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COMPOSITIONAL VARIATION OF PEROVSKITE-GROUP MINERALS FROM THE KHIBINA COMPLEX, KOLA PENINSULA, RUSSIA

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ABSTRACT

Perovskite-group minerals from the Khibina alkaline complex, Kola Peninsula of Russia, are primarily members of the lueshite – perovskite – loparite-(Ce) solid solution series. The widest compositional range is exhibited by perovskite-group minerals from the foidolite series, poikilitic nepheline syenite (rischorrite) and associated pegmatites. The trend of compositional evolution of perovskite-group minerals is from perovskite *sensu stricto* through cerian and cerian niobian perovskite to calcian niobian, niobian calcian and niobian loparite-(Ce), and then to isolueshite, a Na–Nb-dominant member of the perovskite family. This trend corresponds well with the trend established for loparite from the Lovozero stratified intrusion. Loparite in metasomatic rocks of the Khibina complex may represent either a relict assemblage or a late-stage phase crystallized from metasomatic fluids.

Keywords: perovskite, loparite, isolueshite, ultramafite, foidolite, nepheline syenite, albitite, Khibina alkaline complex, Kola Peninsula, Russia.

SOMMAIRE

Les minéraux du groupe de la pérovskite du complexe alcalin de Khibina, péninsule de Kola, en Russie, font partie du système lueshite – pérovskite – loparite-(Ce) et forment une solution solide. L'étendue de compositions la plus importante se trouve dans la série des foidolites, les syénites à néphéline poecilitiques (rischorrites) et les pegmatites qui leurs sont associées. Le tracé évolutif de ces minéraux va de pérovskite *sensu stricto*, et passe de la pérovskite enrichie en cérium ou cérium + niobium vers la loparite-(Ce) calcique et niobifère, niobifère et calcique ou simplement niobifère, et ensuite vers l'isolueshite, membre à dominance de Na–Nb de la famille de la pérovskite. Ce tracé correspond bien à celui qui est établi pour la loparite du complexe alcalin stratiforme de Lovozero. La loparite des roches métasomatiques du complexe de Khibina représente soit une phase relique ou une phase tardive formée aux dépens d'une phase fluide lors d'un épisode de métasomatose.

(Traduit par la Rédaction)

Mots-clés: pérovskite, loparite, isolueshite, roche ultramafique, foidolite, syénite néphélinique, albitite, complexe alcalin de Khibina, péninsule de Kola, Russie.

INTRODUCTION

The Khibina alkaline complex, in the Kola Peninsula of Russia, covers an area of 1327 sq. km, and is the largest intrusion of nepheline syenites and allied rocks in the world. The intrusion was emplaced at the boundary between Archean granite gneisses and Proterozoic volcanic-sedimentary rocks. Emplacement was tectonically controlled by a Middle Paleozoic paleorift zone (Orlova 1993). Structurally, the complex is a differentiated subconical body with contacts dipping from 45° to almost 90°, with inclination angles gradually decreasing with depth (Shablinskii 1963). The intrusion is composed of the following petrographic units (from the western contact inward) (Fig. 1): leucocratic coarse-grained massive nepheline syenite (khibinite) and trachytoid khibinite locally enclosing a rhomb-porphyry complex, a "differentiated" series of melteigite – urtite and associated apatite – nepheline rocks, poikilitic nepheline syenite (rischorrite) and associated juvite, medium-grained aegirine – nepheline syenite (liavochorrite), trachytoid and massive foyaite (Eliseev *et al.* 1939, Galakhov 1975, Kogarko *et al.* 1995, Sørensen 1970, Zak *et al.* 1972). The central plug of foyaite hosts pulaskites,

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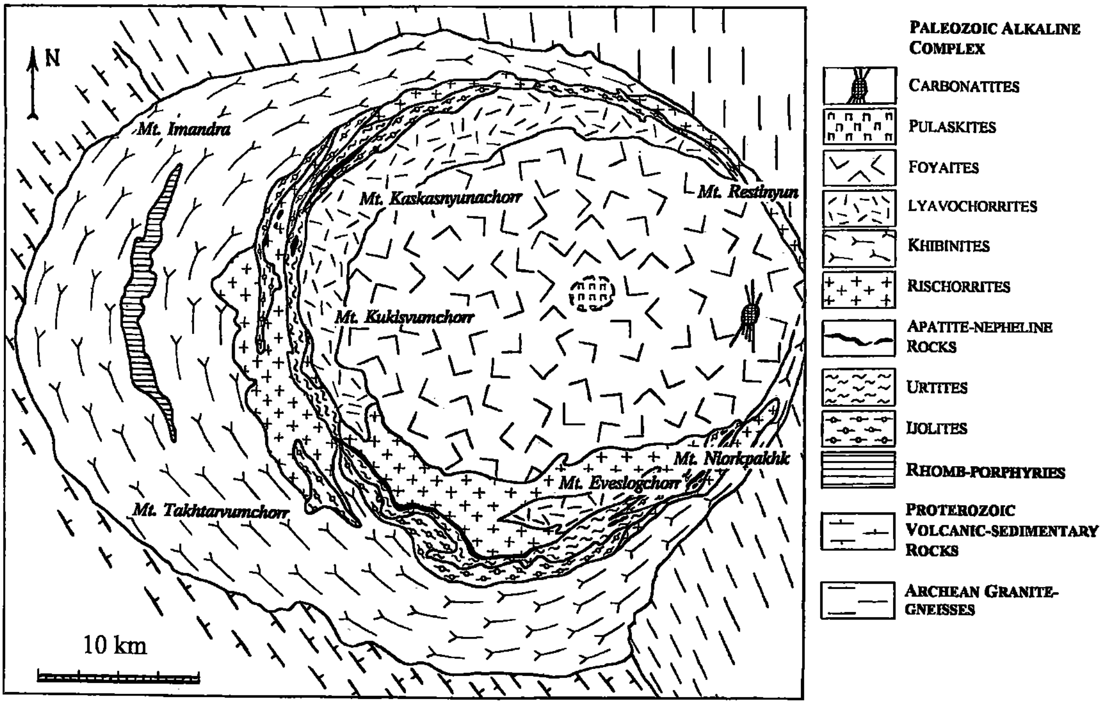

FIG. 1. Schematic geological map of the Khibina alkaline massif, after Zak *et al.* (1972), with additions by Dudkin *et al.* (1984) and Korobeinikov & Pavlov (1990).

which are covered by Quaternary sediments (Korobeinikov & Pavlov 1990). The youngest igneous rocks are, in the order of emplacement: alkali picrite, olivine melanephelinite dikes and diatremes, an alkali gabbro series, nephelinite, phonolite, alkali trachyte dikes and carbonatite (Arzamastsev *et al.* 1988, Dudkin *et al.* 1984).

Rocks of the Khibina complex are derivatives of two distinct parental magmas: nephelinitic (olivine nephelinite) and alkali-basaltic, both of which were present between 377.3 ± 3.9 and 362.4 ± 4.5 Ma (Kramm *et al.* 1993). The nephelinitic source is responsible for the formation of the ultramafic – alkali ultramafic suite represented by peridotite, pyroxenite and melilitolite (Arzamastsev 1990, 1994). These rocks are found as thin dikes in the country-rock-derived fenitized gneisses, and as xenoliths in the later-formed foidolite and nepheline syenite (Galakhov 1966, Shpachenko *et al.* 1990). Nepheline syenites comprising the bulk of the intrusion, alkaline syenites and their hypabyssal analogues are believed to originate from an alkali-basaltic parent (Arzamastsev 1990, Korobeinikov & Pavlov 1990).

The origin of the foidolite and rischorrite series remains uncertain. According to Eliseev *et al.* (1939), Galakhov (1975) and Zak *et al.* (1972), the major intrusive series were emplaced in the sequence observed from the western contact eastward. Kupletskii's (1937) hypothesis, that the intrusion of the foidolites followed the formation of nepheline syenite and rischorrite, is supported by field observations (Sniatkova *et al.* 1986) and by many studies of the mineralogy of Khibina rocks (Kostyleva-Labuntsova *et al.* 1978). As an alternative, some authors interpret the melteigite – urtite series and apatite – nepheline rocks as remnants of an earlier intrusion derived from the nephelinitic source (Arzamastsev 1990, 1994, Dudkin *et al.* 1986). Solodovnikova (1959) and Tikhonenkov (1963) proposed that rischorrite is a metasomatic rock developed after the earlier-formed foidolites or nepheline syenites, whereas Ivanova & Arzamastsev (1985) considered the foidolite series and rischorrite as products of differentiation of a nepheline syenite magma.

Nepheline syenites and country rocks of the Khibina complex underwent large-scale metasomatic alteration which gave rise to modally diverse albite, albite – aegirine, albite – aegirine – astrophyllite metasomatic assemblages (mariupolite) in the former and alkali feldspar – aegirine fenite in the latter (Gorstka 1971). The albite-rich metasomatic suites are especially abundant on both sides of the melteigite – urtite – rischorrite sequence along the contacts with khibinite and foyaite (Kostyleva-Labuntsova *et al.* 1978, Tikhonenkov 1963).

Pegmatite bodies ranging from simple unzoned to complex differentiated varieties occur in all major intrusive units of the complex. Their distribution, geological setting and mineralogy have been described by Slepnev (1962), Tikhonenkov (1963), and Kostyleva-Labuntsova *et al.* (1978). Some pegmatite bodies have experienced intense alteration (with formation of aegirine, albite, natrolite) by late-stage residual melts or fluids (or both).

The Khibina complex is the type locality for loparite, which was initially reported from endocontact khibinites by Kuznetsov (1925). Studies by Tikhonenkova *et al.* (1982) and Bel'kov *et al.* (1988) have shown that this mineral occurs in most petrographic members of the complex and may be present in commercially viable quantities. At Khibina, perovskite was first recognized by Eliseev (1937) in the apatite – nepheline rocks. Studies by Shilin & Yanchenko (1962), Dudkin *et al.* (1964), Galakhov (1966, 1975), Arzamastsev *et al.* (1988) and Shpachenko *et al.* (1990) have demonstrated that perovskite is a common accessory constituent of the plutonic and extrusive alkaline ultramafic rocks in the complex. However, a systematic study of loparite mineralization at Khibina has not been undertaken, and most of the available data on the composition of the Khibina perovskite-group minerals have been obtained by wet-chemical, semiquantitative spectrographic and other bulk methods. As a result, the majority of authors of previous investigations reported unrealistically high contents of Si, Al, K and Mg, probably resulting from inclusions or overgrowths of silicate phases associated with loparite.

