7	15.8	15.9	15.0	15.4
Refractive indices					
<i>n<sub>p</sub></i>	1.596	1.619	1.644	1.578	1.607
<i>n<sub>o</sub></i>	1.609	1.622	1.671	1.585	1.612
<i>D<sub>meas.</sub></i> , g/cm <sup>3</sup>	2.72	2.68	3.31	2.67	2.68
<i>D<sub>calc.</sub></i> , g/cm <sup>3</sup>	2.74	2.74	3.31	2.74	2.70
References	Chao <i>et al.</i> , 1974; Ilyushin <i>et al.</i> , 1981	Boggs, 1988; Pushcharovsky <i>et al.</i> , 2002	Voloshin <i>et al.</i> , 1990; Sokolova <i>et al.</i> , 1991	Khomyakov <i>et al.</i> , 1993; Rastsvetaeva and Khomyakov, 1992	Khomyakov <i>et al.</i> , 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 dodecahedral 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**  $\text{CaZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  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-rhomboidal crystals 0.5 – 0.9 mm in size. In one case it grows on natrolite together

with nenadkevichite, rhodochrosite, polyolithionite, 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:  $(Ca_{0.99}K_{0.01})_{\Sigma 1.00}(Zr_{0.96}Ti_{0.02}Mn_{0.01})_{\Sigma 0.99}(Si_{3.00}Al_{0.01})_{\Sigma 3.01}O_{8.96} \cdot 3H_2O$  (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 porphyreous 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, polyolithionite, ne-

ptunite, 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 crys-

tals 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 material 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, naphite, sodalite, lomonosovite, etc. Its association with minerals of light lanthanides, 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 – villiumite, Na-carbonates, soda-phosphate, in others they are completely leached.

**Pyatenkoite-(Y)**  $\text{Na}_5(\text{Y}, \text{HREE})\text{TiSi}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ , a titanium analogue of sazykinaite-(Y), was described as a new mineral from hydrothermal rock<sup>a</sup> of the Alluaiv Mountain<sup>b</sup> 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 Kukisumchorr 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).

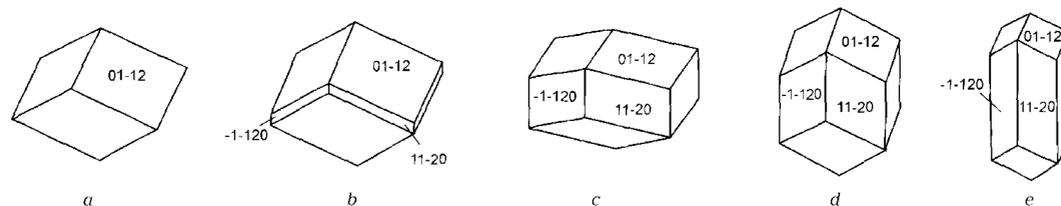
### Chemical Composition

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),  $\text{SrSO}_4$  ( $\text{Sr}^R$ ),  $\text{BaSO}_4$  (Ba), aegirine (Mg),  $\text{MnTiO}_3$  (Mn, Ti), ZnO (Zn), phosphates of individual REE like  $(\text{REE})\text{PO}_4$  (REE = Y and lanthanides),  $\text{ThO}_2$  (Th), Zr (Zr), Hf (Hf), Nb (Nb).

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

Ratio  $\text{Si}/\Sigma\text{M} \approx 3$  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 Kukisumchorr Mountain, Khibiny;  
 c – calciohilairite from the Flora Mountain, Lovozero;  
 d–e – hilairite from the Kukisumchorr Mountain, Khibiny

