Th-rich loparite from the Khibina alkaline complex, Kola Peninsula: isomorphism and paragenesis

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ABSTRACT

Th-rich (up to 18.4 wt.% ThO_2) loparite occurs as an accessory phase in foyaite pegmatites at Mt. Eveslogchorr, Khibina complex, Russia. It is associated with aegirine, astrophyllite, eudialyte, lorenzenite, lamprophyllite, magnesio-arfvedsonite and gerasimovskite. Loparite crystals are zoned from niobian loparite (core) to niobian thorian and thorian niobian loparite (rim). Th-enrichment is accompanied by a decrease in Na, *LREE*, Sr and increase in A-site vacancies. The most Th-rich composition approaches $(Na_{0.39}LREE_{0.19}Th_{0.12}Ca_{0.05}Sr_{0.02})_{\Sigma 0.77}(Ti_{0.76}Nb_{0.27})_{\Sigma 1.03}O_3$. The mineral is partly or completely metamict and after annealing gives an X-ray diffraction powder pattern similar to that of synthetic $NaLaTi_2O_6$ and naturally occurring loparite of different composition. For the Th-rich rim sample, the five strongest diffraction lines (Å) are: 2.72 (100) 110, 1.575 (60) 211, 1.925 (40), 1.368 (30) 220, 1.222 (20) 310; a = 3.867(2) Å. The X-ray diffraction patterns do not exhibit peak splitting or other diffraction lines typical of low-symmetry and ordered perovskite-type structures. Composition determinations, infrared transmission spectroscopy and X-ray diffractometry show that thorian loparite is partly replaced by betafite with *LREE* and Th as dominant *A*-site cations ('ceriobetafite'). Some loparite samples also exhibit thin replacement mantles of belyankinite with high $LREE_2O_3$ and ThO_2 contents. Both 'ceriobetafite' and belyankinite were formed due to metasomatic alteration of loparite.

Introduction

PEROVSKITE-GROUP minerals from alkaline rocks exhibit wide ranges in composition and may serve as sensitive indicators of evolutionary trends (Kukharenko and Bagdasarov, 1961; Mitchell, 1996; Mitchell and Chakhmouradian, 1996; Tikhonenkova *et al.*, 1982). Comprehensive studies of isomorphic substitutions in naturally-occurring perovskites are also very important for understanding the crystal chemistry of synthetic perovskite-type compounds that show a broad spectrum of electric and magnetic properties.

Among the least studied of perovskite-group minerals are species containing large-size high-valency cations, in particular, Th, other tetra-valent actinides and Ce^{4+}. The initial study of naturally-occurring perovskites enriched in actinide elements was undertaken by Borodin (1954), who suggested that accommodation of high-valency elements with large ionic radii in perovskite-group minerals is accompanied by the creation of vacancies at *A* sites in the lattice and partial substitution of oxygen atoms by hydroxyl anions. The generalized formula proposed by Borodin (1954) for hydrous perovskite-group minerals containing considerable amounts of rare-earth or actinide elements is $A_{1-x}BO_{3-x}(OH)_x$ (x = 0–0.5). Borodin and Kazakova (1954) reported the occurrence of Th-rich

(13.0 wt.% ThO_2) loparite (termed 'irinite') with minor amounts of Fe_2O_3 and CaO in a foyaite pegmatite at Mt. Eveslogchorr, in the Khibina alkaline complex, Kola Peninsula. The structural formula deduced from bulk wet-chemical analysis indicated that this mineral had significant cation deficiency at the A sites which was associated with $O^{2-} \rightleftharpoons (OH)^-$ substitution (Borodin and Kazakova, 1954). Recent studies of loparite mineralization at the Khibina complex (Kozyreva et al., 1991; Tikhonenkova et al., 1982) also report the occurrence of Th-rich loparite in foyaite or related pegmatites. Parker and Sharp (1970) have described 'irinite' as an accessory constituent of vermiculite rock at the Gem Park Complex, Colorado. However, identification of this mineral as 'irinite' was based merely on its metamict state and resemblance of the X-ray diffraction pattern of the heated sample to that of Borodin and Kazakova's (1954) material (Parker and Sharp, 1970). Perovskite with ThO_2 content of up to 1.7 wt.% occurs in the Polino carbonatite diatreme, Italy (Lupini et al., 1992), and up to 4.9 wt.% in the carbonatite complexes of Kola Peninsula (Chakhmouradian and Mitchell, 1997). Finally, fenite-like rocks in the carbonatite complexes of the Paraná Basin, South America, host loparite of widely varying SrO, Na_2O, Nb_2O_5, $LREE_2O_3$ and ThO_2 (up to 6.2 wt.%) contents (Mitchell, 1996).