This study was conducted to establish the trends of intra- and intergranular compositional variation of loparite and perovskite from the intrusive rocks, associated pegmatite facies and metasomatic rocks of the Khibina complex, and to compare these data with the compositions of perovskite-group minerals from other alkaline complexes. The material examined was selected by the authors during the field work at Khibina in 1993, 1994 and 1996, and was provided in part by our colleagues from the Geological Institute in Apatity, Kola Peninsula.

OCCURRENCE

The occurrence of perovskite at Khibina is restricted to the undersaturated ultramafic rocks and foidolites, as the mineral is unstable in a paragenesis with feldspars. In ultramafites and foidolites, perovskite occurs as small anhedral to subhedral crystals (40–100 μm) filling interstices between the rock-forming silicates, as polygranular pseudomorphs after titanite, and as relics partly replaced by titanite, ilmenite or aeschynite-(Ce). Veksler & Teptelev (1990) have demonstrated that titanite is an earlier liquidus phase compared to perovskite in the "diopside" part, and *vice versa* in the "nepheline" part of the system nepheline – diopside – titanite. Our observations and published data (Shilin & Yanchenko 1962, Dudkin *et al.* 1964) confirm that pseudomorphs of perovskite after titanite are found in melanocratic rocks such as clinopyroxenite or melteigite, whereas titanite pseudomorphs after perovskite are common in apatite – nepheline rocks and urtite. In ultramafic rocks, perovskite is associated with diopside or augite, phlogopite, apatite, titaniferous magnetite, magnesian ilmenite, and may be also accompanied by olivine, nepheline, calcite, zirconolite and sulfides. In foidolites, the associated minerals are nepheline, diopside, titaniferous magnetite, titanite, apatite and, less commonly, manganoan ilmenite, calzirtite and wöhlerite.

Loparite at Khibina occurs predominantly in pegmatite-facies nepheline syenite and petrographically diverse metasomatic rocks, but is not a common accessory phase in the intrusive series. In the latter, loparite was found in khibinite, ijolite, rischorrite and foyaite. In khibinite and foyaite, loparite forms scarce anhedral to subhedral grains between crystals of nepheline and alkali feldspar. The loparite crystals do not exceed 3–4 mm in size. In ijolite, anhedral grains of loparite are found as inclusions in the rock-forming silicates. The associated minerals are nepheline, aegirine, apatite and titanite. In rischorrite, loparite is a ubiquitous accessory mineral in potassium feldspar – aegirine "veins", conformably developed within the host "normal" rischorrites. Although the geological position of the "veins" may suggest that they are cogenetic with rischorrite, some authors propose a metasomatic origin for these rocks (Bel'kov *et al.* 1988, Kozyreva 1990). Discussion of their genesis is beyond the scope of this work. The potassium feldspar – aegirine "veins" contain minor quantities of nepheline, eudialyte and astrophyllite and also host loparite mineralization of economic value (Bel'kov *et al.* 1988). In these, loparite occurs as interpenetration "fluorite-type" twins of cubic crystals which may enclose minute grains of potassium feldspar. The size of the twinned crystals does not exceed 4–5 mm.

Pegmatites commonly contain accessory loparite as:

1. An early-stage phase in contact zones which, in general, are mineralogically similar to the host rock, and are composed of nepheline, alkali feldspar and, possibly, prismatic aegirine, eudialyte, aenigmatite and arfvedsonite. Single hexahedral and twinned crystals of loparite are included in felsic minerals and microcline – villiaumite intergrowths.

2. A late-stage mineral in an aggregate of fibrous and radial aegirine with titanite, astrophyllite, lamprophyllite and lorenzenite present in smaller quantities (Fig. 2). These aggregates developed by corrosion and metasomatic replacement of the early-stage paragenesis due to interaction with deuteric (?) fluids derived from a pegmatite-forming melt. In the Russian literature, the aegirine zones in the nepheline syenite pegmatites are commonly termed "autometasomatic" (Kostyleva-Labuntsova *et al.* 1978). Loparite forms morphologically diverse twins of cubic and cubo-octahedral crystals.

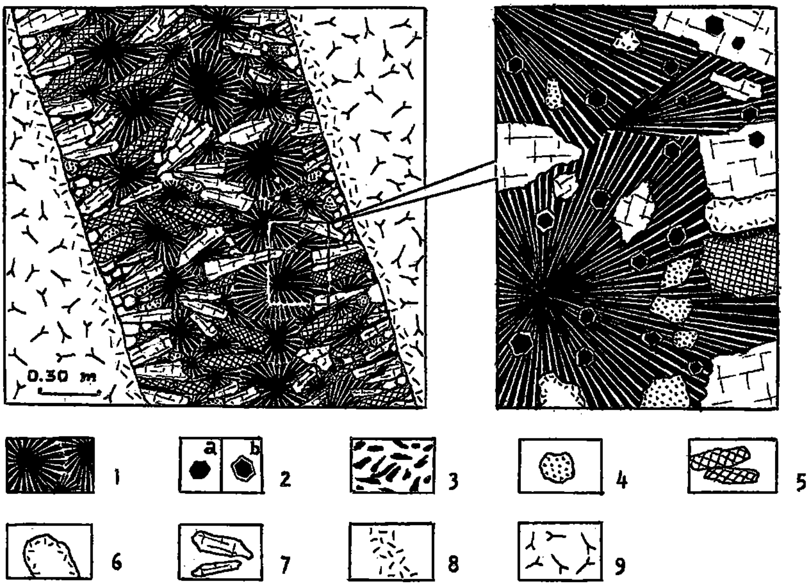

FIG. 2. Schematic drawing of a pegmatite vein in khibinite, Mt. Imandra: 1 radial and fibrous aegirine, 2 loparite-I (a) and loparite-II (b), 3 aenigmatite, 4 eudialyte, 5 arfvedsonite, 6 nepheline, 7 microcline, 8 contact chilled zone, 9 khibinite.

3. A phase associated with sodalite, ordered microcline, natrolite, acicular aegirine and rare Na–Nb, Na–Zr and Na–Ti silicates (nenadkevichite, fersmanite, catapleiite, lovozerite), which commonly occur in the axial zones of strongly differentiated pegmatite bodies, and as coatings on the walls of cavities and vugs developed in occasional "blows". Undoubtedly, this mineral assemblage crystallized from the final products in the evolution of pegmatite-forming systems. Loparite occurs as interpenetration twins of cubo-octahedral crystals.

In this work, these differing loparite-bearing parageneses are referred to as loparite-I, -II and -III, respectively.

Pegmatites in the rocks of the melteigite – urtite series have been noted to contain niobian loparite (Sokolova 1972) and isolueshite (Chakhmouradian *et al.* 1997) as late-stage accessory phases associated with sodalite. Isolueshite has the empirical formula (Na,La, Ca) $(Nb,Ti)O_3$ and, compared to orthorhombic lueshite, the undistorted cubic structure of the perovskite type.

Albite-rich metasomatic rocks commonly contain considerable concentrations of accessory loparite. In these, it occurs as "fluorite-type" twins of equally developed cubic or cubo-octahedral individuals. The twins commonly enclose multiple inclusions of albite, aegirine and eudialyte, that demonstrate crystallization during the latest stages of albitite formation from metasomatizing alkali fluids. In albite – aegirine metasomatites of the North Partomchorr Pass, loparite occurs in two generations. Loparite of the early generation forms large (0.5–1.5 cm) twins with a nonpoikilitic core and a rim "stuffed" with minute platelets of albite. The late generation is represented by small (0.5–2 mm) poikilitic twins with multiple inclusions of albite and aegirine.

ANALYTICAL TECHNIQUES

All mineral compositions were determined by X-ray energy-dispersion spectrometry (EDS) using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn$K\alpha$) at Lakehead University. EDS spectra of loparite were acquired for 300 seconds, and those of perovskite, for 180 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86 nA. X-ray spectra were collected and processed with the LINK ISIS–SEMQUANT software package. Full ZAF corrections were applied to the raw X-ray data. The following standards were used for the determinations of loparite and perovskite compositions: Khibina loparite (Na, La, Ce, Pr, Nd, Nb), Magnet Cove perovskite (Ca, Ti, Fe), synthetic $SrTiO_3$ (Sr), metallic Th and Ta. The accuracy of the method was cross-checked by wavelength-dispersion electron-microprobe analysis of isolueshite using an automated CAMECA SX–50 microprobe located at the University of Manitoba using methods described by Mitchell & Vladykin (1993). At the low beam-currents used for the analyses, back-scattered electron imagery of the samples did not reveal any heterogeneity in the distribution of the major elements. Consequently, each grain of loparite and perovskite was analyzed in several places to ensure that the complete compositional range, if any, was determined.

Compositional data were recalculated into perovskite-group end-members following methods suggested by Mitchell (1996). All perovskite-group minerals examined in this study were found to be essentially members of the $NaNbO_3 - CaTiO_3 - Na(REE)Ti_2O_6$ system. They contain low levels of the $SrTiO_3$ (tausonite), $CaThO_3$, $(REE)_2Ti_2O_7$ and other perovskite-type end members. Accordingly, the ternary system lueshite (isolueshite) – perovskite – loparite is used to illustrate the compositional variation (Figs. 3–8). The system tausonite – perovskite – loparite is used to compare Sr contents in the composition of perovskite and loparite from alkaline ultramafic rocks of the Khibina complex and carbonatite complexes of the Kola Peninsula (Fig. 3b). Variations in major and trace elements in perovskite-group minerals are given in Tables 1–6 and discussed in the text, as they are important for determination of the compositional evolution of these minerals during the formation of the host rocks.