Table 2. Chemical composition of hilairite, calciohilairite and komkovite

	1	2	3	4	5	6	7	8	9	10	11
	wt. %										
Na <sub>2</sub> O	14.77	—	—	13.43	14.32	0.20	0.22	0.24	0.13	0.20	0.00
K <sub>2</sub> O	—	—	—	0.52	0.00	n.c.	n.c.	n.c.	n.c.	n.c.	0.13
CaO	—	13.56	—	0.20	0.00	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 <sub>2</sub> O <sub>3</sub>	—	—	—	0.03	n.c.	2.61	2.59	1.06	0.05	0.28	n.c.
SiO <sub>2</sub>	42.97	43.58	35.28	42.08	44.12	38.81	39.03	39.74	41.16	41.37	34.44
TiO <sub>2</sub>	—	—	—	0.04	0.00	0.09	0.09	0.04	0.04	0.02	0.00
ZrO <sub>2</sub>	29.37	29.79	24.12	29.72	30.43	31.64	32.37	33.37	33.58	32.02	24.94
HfO <sub>2</sub>	—	—	—	n.c.	0.21	n.c.	n.c.	n.c.	n.c.	n.c.	0.46
H <sub>2</sub> O	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
<b>Σefc</b>	<b>2.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.92</b>	<b>1.89</b>	<b>0.90</b>	<b>0.92</b>	<b>0.91</b>	<b>0.92</b>	<b>0.94</b>	<b>0.99</b>
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 <sub>2</sub> O	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<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;  
2 – calculated composition of CaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;  
3 – calculated composition of BaZrSi<sub>3</sub>O<sub>9</sub>·3H<sub>2</sub>O;  
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 <sub>2</sub> O	13.04	2.33	1.02	0.57	0.07	0.00	0.28	0.10	0.00	0.00	0.31
K <sub>2</sub> O	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 <sub>2</sub> O <sub>3</sub>	0.06	0.00	0.00	0.00	0.00	0.03	0.02	0.05	0.03	0.05	1.36
SiO <sub>2</sub>	42.66	43.43	44.58	43.94	44.99	47.40	44.90	41.94	42.64	41.82	43.70
TiO <sub>2</sub>	0.00	0.46	0.58	0.71	0.98	1.07	0.81	0.87	0.92	0.55	0.33
ZrO <sub>2</sub>	28.92	27.41	28.27	28.76	30.41	29.89	29.23	29.51	29.17	29.57	26.46
HfO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.63	0.00	0.79	0.00
Nb <sub>2</sub> O <sub>5</sub>	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	—	—
<b>Σefc</b>	<b>1.99</b>	<b>0.95</b>	<b>0.81</b>	<b>0.79</b>	<b>0.74</b>	<b>0.60</b>	<b>0.78</b>	<b>0.84</b>	<b>0.90</b>	<b>0.93</b>	<b>0.79</b>
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 <sub>2</sub> O	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 <sub>2</sub> O	—	—	3.05	2.49	2.55	4.06	1.82	4.19	2.12	0.14	0.13	0.13
Y <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	—	—	0.00	0.01	0.01	0.05	0.02	0.15	0.00	0.10	0.00	0.00
Ce <sub>2</sub> O <sub>3</sub>	—	—	0.17	0.25	0.66	0.23	0.12	2.65	0.30	0.34	0.00	0.00
Pr <sub>2</sub> O <sub>3</sub>	—	—	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00
Nd <sub>2</sub> O <sub>3</sub>	—	—	0.25	0.06	0.63	0.24	0.17	2.16	0.24	0.60	0.00	0.00
Sm <sub>2</sub> O <sub>3</sub>	—	—	0.38	0.48	0.95	0.63	0.24	0.79	0.32	1.14	0.00	0.32
Eu <sub>2</sub> O <sub>3</sub>	—	—	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00
Gd <sub>2</sub> O <sub>3</sub>	—	—	1.03	0.95	1.22	0.78	0.79	0.91	0.83	1.78	0.00	0.28
Tb <sub>2</sub> O <sub>3</sub>	—	—	0.21	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00
Dy <sub>2</sub> O <sub>3</sub>	—	—	1.26	1.21	1.14	0.98	1.17	0.95	1.19	2.39	0.67	0.76
Ho <sub>2</sub> O <sub>3</sub>	—	—	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.24	0.00	0.00
Er <sub>2</sub> O <sub>3</sub>	—	—	0.79	0.98	0.68	0.67	0.60	0.62	0.88	0.94	1.31	0.93
Tm <sub>2</sub> O <sub>3</sub>	—	—	0.16	0.00	0.00	0.00	0.00	0.00	0.15	0.08	0.00	0.00
Yb <sub>2</sub> O <sub>3</sub>	—	—	0.60	0.57	0.47	0.66	0.42	0.48	0.72	0.14	1.07	0.71
Lu <sub>2</sub> O <sub>3</sub>	—	—	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00
ThO <sub>2</sub>	—	—	0.74	1.07	1.03	0.68	1.08	0.00	0.36	0.36	0.00	1.33
SiO <sub>2</sub>	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 <sub>2</sub>	—	9.79	1.36	1.04	1.40	0.10	0.33	0.40	0.67	8.16	9.64	9.55
ZrO <sub>2</sub>	14.33	—	10.24	9.32	9.30	13.92	13.99	13.60	9.99	0.38	0.00	0.00
Nb <sub>2</sub> O <sub>5</sub>	—	—	1.30	1.34	1.02	0.00	0.36	0.00	1.25	2.68	0.11	2.39
H <sub>2</sub> O	12.58	13.24	12.6	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 <sub>2</sub> O	6.00	6.00	6.25	n.d								