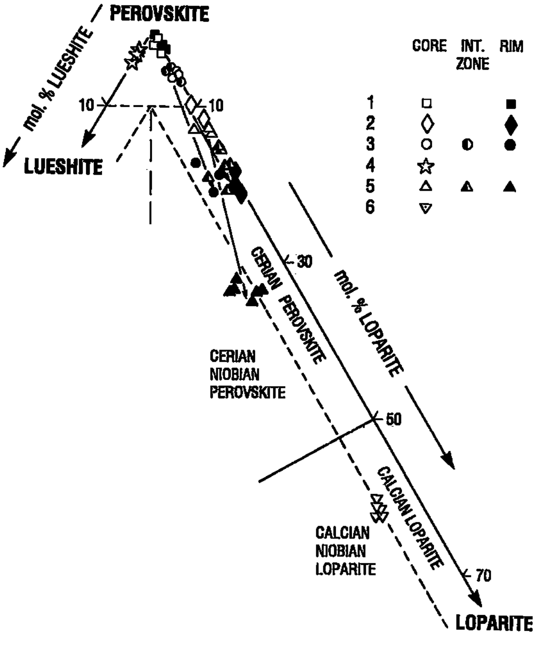

FIG. 3. Compositions (mol.%) of perovskite and loparite from alkaline ultramafic rocks of the Khibina complex in the system lueshite – perovskite – loparite: 1 clinopyroxenite, Mt. Restinyun, 2 clinopyroxenite, Mt. Putelichorr, 3 mica peridotite, R. Tulijok, 4 urtite, Mt. Putelichorr, 5 apatite – nepheline rock, Yukspor Mine, 6 ijolite, Mt. Eveslogchorr.

COMPOSITION

Ultramafic rocks and foidolites

Perovskite from these rocks may or may not exhibit intragranular zonation. It is important to note that perovskite from clinopyroxenite dikes in the country-rock-derived fenitized gneiss shows no compositional zonation (Table 1, anal. 1). Where present, the pattern of zonation is irregular, with a discontinuous rim and occasional "patches" along fractures within the crystals enriched in Na, the light rare-earth elements (*LREE*) and Nb. The zonation trend is from perovskite *sensu stricto* to cerian perovskite or from cerian perovskite to cerian niobian perovskite at essentially constant content of the tausonite end-member (Table 1, anals. 2–10, Fig. 3). Enrichment in Na (up to 4.1 wt.% Na_2O), *REE* (up to 15.0 wt.% REE_2O_3) and Nb (up to 6.3 wt.% Nb_2O_5) from the core toward the rim is always accompanied by increase in Th content (up to 2.0 wt.% ThO_2). This trend culminates with the appearance of calcian niobian loparite-(Ce) in ijolite (Table 1, anals. 11–12, Fig. 3a).

Perovskite and loparite from the Khibina alkaline ultramafic rocks are enriched in Sr (up to 2.8 and 6.9 wt.% SrO) compared to those from the typical alkaline ultramafic complexes of the Kola Peninsula (*e.g.*, Afrikanda, Kovdor). In the latter, the Sr content ranges from 0 to 0.8 wt.% SrO.

Khibinite

Loparite from coarse-grained massive khibinite is calcian niobian loparite-(Ce) with a low concentration of Sr and relatively high concentrations of Th, Ta and Fe. From core to rim, the loparite evolves in composition by depletion in Nb and Sr and enrichment in *LREE*, Ti and Fe (Table 2, anals. 1–2, Fig. 4). Thus, the zonation trend is toward less niobian loparite at slightly decreasing average content of the perovskite end-member (from 12.4 to 11.9 mol.%).

Pegmatites in khibinite

At Mount Takhtarvumchorr, a differentiated pegmatite body hosted by khibinite contains two generations of loparite. Compared to the above-characterized loparite from the host rock, both loparite-I and loparite-II are enriched in Sr (2.0–4.1 wt.% SrO), Nb (9.4–18.6 wt.% Nb_2O_5) and depleted in *LREE* (27.5–36.0 wt.% $\Sigma LREE_2O_3$) (Table 2, anals. 3–6). Loparite-I is niobian calcian loparite-(Ce) with a core-to-rim zonation trend similar to that observed in the loparite in the host khibinite (Fig. 4). Calcian niobian loparite-II from aegirine-bearing autometasomatic rocks compositionally evolves by becoming enriched in Na, Nb, and Th, and depleted in Ca, Ti and Fe (Fig. 4). At the rim, loparite-II is replaced by Nb-rich anatase and rare-earth phosphate [? monazite-(Ce)]. Interestingly, a similar pattern of

TABLE 1. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM ULTRAMAFIC ROCKS AND FOIDOLITES

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12
Nb_2O_5	0.02	0.91	1.48	1.08	1.06	5.02	n.d	1.34	1.24	6.29	5.94	4.82
Ta_2O_5	0.14	0.20	0.24	0.16	0.25	0.37	0.24	0.20	0.13	0.31	0.45	0.79
TiO_2	55.90	55.07	52.28	54.20	54.74	50.65	58. 10	54.37	52.62	48.13	44.17	42.37
FeO	0.84	0.43	0.57	1.71	1.72	1.37	0.33	0.55	0.64	0.63	0.84	0.91
ThO_2	n.d	n.d	0.93	0.07	0.11	0.91	0.19	0.10	0.21	1.78	1.43	1.79
La_2O_3	0.97	0.75	1.60	1.03	0.18	2.58	n.d	1.97	2.84	3.33	8.34	6.72
Ce_2O_3	0.62	2.19	4.55	1.89	1.68	5.57	n.d	3.07	4.42	6.96	15.57	14.54
Pr_2O_3	n.d	0.94	1.31	n.d	0.47	n.d	n.d	n.d	1.00	0.78	0.31	1.43
Nd_2O_3	0.22	1.21	2.94	0.20	0.16	1.03	n.d	1.15	1.61	2.29	2.33	3.19
CaO	38.36	35.17	30.27	37.97	37.51	30.71	38.28	33.39	31.73	23.83	8.92	9.67
SrO	1.89	1.81	1.31	0.62	0.66	0.91	2.14	1.36	1.37	1.58	6.52	6.19
Na_2O	0.09	1.11	2.10	0.77	0.67	2.10	0.70	1.55	1.58	4.10	6.31	6.06
Total	99.05	99.79	99.58	99.70	99.21	101.22	99.98	99.05	99.39	100.01	101.13	98.48
	Structural formulae based on 3 atoms of oxygen											
Nb	0.000	0.010	0.016	0.011	0.011	0.055	0.000	0.014	0.014	0.072	0.074	0.062
Ta	0.001	0.001	0.002	0.001	0.002	0.002	0.001	0.001	0.001	0.002	0.003	0.006
Ti	0.984	0.979	0.965	0.957	0.966	0.920	1.002	0.978	0.965	0.914	0.916	0.908
Fe	0.016	0.008	0.012	0.033	0.034	0.028	0.006	0.011	0.013	0.013	0.019	0.022
Th	0.000	0.000	0.005	0.000	0.001	0.005	0.001	0.000	0.001	0.010	0.009	0.012
La	0.008	0.007	0.014	0.009	0.002	0.023	0.000	0.017	0.026	0.031	0.085	0.071
Ce	0.005	0.019	0.041	0.016	0.014	0.049	0.000	0.027	0.039	0.064	0.157	0.152
Pr	0.000	0.008	0.012	0.000	0.004	0.000	0.000	0.000	0.009	0.007	0.003	0.015
Nd	0.002	0.010	0.026	0.002	0.001	0.009	0.000	0.010	0.014	0.021	0.023	0.032
Ca	0.962	0.891	0.796	0.955	0.944	0.795	0.940	0.856	0.829	0.645	0.263	0.295
Sr	0.026	0.025	0.019	0.008	0.009	0.013	0.028	0.019	0.019	0.023	0.104	0.102
Na	0.004	0.051	0.100	0.035	0.030	0.098	0.031	0.072	0.075	0.201	0.337	0.335
	Mol.% End-members											
$CaThO_3$	0.00	0.00	0.52	0:04	0.06	0.52	0.10	0.05	0.12	1.03	1.12	1.39
$SrTiO_3$	2.58	2.50	1.88	0.85	0.90	1.31	2.84	1.88	1.98	2.33	12.99	12.27
$NaNbO_3$	0.00	0.70	0.72	0.82	0.91	1.78	3.11	1.78	0.00	7.82	4.82	4.09
$Ce_2Ti_2O_7$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.76	0.27
$CaTiO_3$	96.60	87.99	78.10	92.92	93.88	79.66	93.94	85.47	82.64	63.98	31.72	34.02
Loparite	0.82	8.81	18.78	5.37	4.25	16.73	0.00	10.82	15.26	24.84	48.59	47.96

Compositions 1-10 perovskite, 11 & 12 loparite: 1 unzoned crystal from clinopyroxenite (dike in fenitized gneiss), Mt. Restinyun, 2 & 3 core and rim of a zoned crystal from clinopyroxenite (xenolith in urtite), Mt. Putelichorr, 4-6 core, intermediate zone and rim of a zoned crystal from mica peridotite (xenolith in nepheline syenite), R. Tulijok, 7 unzoned crystal from urtite, Mt. Putelichorr, 8-10 core, intermediate zone and rim of a zoned crystal from apatite-nepheline rock, Yukspor Mine, 11 & 12 core and rim of an unzoned crystal from ijolite, Mt. Eveslogchorr. All data this work. Total Fe expressed as FeO; n.d = not detected.

replacement resulting in complete replacement was described for loparite from albitized syenite from Far East Russia (Kalenov *et al.* 1963).

Loparite-I from a simple unzoned vein at Mt. Khibina does not show any compositional zonation. On the diagram $NaNbO_3$–$CaTiO_3$–$NaCeTi_2O_6$, its composition plots near the boundary between calcian niobian and niobian calcian loparite-(Ce) (Fig. 4). Sr, Th, Fe and Ta contents in this loparite are similar to those in loparite from the pegmatite at Mt. Takhtarvumchorr (Table 2, anal. 7).

Among the loparite samples from khibinite pegmatites, those from Mt. Imandra are the most depleted in Ca and Sr (Table 2, anals. 8–13). Compositionally, both loparite-I and loparite-II are calcian niobian loparite-(Ce). Loparite-I exhibits two major trends in core-to-rim zonation trends. One of them is toward the loparite apex of the system $NaNbO_3$–$CaTiO_3$–$NaCeTi_2O_6$, and is thus similar to the trend shown by loparite-I from the Takhtarvumchorr pegmatite body (Fig. 4, A). The other trend is toward compositions enriched in Na and Nb (from 15.1 to 27.2 mol.% $NaNbO_3$), with the $NaCeTi_2O_6$ content decreasing from 77.3 to 67.4 mol.% (Fig. 4, B).

Loparite-II evolves by enrichment in Na and Nb (from 16.7 to 23.2 mol.% $NaNbO_3$) coupled with depletion in *LREE* and Ti (75.8 to 68.4 mol.% $NaCeTi_2O_6$) at essentially constant contents of the perovskite component (7.6–8.5 mol.%) (Fig. 4). At the rim, loparite-II is resorbed and replaced by niobian anatase and ? monazite-(Ce).

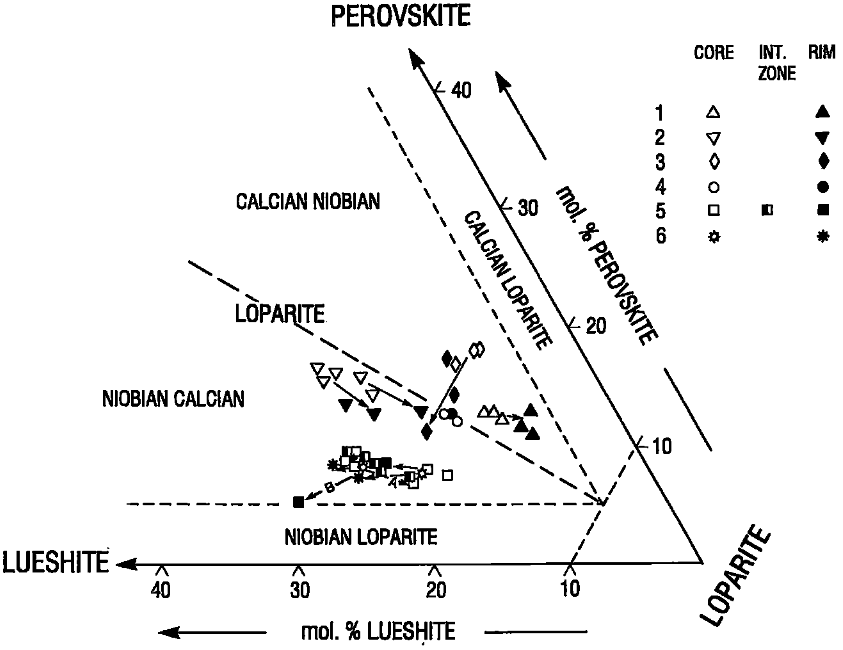

FIG. 4. Compositions (mol.%) of loparite from khibinite (1) and pegmatites in khibinite (2–6): 1 Mt. Takhtarvumchorr, 2 loparite-I, Mt. Takhtarvumchorr, 3 loparite-II, Mt. Takhtarvumchorr, 4 loparite-I, Mt. Khibina, 5 loparite-I, Mt. Imandra, 6 loparite-II, Mt. Imandra.

Rischorrite

Potassium feldspar – aegirine "veins" at Mts. Eveslogchorr and Kaskasnyunachorr contain loparite characteristically enriched in Ca, Fe and Ta, and depleted in Th (Table 3, anals. 1–4, 6–7). Most of the loparite is calcian niobian loparite-(Ce) with a relatively uniform intragranular composition. Intergranular compositional variation is particularly pronounced in loparite from Mt. Eveslogchorr (Fig. 5). The rims of some crystals from both localities are enriched in Na (up to 9.8 wt.% Na_2O) and Nb (up to 20.5 wt.% Nb_2O_5). Such rims are Fe- and Ta-poor, and Th-rich (Table 3, anals. 5, 8). Undoubtedly, this patchy zonation is due to interaction of the early-formed loparite with late-stage Nb-bearing alkali-rich fluids.

Pegmatites in rischorrite

Loparite-I from two pegmatite veins at Mt. Marchenko are compositionally close to the loparite from rischorrite, being calcian niobian loparite-(Ce) relatively rich in Fe and Ta and depleted in Th (Table 3, anals. 9–12, Fig. 5). In common with the loparite from rischorrite, some grains are occasionally enriched in Na and Nb at their rim (Table 3, anal. 13). The "patchy" zonation observed in the loparite from the rischorrite and rischorrite pegmatites also has been established in specimens of loparite from the Eudialyte Pass (Mitchell *et al.* 1996), originally described by Tikhonenkov & Kazakova (1957) as "nioboloparite". The mineral is associated with natrolite, murmanite, pyrochlore, and some other minerals typical of the parageneses with loparite-III. However, the compositional features of "nioboloparite" suggest that it is loparite-I.

Loparite-III from highly differentiated pegmatite veins in rischorrite has been studied by Mitchell *et al.* (1996) and found to be niobian calcian and niobian loparite-(Ce), with trends of core-to-rim zonation similar to those determined for loparite from khibinite and some loparite generations from pegmatites in khibinite (see above). The compositions and zonation trends of the loparite-III are shown on Figure 5.

Pegmatites in foidolites

Pegmatite veins in foidolites contain Na- and Nb-rich members of the perovskite family. At Mt. Koashva, loparite-III is niobian loparite-(Ce) with high Na and Nb (10.3–11.8 wt.% Na_2O and 25.7–35.6 wt.% Nb_2O_5, respectively), and low Ca, Sr, Ta and Fe contents (Table 4, anals. 1–2). The composition and trend of core-to-rim zonation are similar to those of loparite-III from the vein in rischorrite (Fig. 5).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM KHIBINITE AND PEGMATITES IN KHIBINITE

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
Nb_2O_5	8.92	6.69	18.51	13.88	7.30	13.17	11.75	19.36	15.83	14.14	24.35	15.01	19.95
Ta_2O_5	0.95	1.11	1.19	0.45	0.89	1.17	0.46	1.05	0.87	0.90	0.40	1.24	0.78
TiO_2	39.89	40.08	36.13	37.72	41.15	35.78	39.42	33.17	36.05	37.27	31.11	37.84	34.48
FeO	0.15	0.57	0.08	0.09	0.32	0.08	0.01	0.15	n.d	0.12	0.04	0.09	0.14
ThO_2	1.12	1.44	0.55	1.29	0.76	1.38	0.98	0.50	0.89	0.62	0.92	0.52	0.68
La_2O_3	11.09	10.63	9.48	10.38	10.38	8.58	10.08	9.53	10.49	9.94	8.91	9.82	9.06
Ce_2O_3	19.88	19.79	15.61	17.20	19.31	17.17	19.17	17.03	18.46	18.92	15.03	18.95	16.67
Pr_2O_3	1.79	2.54	0.92	1.66	1.89	4.16	1.04	3.08	1.39	2.18	3.01	0.68	1.80
Nd_2O_3	3.68	4.76	1.91	3.57	4.40	4.25	4.20	3.38	3.09	3.08	2.94	2.97	2.88
CaO	2.98	2.69	3.46	2.91	3.99	2.47	2.80	1.64	1.52	1.69	1.22	1.64	1.63
SrO	2.04	1.84	2.78	2.42	2.51	2.48	1.71	2.38	2.12	1.98	2.34	1.89	2.44
Na_2O	8.41	8.19	9.18	8.86	7.63	8.52	8.72	9.47	9.10	9.26	10.46	9.22	9.94
Total	100.90	100.33	99.80	100.43	100.53	99.21	100.34	100.74	99.81	100.10	100.73	99.87	100.45
Structural formulae based on 3 atoms of oxygen													
Nb	0.116	0.089	0.237	0.180	0.095	0.176	0.152	0.254	0.208	0.185	0.317	0.195	0.258
Ta	0.007	0.009	0.009	0.004	0.007	0.009	0.004	0.008	0.007	0.007	0.003	0.010	0.006
Ti	0.866	0.884	0.769	0.814	0.891	0.797	0.849	0.725	0.788	0.811	0.673	0.816	0.742
Fe	0.004	0.014	0.002	0.002	0.008	0.002	0.000	0.004	0.000	0.003	0.001	0.002	0.003
Th	0.007	0.010	0.003	0.008	0.005	0.009	0.006	0.003	0.006	0.004	0.006	0.003	0.004
La	0.118	0.115	0.099	0.110	0.110	0.094	0.106	0.102	0.112	0.106	0.094	0.104	0.096
Ce	0.210	0.212	0.162	0.181	0.203	0.186	0.201	0.181	0.196	0.200	0.158	0.199	0.175
Pr	0.019	0.027	0.009	0.017	0.020	0.045	0.011	0.032	0.015	0.023	0.032	0.007	0.019
Nd	0.038	0.050	0.019	0.036	0.045	0.045	0.043	0.035	0.032	0.032	0.030	0.030	0.029
Ca	0.092	0.084	0.105	0.090	0.123	0.078	0.086	0.051	0.047	0.052	0.038	0.050	0.050
Sr	0.034	0.031	0.046	0.040	0.042	0.043	0.028	0.040	0.036	0.033	0.039	0.031	0.040
Na	0.471	0.466	0.504	0.493	0.426	0.489	0.484	0.533	0.513	0.519	0.584	0.513	0.551
Mol.% End-members													
$CaThO_3$	1.00	1.29	0.52	1.18	0.67	1.29	0.90	0.48	0.86	0.58	0.90	0.51	0.65
$SrTiO_3$	4.63	4.21	6.67	5.66	5.64	5.93	4.00	5.82	5.25	4.76	5.82	4.69	5.98
$NaNbO_3$	8.40	6.56	17.98	12.89	6.86	12.92	10.97	19.06	15.78	13.75	23.86	15.23	19.51
$Ce_2Ti_2O_7$	3.87	3.66	3.48	3.70	5.54	6.91	3.46	8.72	6.36	3.63	5.70	3.57	3.45
$CaTiO_3$	11.51	10.07	14.82	11.38	15.89	9.61	11.21	6.93	6.09	6.92	4.71	7.01	6.73
Loparite	70.59	74.21	56.53	65.19	65.40	63.34	69.46	58.99	65.66	70.36	59.01	68.99	63.68

Compositions: 1-6 Mt. Takhtarvumchorr, 1 & 2 core and rim of a zoned crystal from khibinite; 3 & 4 core and rim of a zoned loparite-I crystal from pegmatite in khibinite; 5 & 6 core and rim of a zoned loparite-II crystal from pegmatite in khibinite; 7 unzoned loparite-I crystal from pegmatite in khibinite, Mt. Khibina; 8-13 Mt. Imandra, 8 & 9 core and rim of a zoned loparite-I crystal from pegmatite in khibinite (Fig. 4, trend A); 10 & 11 core and rim of a zoned loparite-I crystal from pegmatite in khibinite (Fig. 4, trend B); 12 & 13 core and rim of a zoned loparite-II crystal from pegmatite vein in khibinite. All data this work. Total Fe expressed as FeO; n.d = not detected.