**Notes:**

- 1 — calculated composition of Na<sub>3</sub>Y<sub>2</sub>ZrSi<sub>6</sub>O<sub>18</sub>·6H<sub>2</sub>O;
- 2 — calculated composition of Na<sub>3</sub>YTiSi<sub>6</sub>O<sub>18</sub>·6H<sub>2</sub>O;
- 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

and Nb are only a small admixtures, down to almost total absence. Yttrium and lanthanides are absent in quantities determined by the electron microprobe ( $> 0.05 - 0.1 \%$ ) in hilairite and calciohilairite. These regularities are also fair for komkovite (Table 2).

Yttrium in all cases dominates among REE in sazykinaite and pyatenkoite. In investigated samples of these minerals from Khibiny, heavy lanthanides sharply prevail in lanthanide spectrum with DyGd-maximum in sazykinaite and Er-maximum in pyatenkoite.

In barium-containing calciohilairite from the Lepkhe Nel'm Mountain, Lovozero, the admixture of aluminum was discovered: 1.4 wt. % of  $Al_2O_3$  (analysis 22 in Table 2).

The structure of large (alkaline and alkaline-earth) cations in investigated hilairite and calciohilairite samples varies rather widely:  $Na_2O$  0.0–13.0 wt. %,  $CaO$  0.7–11.5 %,  $K_2O$  0.0–3.2 %,  $SrO$  0.0–1.3 %,  $BaO$  0.0–6.2 %. Such high contents of admixtures of K, Sr, and Ba in hilairite and calciohilairite were not known earlier. Amounts of others low-valent cations (Mg, Mn, Fe, Zn) are small – less than 1 wt. % in all analyses. Zonal crystals whose core are enriched with Na and correspond to high-calcium variety of hilairite (analysis 13 in Table 2) while peripheral parts correspond calciohilairite (analysis 16 in Table 2) were discovered in Lovozero hydrothermal rocks. Transitions between zones are gradual, which allows to suppose continuous isomorphism between large extra-framework cations and, respectively, about isomorphous series hilairite – calciohilairite.

In sazykinaite-(Y) and pyatenkoite-(Y) alkaline-earth and other bivalent cations are practically absent and Na is the main extra-framework cation: pyatenkoite is almost purely sodic mineral; all samples of sazykinaite contain appreciable admixture of K (1.8–4.2 wt. %  $K_2O$ ).

The total contents of alkaline and alkaline-earth cations is variable in calciohilairite from Lovozero. In addition to stoichiometric varieties, there are also cation-deficient varieties, in which the total of extra-framework cations little exceeds 0.5 of formula unit (at calculation to  $Si_3$ ).