Representative compositions of isolueshite from the type locality are given in Table 4, anals. 3–6. This mineral is a cubic polymorph of $NaNbO_3$ and contains considerable levels of *LREE*, Ti and Th. The zonation trend of isolueshite is essentially identical to those described above for loparite-III from different occurrences (Fig. 5). In isolueshite, this trend culminates with the appearance of loparite as a thin (less than 10 μm) outermost zone. It contains approximately 68 mol.% of the $NaLaTi_2O_6$ end-member and should be classified as loparite-(La), following the principles of nomenclature suggested by Levinson (1966) for rare-earth minerals. A detailed discussion on the chemical composition of isolueshite can be found in Mitchell *et al.* (1996) and Chakhmouradian *et al.* (1997).

Foyaite

Loparite from foyaite is niobian calcian loparite-(Ce) with low Ca, Sr, Fe and Ta contents. The Th content is generally much higher than in the above-characterized samples, and ranges from 1.2 to 6.9 wt.% ThO_2 (Table 5, anals. 1–3). This loparite is, as a rule, complexly zoned, with occasional regions enriched in Na and Nb (up to 10.4 wt.% Na_2O and 20.1 wt.% Nb_2O_5) (Fig. 6).

Pegmatites in foyaite

In foyaite pegmatites at Mt. Niorkpakhk, both loparite-I and loparite-II are niobian calcian loparite-(Ce). Both generations have similar low Ca, Sr and Fe contents. Compared to loparite-I, loparite-II is enriched in Na, Nb, and depleted in *LREE*, Ti and Th (Table 5, anals. 4–11). The two generations also differ in their core-to-rim patterns of zonation. Loparite-I evolves compositionally by becoming enriched in *LREE* and Ti (from 73.6–74.2 mol.% $NaCeTi_2O_6$ at the core to 77.8–78.5 mol.% $NaCeTi_2O_6$ at the rim), and correspondingly

TABLE 3. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM RISCHORRITE AND PEGMATITES IN RISCHORRITE

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
Nb_2O_5	10.68	9.15	11.40	9.94	12.32	8.26	9.06	20.51	10.54	10.28	10.84	10.86	13.53
Ta_2O_5	1.58	1.33	1.55	1.29	1.09	0.62	0.63	0.25	1.09	0.78	1.21	1.21	1.47
TiO_2	39.34	39.48	38.41	39.37	38.65	41.02	40.88	34.52	38.65	39.26	37.94	38.37	36.76
FeO	0.20	0.12	0.36	0.21	0.17	0.41	0.15	0.26	0.25	0.16	0.29	0.13	0.23
ThO_2	0.33	0.46	0.60	0.65	0.72	0.27	0.34	2.04	0.52	1.09	0.70	0.58	0.60
La_2O_3	10.61	10.82	9.09	9.99	9.84	9.69	9.70	10.50	9.95	10.07	10.78	11.28	10.28
Ce_2O_3	19.22	19.66	17.88	18.81	17.94	18.14	18.83	14.37	18.19	18.41	17.70	18.25	16.21
Pr_2O_3	0.63	1.48	3.40	2.76	2.32	1.04	1.61	0.81	2.57	1.55	2.10	1.95	2.44
Nd_2O_3	3.02	2.95	3.31	3.41	2.86	2.73	3.05	1.49	4.06	3.31	2.51	3.18	3.52
CaO	3.90	3.62	4.14	3.64	3.30	6.85	4.91	2.96	4.66	4.40	4.67	4.23	4.70
SrO	1.46	1.95	2.34	1.94	2.54	2.05	2.18	2.50	1.63	2.67	2.14	1.79	2.21
Na_2O	8.62	8.44	8.03	7.83	8.42	7.36	7.70	9.84	7.98	8.08	7.71	7.99	8.02
Total	99.59	99.46	100.51	99.84	100.17	98.44	99.04	100.05	100.09	100.06	98.59	99.82	99.97
Structural formulae based on 3 atoms of oxygen													
Nb	0.139	0.120	0.148	0.130	0.160	0.107	0.117	0.264	0.137	0.134	0.143	0.142	0.176
Ta	0.012	0.010	0.012	0.010	0.008	0.004	0.005	0.002	0.009	0.006	0.010	0.010	0.012
Ti	0.850	0.862	0.830	0.857	0.834	0.882	0.881	0.738	0.839	0.850	0.834	0.836	0.798
Fe	0.005	0.003	0.009	0.005	0.004	0.010	0.004	0.006	0.006	0.004	0.007	0.003	0.006
Th	0.002	0.003	0.004	0.004	0.005	0.002	0.002	0.013	0.003	0.007	0.005	0.004	0.004
La	0.112	0.116	0.096	0.107	0.104	0.102	0.103	0.110	0.106	0.107	0.116	0.121	0.109
Ce	0.202	0.209	0.188	0.199	0.188	0.190	0.198	0.150	0.192	0.194	0.189	0.194	0.171
Pr	0.007	0.016	0.036	0.029	0.024	0.011	0.017	0.008	0.027	0.016	0.022	0.021	0.026
Nd	0.031	0.031	0.034	0.035	0.029	0.028	0.031	0.015	0.042	0.034	0.026	0.033	0.036
Ca	0.120	0.113	0.128	0.113	0.101	0.210	0.151	0.090	0.144	0.136	0.146	0.131	0.145
Sr	0.024	0.033	0.039	0.033	0.042	0.034	0.036	0.041	0.027	0.045	0.036	0.030	0.037
Na	0.480	0.475	0.448	0.440	0.468	0.408	0.428	0.542	0.446	0.451	0.437	0.449	0.449
Mol.% End-members													
$CaThO_3$	0.30	0.41	0.54	0.60	0.66	0.23	0.30	1.93	0.46	0.96	0.63	0.52	0.54
$SrTiO_3$	3.33	4.42	5.36	4.54	5.93	4.41	4.91	6.02	3.66	5.97	4.92	4.09	5.07
$NaNbO_3$	10.33	10.28	11.01	9.77	11.81	7.25	8.28	19.41	9.80	9.36	10.36	10.31	12.90
$Ce_2Ti_2O_7$	2.36	4.90	6.89	7.43	4.84	3.34	4.32	0.69	6.69	4.03	7.13	7.19	8.43
$CaTiO_3$	16.13	14.77	16.98	15.13	13.58	27.02	20.12	11.25	18.88	17.21	19.20	17.33	19.40
Loparite	67.55	65.22	59.23	62.53	63.18	57.75	62.07	60.70	60.51	62.47	57.76	60.56	53.66

Compositions: 1-5 rischorrite, Mt. Kaskasnyunachorr, 1 & 2 core and rim of an unzoned crystal, 3 & 4-5 core and rim of a patchy zoned crystal; 6 & 7-8 core and rim of a patchy zoned crystal from rischorrite, Mt. Eveslogchorr; 9-13 pegmatite veins in rischorrite, Mt. Marchenko, 9 & 10 core and rim of an unzoned loparite-I crystal; 11 & 12-13 core and rim of a patchy zoned loparite-I crystal. All data this work. Total Fe expressed as FeO.

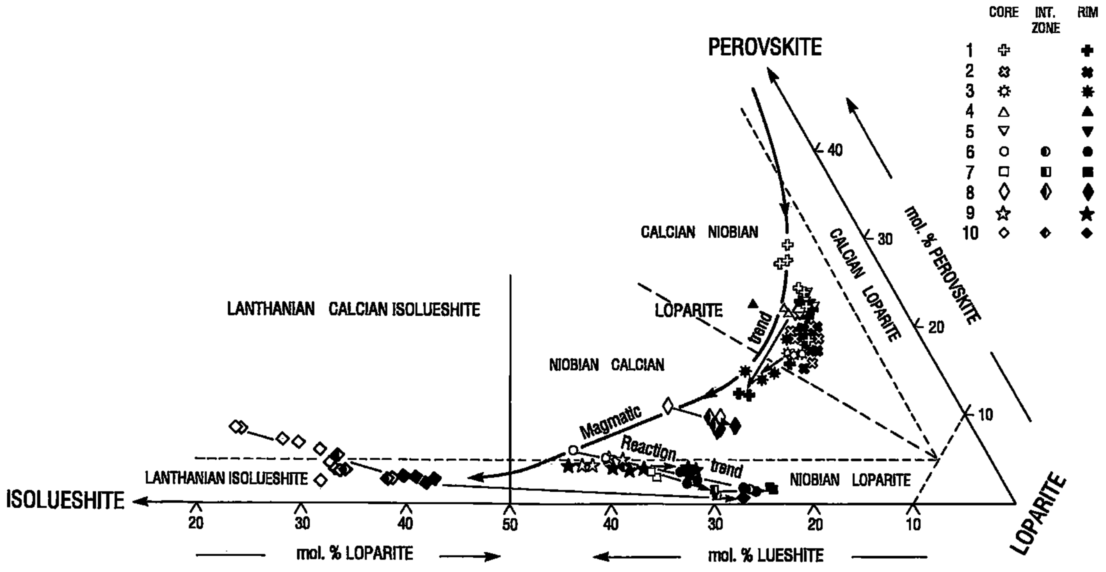

FIG. 5. Compositions (mol.%) of loparite from rischorrite (1–2), pegmatites in rischorrite (3–8) and of loparite and isolueshite from pegmatites in foidolites (9–10). Compositions 1–5, 9 and 10: this work, 6–8 after Mitchell *et al.* (1996). 1 Mt. Eveslogchorr, 2 Mt. Kaskasnyunachorr, 3 and 4 loparite-I, Mt. Marchenko, 5 loparite-I, Eudialyte Pass, 6 and 7 loparite-III, Mt. Kukisvumchorr, 8 loparite-III, Mt. Kaskasnyunachorr, 9 loparite-III, Mt. Koashva, 10 isolueshite, Mt. Kukisvumchorr.

TABLE 4. REPRESENTATIVE COMPOSITIONS OF LOPARITE AND ISOLUESHITE FROM PEGMATITES IN FOIDOLITES

Wt.%	1	2	3	4	5	6
Nb_2O_5	35.59	26.87	52.31	41.55	40.22	25.25
Ta_2O_5	n.d	n.d	0.39	0.75	0.70	0.17
TiO_2	25.51	32.40	17.62	22.38	22.60	29.68
FeO	0.28	0.05	0.08	n.d	n.d	n.d
ThO_2	0.30	0.88	1.38	5.35	2.54	0.33
La_2O_3	10.01	10.62	5.44	6.87	7.92	15.18
Ce_2O_3	11.17	13.87	3.22	5.35	7.81	13.10
Pr_2O_3	0.83	n.d	0.17	0.20	0.47	0.73
Nd_2O_3	1.42	2.03	0.65	0.44	0.87	1.24
CaO	0.86	0.97	2.80	2.09	1.39	0.22
SrO	2.29	2.18	2.11	1.71	1.37	0.94
Na_2O	11.81	10.97	13.80	12.27	12.67	11.21
Total	100.07	100.84	99.97	98.96	98.56	98.05
	Structural formulae based on 3 atoms of oxygen					
Nb	0.457	0.340	0.650	0.533	0.519	0.337
Ta	0.000	0.000	0.003	0.006	0.005	0.001
Ti	0.545	0.683	0.364	0.477	0.485	0.658
Fe	0.007	0.001	0.000	0.000	0.000	0.000
Th	0.002	0.006	0.009	0.034	0.016	0.002
La	0.105	0.110	0.055	0.072	0.083	0.165
Ce	0.116	0.142	0.032	0.056	0.082	0.141
Pr	0.009	0.000	0.002	0.002	0.005	0.008
Nd	0.014	0.020	0.002	0.004	0.009	0.013
Ca	0.026	0.029	0.082	0.064	0.042	0.007
Sr	0.038	0.035	0.034	0.028	0.023	0.016
Na	0.651	0.596	0.735	0.675	0.702	0.641
	Mol.% End-members					
$CaThO_3$	0.31	0.89	0.92	3.87	1.75	0.33
$SrTiO_3$	6.08	5.62	3.57	3.15	2.41	2.42
$NaNbO_3$	36.83	26.98	68.37	59.71	55.10	25.42
$Ce_2Ti_2O_7$	6.12	1.99	0.00	0.00	0.00	2.76
$CaTiO_3$	3.91	3.73	7.83	3.25	2.76	0.71
Loparite	46.75	60.79	19.31	30.02	37.99	68.36

Compositions 1 & 2 loparite-(Ce), 3-5 isolueshite, 6 "loparite-(La)" (not a valid mineral name). 1 & 2 core and rim of a zoned loparite-III crystal from pegmatite in apatite-nepheline rock, Mt. Koashva, 3, 4 & 5-6 core, intermediate zone and rim of a zoned crystal, respectively, pegmatite in ijolite, Mt. Kukisvumchorr. All data this work. Total Fe expressed as FeO; n.d = not detected.

depleted in Na and Nb (16.9–18.3 to 14.7–15.0 mol.% $NaNbO_3$). Loparite-II shows an opposite trend of zonation, similar to that of loparite-II from the Imandra khibinite pegmatites (Fig. 6).

At Mt. Eveslogchorr, loparite-II from aegirine – astrophyllite spherulites is similar in composition to the above-described loparite-II from Mt. Niorkpakhk. This loparite also evolves by enrichment in Na and Nb (Table 5, anals. 12, 13). Some grains of loparite-II were found to be significantly enriched in Th (up to 18.4 wt.% ThO_2). Previously, thorian loparite was described from a foyaite pegmatite and an albitized foyaite by Borodin & Kazakova (1954) and Tikhonenkova *et al.* (1982), respectively. A detailed study of this mineral has been provided by Mitchell & Chakhmouradian (1998).

Metasomatic rocks

Loparite from albite – aegirine metasomatic rocks at the North Partomchorr Pass, Mts. Niorkpakhk, Eveslogchorr and Kukisvumchorr are all compositionally similar to loparite from foyaite and foyaite pegmatites. It consists of niobian calcian loparite-(Ce) with low Ca, Sr and Fe contents (Table 6, anals. 1–10). Some grains are enriched in Ta and Th. From core to rim, these grains of loparite evolve by enrichment in *LREE* and Ti (from 60.5 to 84.3 mol.% $NaCeTi_2O_6$) coupled with depletion in Na and Nb (from 22.9 to 10.0 mol.% $NaNbO_3$) (Fig. 7). According to Chakhmouradian *et al.* (1995), loparite from the parental rocks was dissolved and then reprecipitated from an alkaline metasomatizing fluid. Our findings confirm that the composition of loparite was not affected by the fluid. A similar conclusion has been drawn for loparite from metasomatic assemblages at Lovozero by Mitchell & Chakhmouradian (1996).

An albite rock that developed along the contact between loparite-bearing rischorrite and foyaite at Mt. Kaskasnyunachorr contains resorbed grains of calcian-niobian loparite-(Ce) that is compositionally close to loparite from the non-albitized rischorrite (*cf.* Table 3, anals. 1–4, Table 6, anals. 11–12). In common with the loparite from rischorrite, that from the Kaskasnyunachorr albitite is irregularly zoned, with the rim of some grains enriched in Na and Nb (Table 6, anal. 13). The similarity in composition and zonation trend (*cf.* Figs. 5, 7) suggests that at this locality, the loparite mineralization was "inherited" from the substrate rock (K-feldspar – aegirine "veins").

The ratio Ce/La in loparite

Our data (Tables 2–6) show that the ratio Ce/La in loparite at Khibina increases from the earliest generation, in the intrusive series and contact zones of the pegmatites, to the latest generations of loparite in aegirine-rich autometasomatic assemblages, albite – aegirine metasomatic rocks, and natrolite- and sodalite-rich zones in rischorrite pegmatites (Table 7). This trend presumably reflects fractionation of lanthanum into the most evolved portions of peralkaline magma undergoing differentiation processes. This observation is in accord with the presence of La-dominant isolueshite ($0.5 < Ce/La < 1.0$) in a highly evolved calcite-, natrolite- and sodalite-bearing pegmatite vein within ijolite – urtite (Mitchell *et al.* 1996, Chakhmouradian *et al.* 1997).

DISCUSSION

Perovskite from alkaline ultramafic rocks of the Khibina complex exhibits a distinct trend of compositional evolution, characterized by enrichment in Na, *LREE*, Nb and Th. This trend is essentially toward the

TABLE 5. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM FOYAITE AND PEGMATITES IN FOYAITE

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
Nb_2O_5	18.05	17.42	20.04	16.46	13.91	16.75	12.77	17.14	18.88	17.39	19.63	15.40	19.60
Ta_2O_5	0.58	0.31	0.47	0.28	0.36	1.12	0.50	0.84	0.54	0.70	0.46	0.21	0.16
TiO_2	35.02	35.66	34.47	35.90	38.13	36.06	39.35	34.04	33.39	36.15	35.12	35.26	34.83
FeO	0.05	0.07	n.d	0.09	n.d	0.08	n.d	0.08	0.21	0.04	0.07	0.06	0.03
ThO_2	4.02	4.39	1.49	1.28	1.52	1.37	1.86	1.15	0.91	1.20	1.17	2.60	1.80
La_2O_3	9.75	10.14	12.26	12.29	12.82	11.51	11.65	12.43	11.39	11.49	11.98	13.20	11.95
Ce_2O_3	16.50	17.03	16.28	17.28	17.80	16.26	17.96	16.57	16.01	16.48	16.40	17.02	16.14
Pr_2O_3	0.58	1.18	n.d	1.75	1.44	0.15	0.76	1.97	3.50	1.44	0.53	0.85	1.45
Nd_2O_3	1.69	2.06	1.71	2.19	2.27	1.91	1.95	2.02	2.57	1.57	1.00	2.39	1.70
CaO	1.95	1.95	2.00	1.81	1.70	1.97	1.79	1.79	1.86	1.86	2.02	1.86	1.75
SrO	1.31	1.46	1.68	1.67	1.75	2.06	1.75	1.42	1.44	2.04	2.03	2.05	1.85
Na_2O	9.65	9.55	9.94	9.21	9.16	9.64	8.78	9.40	9.36	9.32	9.58	9.19	10.14
Total	99.15	101.22	100.34	100.21	100.86	98.88	99.12	98.85	100.06	99.68	99.99	99.99	101.40
Structural formulae based on 3 atoms of oxygen													
Nb	0.238	0.226	0.259	0.215	0.180	0.219	0.166	0.228	0.249	0.226	0.254	0.204	0.252
Ta	0.004	0.002	0.004	0.002	0.003	0.009	0.004	0.007	0.004	0.005	0.004	0.002	0.001
Ti	0.765	0.770	0.741	0.781	0.822	0.785	0.853	0.755	0.733	0.782	0.755	0.778	0.745
Fe	0.001	0.002	0.000	0.002	0.000	0.002	0.000	0.002	0.005	0.001	0.002	0.002	0.001
Th	0.027	0.029	0.010	0.008	0.010	0.009	0.012	0.008	0.006	0.008	0.008	0.017	0.012
La	0.104	0.107	0.129	0.131	0.136	0.122	0.124	0.135	0.122	0.122	0.126	0.142	0.125
Ce	0.176	0.179	0.170	0.183	0.187	0.172	0.190	0.179	0.171	0.173	0.172	0.183	0.168
Pr	0.006	0.012	0.000	0.018	0.015	0.002	0.008	0.021	0.037	0.015	0.006	0.009	0.015
Nd	0.018	0.021	0.017	0.023	0.023	0.020	0.020	0.021	0.027	0.016	0.010	0.025	0.017
Ca	0.061	0.060	0.061	0.056	0.052	0.061	0.055	0.057	0.058	0.057	0.062	0.058	0.053
Sr	0.022	0.024	0.028	0.028	0.029	0.035	0.029	0.024	0.024	0.034	0.034	0.035	0.030
Na	0.544	0.532	0.551	0.517	0.509	0.541	0.491	0.538	0.530	0.520	0.531	0.523	0.559
Mol.% End-members													
$CaThO_3$	4.04	4.31	1.44	1.23	1.44	1.32	1.83	1.11	0.88	1.18	1.15	2.47	1.70
$SrTiO_3$	3.36	3.65	4.13	4.10	4.23	5.07	4.39	3.51	3.56	5.09	5.06	4.96	4.46
$NaNbO_3$	18.37	17.16	19.47	15.91	13.31	16.72	12.79	16.99	18.51	17.33	19.35	14.64	18.51
$Ce_2Ti_2O_7$	0.19	1.89	3.20	6.15	3.77	0.38	2.37	5.88	8.92	4.32	4.51	4.49	2.17
$CaTiO_3$	5.19	4.70	7.65	6.97	6.15	7.64	6.47	7.05	7.61	7.40	8.16	5.85	6.09
Loparite	68.85	68.29	64.11	65.64	71.10	68.87	72.15	65.46	60.52	64.68	61.77	67.59	67.07