### The X-ray Data

The crystal structure of calciohilairite – the unique representative of the group, which structure remained unstudied until recently –

was studied (Pushcharovsky *et al.*, 2002) in a single crystal from the Flora Mountain (Lovozero). Even the sizes of unit cell of this mineral were not authentically known. R.C.Boggs (1988) has stated a trigonal cell, twice as big in direction  $a$  than in other members of the group:  $a = 20.90$ ,  $c = 16.05$  Å. However, poor quality of single crystals from Golden Horn left doubts in correctness of these results. The data received for the Lovozero cation-deficient calciohilairite with the help of single crystal diffractometer Siemens P4 show that the unit cell of this mineral by  $a$  is the same as in all other representatives of the group, and by  $c$  is less:  $a = 10.498$ ,  $c = 7.975$  Å (Pushcharovsky *et al.*, 2002). Thus, it appeared four times smaller in volume than R.C.Boggs (1988) supposed it. The space group of calciohilairite is  $R32$ , as well as of all other members of the group (Table 1), but the parameter  $c$  of its cell is equal to the repeatability period of M-octahedra (~8 Å) and, respectively, the «step» of a screwed chain ( $Si_3O_9$ ), which includes three Si-tetrahedra. The other members of the group contain in cell two periods of chain in height and two M-octahedra, which is related to the arrangement of extra-framework cations and water molecules (see, for example, Ilyushin *et al.*, 1981). In calciohilairite with disordered as compared to hilairite structure, one position of extra-framework cations (with dominating Ca) is realized instead of two nonequivalent in other members of the group, which provokes halved parameter  $c$ .

A similar mixed framework of hilairite-group minerals results in similarity of their X-ray powder patterns. Only members containing large octahedron occupied with Y and Ln in the framework may be separated in X-ray powder patterns from REE-free members (Table 4). Obviously, as well as in case of aluminosilicate zeolites, character of «filler» of extensive cages (alkaline and alkaline-earth cations and water molecules) does not render essential influence on parameters of cell and X-ray powder pattern.

Table 4 shows X-ray powder data for calciohilairite from the Flora Mountain (Lovozero), indicated in parameters of true, i.e. small cell determined by single crystal method in comparison with X-ray powder data of other members of the group. At choice of indices  $hkl$  for calciohilairite, the data on intensity, received from its crystal structure data, were taken into account.

Table 4. X-ray powder data for hilairite-group minerals

1			2		3		4		5		
<i>I</i>	<i>d</i> , Å	<i>hkl</i>	<i>I</i>	<i>d</i> , Å	<i>hkl</i>						
90	6.02	011	90	6.03	10	5.96	32	6.03	60	5.99	012
90	5.20	110	70	5.25	100	5.23	63	5.40	30	5.36	110
5	4.00	201			10	3.94					202
							2	3.776			113
5	3.65	102	5	3.62	80	3.59	4	3.645			104
							3	3.453	20	3.43	211
100	3.15	121	90	3.14	20	3.13	84	3.236	100	3.21	122
100	3.01	300, 022	100	3.01	80	3.02	88	3.127	40	3.093	300
					90	2.96	100	3.030	85	2.990	024
					10	2.880					123
					20	2.840					302
					40	2.615	19	2.708	40	2.661	220, 033
40	2.60	212	50	2.62	60	2.571	8	2.641	20	2.608	214, 205
							3	2.565			131
			10	2.41	30	2.393	9	2.472	5	2.439	312
							4	2.407			223
25	2.37	113	10	2.35	20	2.327	5	2.371	22	2.353	116
			10	2.19			7	2.248	10	2.210	042
35	2.12	132	20	2.13	20	2.124	14	2.175	24	2.148	134
					60	2.106	2	2.134			321, 230
			5	2.02	10	2.026	13	2.077	10	2.050	232
50	1.99	410, 303	70	2.00	30	1.984	7	2.046			410, 306
							18	2.018	55	1.998	404, 306
					30	1.960					008
					10	1.931					233
					10	1.911	3	1.909	17.5	1.881	217, 143, 018
20	1.83	322, 024	40	1.86	40	1.841	13	1.890	17.5	1.870	324, 226
					20	1.829					500
			10	1.83	50	1.796	4	1.825	12	1.808	502, 208
20	1.74	330	20	1.755	20	1.750	21	1.805	24	1.781	330
									5	1.746	009, 241
					10	1.736					235
10	1.71	421, 124	10	1.714	50	1.700	11	1.730	10	1.712	422, 128
15	1.68	052	10	1.693	10	1.656	12	1.696	26	1.676	054
									5	1.648	511
30	1.65	151	30	1.660	30	1.642	4	1.648	5	1.627	152, 243
15	1.59	413	10	1.598	10	1.579	7	1.618	26	1.598	244, 416
5	1.57	105	5	1.559	10	1.564	2	1.577	5	1.556	318, 1.0.10, 153
5	1.51	600, 512			50	1.546	5	1.564			131, 600
					10	1.527					237
					20	1.505	4	1.549	5	1.532	514
			40	1.468			5	1.514			342, 253
					10	1.480					2.0.10
40	1.45	520, 333	30	1.442	20	1.460	13	1.503	44	1.481	520, 603
							5	1.491			336