Compositions: 1 & 2 core and rim of a zoned crystals from foyaite, Mt. Eveslogchorr; 3 unzoned crystal from foyaite, Mt. Eveslogchorr; 4-11 pegmatites in foyaite, Mt. Niorkpakhk, 4 & 5 core and rim of a zoned loparite-I crystal, vein # 1, 6 & 7 core and rim of a zoned loparite-I crystal, vein # 2, 8 & 9 core and rim of a zoned loparite-II crystal, vein # 1, 10 & 11 core and rim of a zoned loparite-II crystal, vein # 2. 12 & 13 core and rim of a zoned loparite-II crystal from pegmatite in foyaite, Mt. Eveslogchorr. All data this work. Total Fe expressed as FeO, n.d = not detected.

loparite-(Ce) apex of the ternary systems lueshite (or tausonite) – perovskite – loparite-(Ce). Rare loparite from melanocratic members of the foidolite series is enriched in Ca and Ti and depleted in Na, *LREE* and Nb contents, compared to loparite from nepheline syenites, associated pegmatites and metasomatic rocks. We interpret the observed perovskite – loparite evolutionary trend to result from two different, although perhaps interfering, processes. In some cases [*e.g.*, perovskite partly replaced by aeschynite-(Ce) from mica peridotite: Table 1, anals. 4–6], Na–*LREE*–Nb–Th-enrichment is metasomatic and caused by the interaction of perovskite with alkali-rich fluids derived from nepheline syenite melt. A very similar compositional trend has been established for perovskite from the Schryburt Lake complex, Ontario (Platt 1994). However, at Schryburt Lake, perovskite enrichment in Na, *LREE* and Nb was more likely brought about by fluids derived from a carbonatite source (Platt 1994). In the foidolites, where no evidence of late-stage metasomatic overprint exists, the perovskite – loparite trend presumably reflects enrichment of successive portions of the differentiating magma in Na and incompatible elements. If the foidolite and rischorrite series represent complementary products of the evolution of a parental magma, the described trend may be further traced in loparite from rischorrite and associated pegmatites (see below).

Loparite from nepheline syenite, nepheline syenite pegmatite and albite – aegirine metasomatic rocks of the Khibina complex are calcian niobian, niobian calcian and niobian loparite-(Ce). "Loparite-(La)" was found only as a thin rim on the crystals of isolueshite. There are three major zonation trends in the Khibina loparite:

1. Enrichment in *LREE* and Ti coupled with depletion in Na and Nb at essentially constant or slightly decreasing Ca content. This trend is observed in loparite from khibinite and aegirine – albite metasomatic rocks, early generations of loparite from khibinite and foyaite pegmatites, and, paradoxically, in the most Nb-enriched loparite-III and isolueshite from highly evolved pegmatite

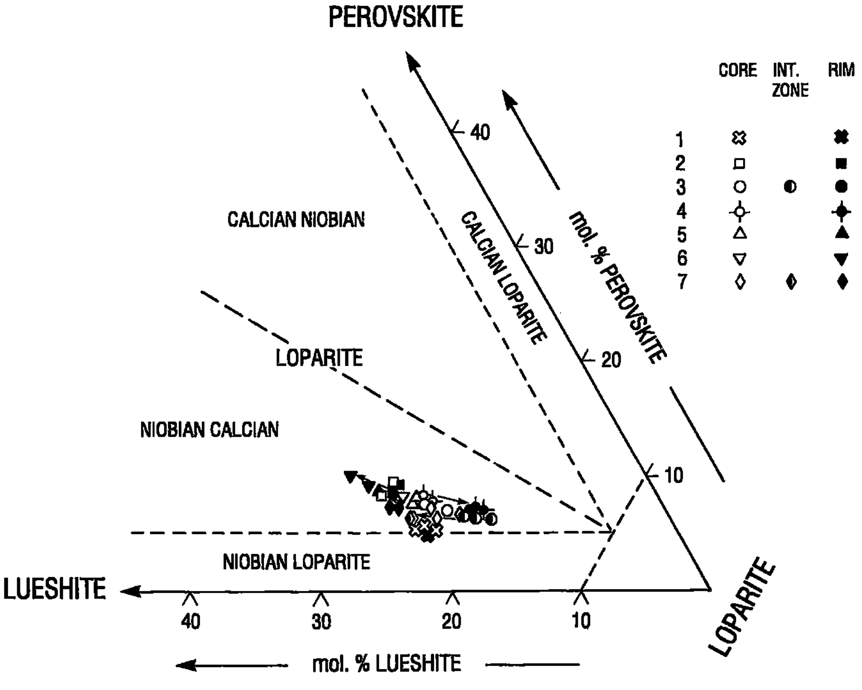

FIG. 6. Compositions (mol.%) of loparite from foyaite (1 and 2) and pegmatites in foyaite (3–7): 1 and 2 Mt. Eveslogchorr, 3 and 4 loparite-I, Mt. Niorkpakhk, 5 and 6 loparite-II, Mt. Niorkpakhk, 7 loparite-II, Mt. Eveslogchorr.

bodies in rischorrite and foidolites. This latter trend is termed the reaction trend in Figure 5.

2. Enrichment in Na, Nb and depletion in *LREE* at constant or increasing Ca content. This zonation pattern is typically present in loparite-II from khibinite and foyaite pegmatites.

3. Enrichment in Na, Nb, Th and depletion in Ca and Fe. This trend, termed the magmatic trend in Figure 5, is characteristic of calcian niobian loparite-(Ce) from rischorrite and the derived albitite, and the loparite-I from rischorrite pegmatites.

None of these trends can be easily explained on the basis of available experimental data. During crystallization from the pseudobinary system loparite – nepheline at decreasing temperature, loparite evolves toward compositions enriched in Nb and Sr (Veksler *et al.* 1985). The experiments on crystallization of the mineral from a lujavrite (melanocratic nepheline syenite) melt have not revealed a similar trend (Veksler & Teptelev 1990: Appendix 4). The close correspondence between intragranular patterns of zonation exhibited by loparite from intrusive rocks and those formed under hydrothermal conditions (Trend 1) presumably results from the crystallization of the mineral in open systems that geochemically evolved toward *LREE*-enriched compositions. Alternatively, crystallization of loparite in "autometasomatic" aegirine zones within pegmatite bodies took place in a closed environment from deuteric fluids enriched in Na and Nb (Trend 2). The irregular pattern of zonation exhibited by the loparite from rischorrite (Trend 3) most likely is an overprint of fluids derived from later-crystallized batches of a parental magma.

Perovskite-group minerals from the foidolites, rischorrite and related pegmatites show the widest compositional range, which is similar to the general trend of compositional evolution of loparite from Lovozero (Fig. 8). At Khibina, the main magmatic trend is from perovskite through cerian and cerian niobian perovskite to calcian niobian loparite, and then to niobian loparite and isolueshite. The earliest generations of loparite from rischorrite are compositionally similar to loparite from the poikilitic feldspathoid syenite and related pegmatites, whereas the latest approach the composition of *LREE*–Ti-enriched lueshite developed in the eudialyte lujavrite of the Lovozero complex (Mitchell & Chakhmouradian 1996). This observation indicates a higher degree of differentiation of a foidolitic–rischorritic melt compared to melts that produced "normal" nepheline syenites.

Perovskite-group minerals evolve along the main magmatic trend during their crystallization, but may be

TABLE 6. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM ALBITE AND ALBITE – AEGIRINE METASOMATIC ASSEMBLAGES

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
Nb_2O_5	15.09	10.00	18.24	12.54	17.64	11.26	20.54	17.48	19.82	14.43	9.29	10.25	14.82
Ta_2O_5	0.42	0.10	1.00	0.86	0.50	0.27	0.34	0.40	0.18	0.26	1.33	1.45	0.78
TiO_2	35.24	38.65	34.61	39.12	36.18	40.19	32.33	34.19	33.66	36.19	39.42	39.13	36.24
FeO	0.05	0.07	0.01	0.07	0.12	0.11	0.10	0.17	0.15	0.04	0.19	0.09	0.08
ThO_2	1.41	1.60	1.02	1.80	1.03	1.84	0.93	1.61	1.37	2.40	0.52	0.67	1.29
La_2O_3	12.06	13.66	12.46	12.22	12.72	13.28	10.79	11.60	11.89	12.09	11.02	11.34	10.94
Ce_2O_3	16.99	18.73	16.82	18.36	16.90	19.15	16.68	17.57	15.53	17.72	19.98	19.42	18.68
Pr_2O_3	3.96	3.59	1.03	0.28	0.37	0.22	3.43	1.93	0.70	2.33	1.49	1.12	1.18
Nd_2O_3	2.13	2.95	1.19	1.75	1.55	1.56	2.64	2.22	2.71	2.59	2.78	2.50	2.90
CaO	1.77	1.54	2.20	2.00	2.30	2.25	1.70	1.67	1.81	1.53	3.68	3.11	1.66
SrO	1.69	1.76	1.06	1.09	1.10	0.95	0.78	0.71	2.05	1.03	1.63	1.78	1.63
Na_2O	9.02	8.92	9.57	8.98	9.56	8.90	10.09	10.19	9.45	9.75	8.12	8.30	9.17
Total	99.83	101.57	99.21	99.07	99.97	99.98	100.35	99.74	99.32	100.36	99.45	99.16	99.37
Structural formulae based on 3 atoms of oxygen													
Nb	0.201	0.132	0.239	0.164	0.228	0.146	0.270	0.231	0.261	0.190	0.122	0.135	0.196
Ta	0.003	0.001	0.008	0.007	0.004	0.002	0.003	0.003	0.001	0.002	0.010	0.011	0.006
Ti	0.780	0.847	0.755	0.850	0.777	0.866	0.708	0.751	0.736	0.794	0.862	0.856	0.797
Fe	0.001	0.002	0.002	0.002	0.003	0.003	0.002	0.004	0.004	0.001	0.005	0.002	0.002
Th	0.009	0.011	0.007	0.012	0.007	0.012	0.006	0.011	0.009	0.016	0.003	0.004	0.009
La	0.131	0.147	0.133	0.130	0.134	0.140	0.116	0.125	0.128	0.130	0.118	0.122	0.118
Ce	0.183	0.200	0.179	0.194	0.177	0.201	0.178	0.188	0.165	0.189	0.213	0.207	0.200
Pr	0.042	0.038	0.011	0.003	0.004	0.002	0.036	0.020	0.007	0.025	0.016	0.012	0.013
Nd	0.022	0.031	0.012	0.018	0.016	0.016	0.027	0.023	0.028	0.027	0.029	0.026	0.030
Ca	0.056	0.048	0.068	0.062	0.070	0.069	0.053	0.052	0.056	0.048	0.115	0.097	0.052
Sr	0.029	0.030	0.018	0.018	0.018	0.016	0.013	0.012	0.035	0.017	0.027	0.030	0.028
Na	0.515	0.504	0.538	0.503	0.530	0.494	0.570	0.577	0.533	0.552	0.458	0.468	0.520
Mol.% End-members													
$CaThO_3$	1.34	1.44	0.99	1.76	0.99	1.74	0.89	1.52	1.35	2.25	0.47	0.62	1.24
$SrTiO_3$	4.10	4.05	2.62	2.71	2.70	2.29	1.90	1.70	5.15	2.46	3.74	4.19	4.01
$NaNbO_3$	14.50	9.03	18.18	12.65	17.15	10.75	19.69	16.57	19.51	13.57	9.02	10.21	14.65
$Ce_2Ti_2O_7$	1.86	4.49	4.85	1.44	3.62	1.42	6.59	1.43	6.43	1.26	5.12	4.65	4.68
$CaTiO_3$	6.59	5.10	9.07	7.43	9.43	8.29	6.76	5.89	7.05	4.50	15.15	12.91	6.30
Loparite	66.21	75.89	64.29	74.01	66.11	75.51	64.17	72.89	60.51	75.96	66.50	67.42	69.12

Compositions: 1 & 2 core and rim of a zoned crystal, Mt. Niorkpakhk; 3 & 4 core and rim of a zoned crystal of early generation, North Partomchorr Pass; 5 & 6 core and rim of a zoned crystal of late generation, North partomchorr Pass; 7 & 8 core and rim of a zoned crystal, Mt. Kukisvumchorr; 9 & 10 core and rim of a zoned crystal, Mt. Eveslogchorr; 11 & 12-13 core and rim of a patchy-zoned crystal, Mt. Kaskasnyunachorr. All data this work. Total Fe expressed as FeO.

affected by subsequent deuteric alteration. The latter is recognizable as reaction trends away from the main magmatic trend toward the loparite apex of the $CaTiO_3$ – $Na\mathit{REE}Ti_2O_6$ – $NaNbO_3$ system (Fig. 5).

Compared to Khibina, loparite from the Burpala complex of nepheline and alkaline syenites are Ca, Sr and Nb-poor members of the lueshite – perovskite – loparite-(Ce) solid solution series (Fig. 8). At Burpala, this loparite-(Ce) (*sensu stricto*) is a common accessory phase in albite-, aegirine- and microcline-rich metasomatic assemblages, but does not occur in the intrusive series and pegmatites (Semenov *et al.* 1974).

Compared to perovskite-group minerals from the Khibina complex, those from the carbonatite complexes of the Kola Peninsula exhibit a similar compositional range (Fig. 8). However, loparite from the carbonatite complexes is calcian or calcian niobian loparite-(Ce) with comparatively low Nb and Sr contents.

CONCLUSIONS

Our study of the compositional variations in perovskite-group minerals from alkaline rocks of the Khibina complex shows that:

1. Perovskite from the alkaline ultramafic rocks compositionally evolves by becoming enriched in Na, *LREE*, Nb and Th, owing to (a) a metasomatic overprint and (b) successive enrichment of the differentiating parental magma in Na and incompatible elements.

2. At Khibina, the suite of loparite essentially corresponds to members of the lueshite – perovskite – loparite-(Ce) solid-solution series having relatively low contents of other perovskite-type end-member compounds ($SrTiO_3$, $Ce_2Ti_2O_7$).

3. Three major patterns of intragranular zonation exist in loparite at Khibina. These compositional trends presumably reflect the geochemical evolution of mineral-forming systems during the course of loparite crystallization.

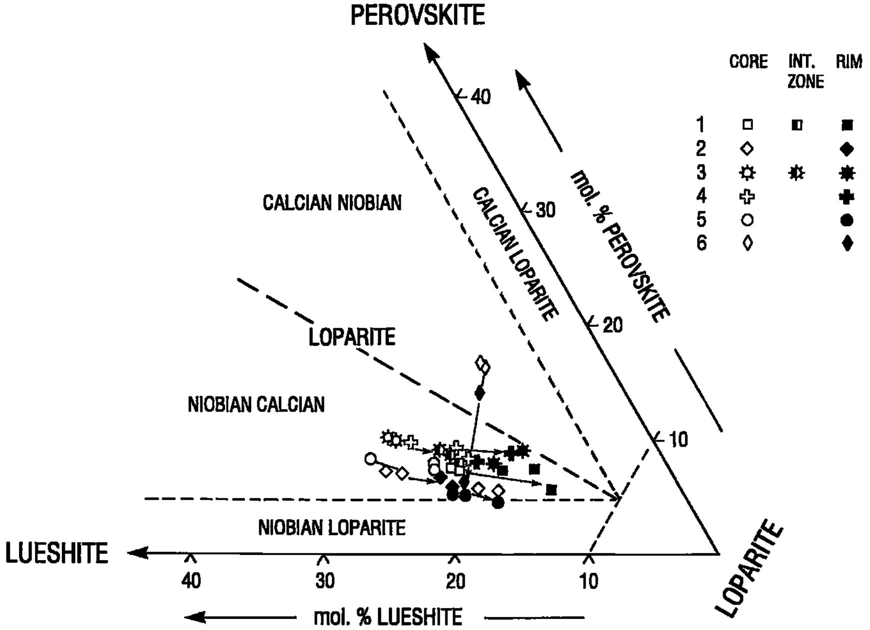

FIG. 7. Compositions (mol.%) of loparite from albite and aegirine – albite metasomatic rocks: 1 Mt. Niorkpakhk, 2 Mt. Kukisvumchorr, 3 early generation, N. Partomchorr Pass, 4 late generation, N. Partomchorr Pass, 5 Mt. Eveslogchorr, 6 Mt. Kaskasnyunachorr.

4. The general trend of the compositional evolution of perovskite-group minerals in the Khibina complex closely corresponds to the trend established for loparite at Lovozero and demonstrates that the character of the evolution of peralkaline magma at the two complexes was similar.

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TABLE 7. La/Ce VALUES IN LOPARITE AND ISOLUESHITE FROM THE KHIBINA COMPLEX

ROCK TYPE	La/Ce
Ijolite	0.48-0.59
Khibinite	0.55-0.57
Pegmatites in khibinite	
Loparite-I	0.42-0.65
Loparite-II	0.44-0.72
Rischorrite	
Not evolved crystals	0.50-0.58
Nb-enriched rims	0.56-0.74
Pegmatites in rischorrite	
Loparite-I	0.50-0.65
Loparite-III	0.61-0.83
Pegmatites in foidolites	
Loparite-III	0.71-0.92
Isolueshite	1.00-2.00
Foyaite	0.59-0.76
Pegmatites in foyaite	
Loparite-I	0.68-0.74
Loparite-II	0.70-0.78
Metasomatites	0.63-0.78

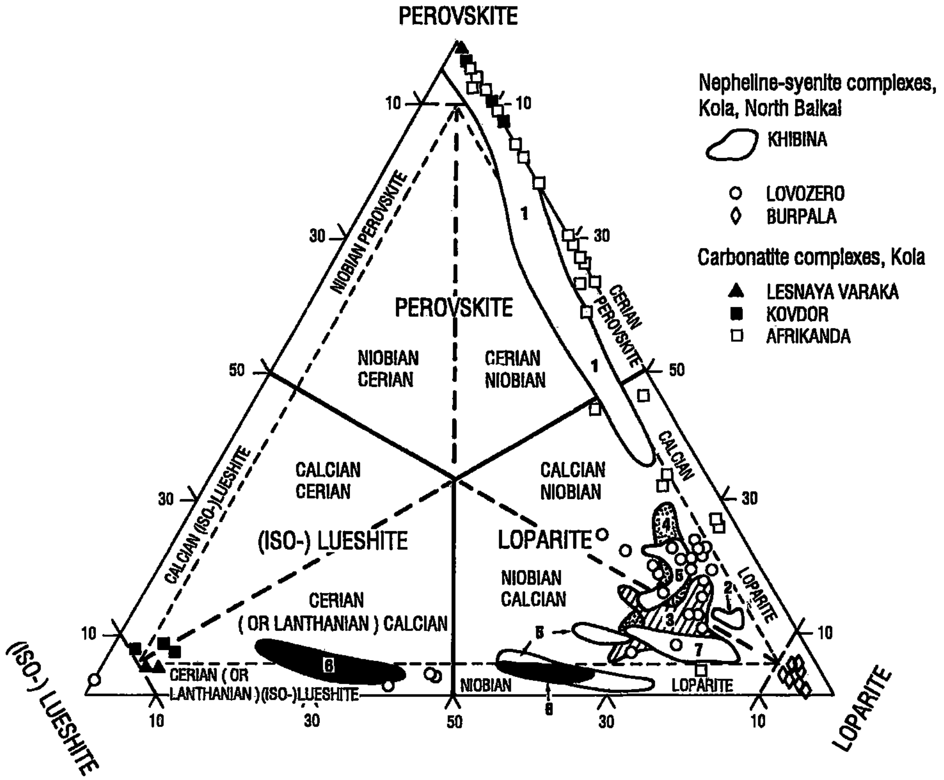

FIG. 8. Composition (mol.%) of perovskite, loparite and isolueshite from the Khibina complex compared to that of perovskite, loparite and lueshite from the Lovozero and Burpala nepheline syenite plutons and from the Afrikanda, Kovdor and Lesnaya Varaka carbonatite complexes (all data obtained in this study): 1–7 Khibina; 1 ultramafites and foidolites, 2 khibinite, 3 pegmatites in khibinite, 4 rischorrite, 5 pegmatites in rischorrite, 6 pegmatites in foidolites, 7 foyaite, pegmatites in foyaite, albite and albite – aegirine metasomatic rocks.

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