**Notes:**

- 1 – calciohilairite, the Flora Mountain, Lovozero (camera RKD-57.3, FeK-radiation);
- 2 – hilairite, the Kukisvumchorr Mountain, Khibiny (camera RKD-57.3, FeK-radiation);
- 3 – komkovite, Vuorijarvi (Voioshin *et al.*, 1990);
- 4 – sazykinaite-(Y), the Koashva Mountain, Khibiny (Khomyakov *et al.*, 1993);
- 5 – pyatenkoite-(Y), the Aluaiv Mountain, Lovozero (Khomyakov *et al.*, 1996).

### IR-spectroscopy

The IR-spectroscopic data on hilairite-group minerals are rather dispersed, and the IR-spectrum of calciophilairite was not published at all. A.V.Voloshin with co-authors (1989) gives spectra of water alkaline Zr-silicates – cataleite, gaidonnayite, georgechaoite and hilairite and fairly notes that the IR-spectroscopy is quite convenient for diagnostics of these minerals. A.P.Khomyakov with co-authors (1996) note that the IR-spectrum of pyatenkoite is generally close to the spectra of sazykinaite, hilairite and komkovite. However, it is difficult to agree without reserves with this statement. Fig. 2 shows IR-spectra of all members of hilairite group and serious distinctions between them are well visible.

Really, the IR-spectroscopy can be proposed as a reliable and fast method not only to distinguish hilairite-group minerals from representatives of other structural types, but also for their diagnostics inside the group. Only hilairite and calciophilairite can be confused by IR-spectra, whereas other minerals have individual sets of features expressed in appearance, disappearance, or shift of this or that spectrum band and/or redistribution of their intensities.

The IR-spectrum of pyatenkoite is most sharply distinguished, which is related to entry of Ti instead of Zr. The distinctions consist both in occurrence of own bands related to vibrations Ti-O (first of all, this is a doublet in the band  $700\text{ cm}^{-1}$  instead of single at zirconium minerals) and in strong polarization by Ti, as against Zr, bond Si-O that results in splitting the main Si-O band of stretching vibrations in pyatenkoite spectrum into two comparable by intensity components at  $\sim 900$  and  $\sim 1020\text{ cm}^{-1}$ . Such character of splitting gives completely individual structure to the main band in spectrum of pyatenkoite allowing to confidently distinguish this mineral from zirconium members of the group.

Very serious distinctions are observed in the area of absorption bands corresponding to vibrations of water molecules – stretching ( $2900 - 3550\text{ cm}^{-1}$ ) and bending ( $\sim 1600\text{ cm}^{-1}$ ). So, splitting of the band of molecular water bending vibrations in komkovite and sazykinaite spectra indicates the presence in these minerals of water molecules at two structural positions, as against three other members of the group, where, considering single band near  $\sim 1600\text{ cm}^{-1}$ ,  $\text{H}_2\text{O}$  positions are of one type. An intensive wide band near  $\sim 2900\text{ cm}^{-1}$  in the sazykinaite spectrum indicates the existence of strong hydrogen bonds, which are not ob-

served in pyatenkoite. At last, a wide band near  $\sim 3200\text{ cm}^{-1}$  may indicate the presence of  $(\text{H}_3\text{O})^+$  in hilairite-group minerals; most strongly this band is manifested in hilairite and calciophilairite.

### Discussion

New finds of hilairite-group minerals in the Khibiny-Lovozero complex show that these minerals are not so rare as it was supposed earlier. The received data on their cation composition appreciably expand our knowledge about isomorphous capacity of hilairite structural type. So, variations in crystals from the Flora Mountain (Lovozero) composition unequivocally show the existence in nature of extended isomorphous series hilairite – calciophilairite and also indicate possibility of entry of significant amounts of K and Sr admixtures in these minerals. Finds of high-

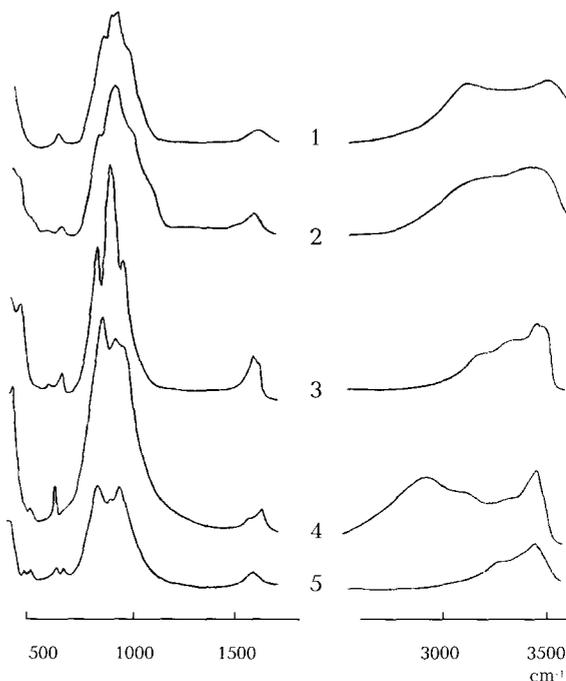
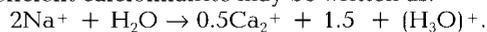


Fig. 2. IR spectra of hilairite-group minerals:

- 1 – hilairite (Alluaive Mountain, Lovozero),
- 2 – calciophilairite (Flora Mountain, Lovozero),
- 3 – komkovite (Vuoriharvi),
- 4 – sazykinaite-(Y) (Koashva Mountain, Khibiny),
- 5 – pyatenkoite-(Y) (Kukisvumchorr Mountain, Khibiny)

barium varieties of calciohilairite (Lepkhe Nel'm Mountain, Lovozero, — analysis 22 in Table 2) allows to assume the probability of realization of the isomorphous series calciohilairite — komkovite.

Results of study of cation-deficient calciohilairite structure from Lovozero (Pushcharovsky *et al.*, 2002) enlightens the nature of non-stoichiometry in compounds with hilairite structural type. In addition to usual heterovalent replacements  $\text{Ca}^{2+} + \leftrightarrow 2\text{Na}^+$ , partial occupancy of cations  $(\text{H}_3\text{O})^+$  in the position usually only occupied with water molecules was revealed here. Significant sizes of cages in the framework allow to placed here such a large cation as hydronium, which compensate the lack of positive charge caused by the reduction of contents of «usual» cations — of alkaline and alkali-earth metals. The presence of hydronium is directly proved by IR-spectroscopy and indirectly — by overestimate of ratios for Si and M-cations at calculation of formulas of cation-deficient varieties by  $\text{O}_9$  (see analyses 14 through 18 and 22 in Table 2). As a result, the idealized general scheme of isomorphism resulting in observed compositions of cation-deficient calciohilairite may be written as:



Taking into account that core of cation-deficient calciohilairite crystals from the Flora Mountain are quite often appreciably enriched with Na in comparison with high-calcium peripheral zones (analyses 13 and 16 in Table 2), it is possible to assume that this scheme of isomorphism at the same time is also the scheme of reaction of natural ion-exchanging process, which results in transition of hilairite, crystallized from alkali-rich solutions, into calciohilairite at late hydrothermal phases in conditions of reduced alkalinity (as is known, reduction of activity of alkalis is rather typical of late phases of apgaitic system evolution). The presence of such open channels in hilairite type structure makes easy ionic exchange and it is thought that this phenomenon in general may be characteristic of hilairite-group minerals, responsible, in some cases, for the composition of extra-framework cations and water contents.

Isomorphism in the frame work is not so wide. So, strict order of two types of M-cations with different sizes — (Zr,Ti) and (Y,Ln) in structures of sazykinaite and pyatenkoite (Rastsvetaeva, Khomyakov, 1992, 1996), as well as absence of REE in hilairite, calciohilairite and komkovite, indicate that isomorphous series between rare-earth and rare-earth-free members of the group are absent.

Thus, in the hilairite group, it is possible to distinguish two independent subgroups: with the same filling of both M-octahedra (hilairite, calciohilairite and komkovite) and with the ordered distribution of M-cations of two types in positions M1 and M2 — sazykinaite-(Y) and pyatenkoite-(Y). Continuous isomorphism between Zr and Ti(Nb) even in isostructural sazykinaite and pyatenkoite is not discovered yet and it is possible that compete series between them are not realized at all owing to serious distinctions in crystallochemical features of Zr and Ti, in detail discussed by Yu.A. Pyatenko and A.A. Voronkov (1977). Presence of Al in hilairite-group minerals is only reported for calciohilairite: from the Golden Horn (Boggs, 1988, — see analyses 6–8 in Table 2) and from the Lepkhe Nel'm Mountain, Lovozero (analysis 22 in Table 2). The structure of Al-containing calciohilairite was not studied, it is only possible to note that the mineral from the Golden Horn has increased content of Al at some deficiency of Si, and in that from Lovozero — a deficiency of Zr.

Thus, stable composition of mixed octahedral-tetrahedral framework at widely varying contents and ratios of extra-framework cations (including hydronium) and a variable quantity of molecular water are characteristic of hilairite-group minerals. A number of attributes indicate easy ionic exchange and de-cationing in hilairite-like phases. All these features could be very well explained if *to consider hilairite-group minerals as specific zeolites with a combined framework*.

Currently large scientific and practical interest call zeolite materials of new type, which framework includes five and six-coordinated cations Ti, Nb, Al, Ga, V, etc. together with tetrahedral fragments (see, for example, the review of Rocha *et al.*, 1996). These «zeolites» are characterized by wide spectrum of structural types and quite often have unique properties. Among minerals good example of microporous materials with combined octahedral-tetrahedral framework are Ti, Nb-silicates of the labuntsovite group (Chukanov *et al.*, 2002; Pekov *et al.*, 2002).

Members of the hilairite group are also bright representatives of natural rare-metal «zeolites». They have a unique structure in which apex-connected silica tetrahedra form chains and isolated M-octahedra are occupied with atoms of Zr, less often Ti(Nb) and Y(HREE), joining to pendent apices of Si-tetrahedra, complete the framework. It is interesting that this picture is opposite to what is observed in labuntsovite-like minerals,

where chained motif is formed by interconnected by apices Ti,Nb-octahedra, while isolated four-member rings of Si-tetrahedra act as a binding element. These two contrast examples well illustrate the possibilities of topological variety of rare-metal «zeolite» structures. The density of framework of hilairite-group minerals varies from 15 to 16 framework atoms (Si + M) by 1000 Å<sup>3</sup>; such values are characteristic of «true» aluminosilicate zeolites with «loose» frameworks.

The thermal data also unequivocally specify the zeolite character of hilairite-like minerals. So, dehydration of hilairite at heating completely terminate at 220° C and then de-watered material preserves the hilairite structure minimum to 855° C. At return cooling, rehydration also begins at 220° C and in 15 hours at room temperature the mineral absorbs about 95 % from initial quantity of water; the rehydration product is meat-red, porcelain-like, gives the X-ray diagram of hilairite (Chao *et al.*, 1974). The main quantity of water from sazykinaite-(Y) flashes out below 250° C (more than 80 wt. % from all the loss, by the published thermal curve). After heating up to 500° C, grown white and turbid crystals give the X-ray powder pattern of sazykinaite with weakened diffusion lines (Khomyakov *et al.*, 1993).

It is possible that massive pink to red opal- and porcelain-like varieties of hilairite described from Saint-Hilaire (Chao *et al.*, 1974) and Karnasurt Mountain in Lovozero (Khomyakov, Chernitsova, 1980) could arise owing to dewatering of «normal» crystalline hilairite at additional heating of a pegmatitic system after the crystallization of mineral and its rehydration at cooling.

Large enough Y cation participates in the sazykinaite and pyatenkoite framework, which is rare for similar «zeolites». Probably, the framework-forming role demanding in this case the minimization of coordination polyhedron volume interferes with entry of ions of light lanthanides – largest of REE<sup>3+</sup> – into these phases in essential quantities. Only one analysis of sazykinaite is known where Ce prevails in Ln spectrum, but here Y remains dominant M2-cation (analysis 8 in Table 3). Zeolite nature of hilairite-group minerals is also proved by the ease of entry of additional Na<sup>+</sup> cation (in relation to REE-free members of the group), necessary to compensate the deficiency of positive charge arising at heterovalent replacement (Zr,Ti)<sup>4+</sup> → Y<sup>3+</sup> in channels of sazykinaite and pyatenkoite. As is known, just this is the charge balance mechanism in very

many «true» zeolites with wide limits of isomorphism between Si<sup>4+</sup> and Al<sup>3+</sup> in tetrahedra (Gottardi, Galli, 1985).

A triple system hilairite Na<sub>2</sub>{ZrSi<sub>3</sub>O<sub>9</sub>}·3H<sub>2</sub>O – calciohilairite Ca{ZrSi<sub>3</sub>O<sub>9</sub>}·3H<sub>2</sub>O – komkovite Ba{ZrSi<sub>3</sub>O<sub>9</sub>}·3H<sub>2</sub>O has a peculiar analogue by a set of extra-framework cations among «true» zeolites: natrolite Na<sub>2</sub>{Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>}·2H<sub>2</sub>O – scolecite Ca{Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>}·3H<sub>2</sub>O – edingtonite Ba{Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>}·4H<sub>2</sub>O. Moreover, isostructural natrolite and scolecite show a complete miscibility, while structurally close edingtonite rarely contains appreciable admixtures of other cations (see: Gottardi, Galli, 1985).

Due to its zeolite-like structure causing multicomponent composition and significant variations in contents of cations (especially extra-framework cations) and water, hilairite-group minerals are sensitive indicators of chemical environments at mineral formation. As shows the analysis of their occurrence conditions and paragenesis, the temperature interval of crystallization of these most rich in water Zr-silicate phases is narrow: appearance of hilairite-group minerals from hydrothermal solutions at temperatures above 150°C is little probable. At the same time, geochemical settings of their formation may differ strongly. So, the particular type of hydrothermal rocks related to carbonatites of the Vuoriyarvi massif has sharp barium specificity manifested, in particular, by the presence of komkovite; decomposition of abundant eudialyte containing admixtures of Y and HREE (Koashva, Khibiny) in hyperalkaline hydrothermal conditions has resulted in crystallization of sazykinaite-(Y) in leaching cavities – the mineral, which has concentrated these elements (Pekov, 1998).

In some cases the composition of hilairite-like minerals reflects the chemical environment of late solutions – the stage of decationing of these phases or ionic exchange. This could be the way of formation of the secondary concentric zonality – so we interpret the structure of crystals from the Flora Mountain in the Lovozero massif.

## Conclusions

So, basing on the results of study of new finds of hilairite-group minerals in the Khibiny-Lovozero alkaline complex and on earlier published data from all known occurrences of the world, we attempted to illustrate zeolite character of these minerals and to characterize from this viewpoint their composition and some cry-

stallochemical features. Hilaireite-group minerals form a very original type of natural rare-metal «zeolites» with a peculiar combined framework. Their properties demand detailed study: it is possible that they are not only unusual, but also interesting in practical application.

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