Initial synthesis of Th-bearing perovskite-type oxides produced compounds of the type $AThO_3$ (A = Ca, Sr, Ba, Pb), in which Th^{4+} occupies octahedrally-coordinated B-sites (Náray-Szabó, 1947; Smith and Welch, 1960). Subsequently, Kovba and Trunov (1962) synthesized a series of niobates and tantalates accommodating Th, U and Ce^{4+} at twelve-coordinated A-sites in the perovskite structure. These compounds were highly cation-deficient relative to ideal ABX_3 perovskite, having the general formula $A_{1/4}BO_3$ (A = Th, U, Ce; B = Nb, Ta). Trunov and Kovba (1963) also prepared perovskite-type tungstates of Th, tolerating even higher cation deficiency at the A sites i.e. $Th_{1/4}WO_3$ to $Th_{1/30}WO_3$. Other synthetic perovskites with A-site Th include $CaThV_2O_6$ and $SrThV_2O_6$ (Vidyasagar and Gopalakrishnan, 1982), $Na_{2/3}Th_{1/3}TiO_3$ (Zhu and Hor, 1995) and the solid solution series $NaNbO_3-Th_{0.25}NbO_3$ (Labeau and Joubert, 1978). The above examples demonstrate that: (i) Th^{4+} in perovskite-type compounds may occupy either twelve-coordinated A sites or smaller octahedral B sites, depending on the type of associated cations; (ii) accommodation of Th in the perovskite structure may or may not be accompanied by the appearance of vacancies at the A sites.

The current study was undertaken to determine how Th is accommodated in the structure of loparite, a Na-$LREE$-Ti member of the perovskite family containing significant amounts of Nb, Ca and Sr. A second objective was to study the paragenesis of Th-rich loparite.

Analytical methods

All mineral compositions were determined by X-ray energy-dispersion spectrometry using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm MnK) at Lakehead University, Ontario. EDS spectra of loparite, betafite and belyankinite were acquired for 300 seconds and those of silicates for 100 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86 nA. The following well-characterized natural and synthetic standards were employed for the determination of mineral compositions: Khibina loparite (Na, $LREE$, Nb), Magnet Cove perovskite (Ca, Fe, Ti), jadeite (Al, Si), periclase (Mg), orthoclase (K), manganoan fayalite (Mn), synthetic $SrTiO_3$ (Sr), $BaSiO_3$ (Ba), metallic Th, Ta and Zr. The accuracy of the method was cross-checked by wave-length-dispersion electron microprobe analysis using an automated CAMECA SX-50 microprobe located at the University of Manitoba following methods described by Mitchell and Vladykin (1993).

X-ray diffraction (XRD) powder patterns (Cu radiation) were obtained with a Philips 3710 diffractometer at Lakehead University using a Philips Debye-Scherer type camera with a diameter of 114.6 mm. The diffractometer was operated at 40 kV and 25 mA. Relative intensities of the diffraction lines were estimated visually from the films.

Infra-red transmission spectra were recorded with a FTIR spectrometer IFS-66 equipped with a microscope. Spectra were obtained on 0.2−0.3 mm thick unfractured slabs of loparite from 256 scans using the 0.3-mm aperture of the microscope. For each measurement, the reference spectrum was obtained from 256 scans at the same operating conditions in order to eliminate the effect of H_2O vapour apparently present in the spectrometer.

Occurrence

Until recently, loparite with the ThO_2 content of more than 10 wt.% has been recognized only from the Khibina alkaline complex, in the Kola Peninsula, Russia. Its occurrence is restricted mainly to foyaite and related pegmatoid and metasomatic rocks comprising the central part of the Khibina pluton. The general geology, petrology and mineralogy of the complex have been described in detail by Galakhov (1975), Kostyleva-Labuntsova et al. (1978a,b), Zak et al. (1972) and summarized by Kogarko et al. (1995).

Th-rich loparite examined in the current study occurs in foyaite pegmatites exposed on the southern slope of Mt. Eveslogchorr, south Khibina. Most of the pegmatites are simple poorly-differentiated veins emplaced into fine-to-medium grained nepheline syenite of gneissoid texture. The veins are composed mainly of alkali feldspar, nepheline, aegirine and astrophyllite. The latter two minerals occur in intimate inter-growths as fibrous or radial aggregates partly or entirely replacing the earlier formed paragenesis of alkali feldspar and nepheline. In Russian mineralogical literature, the late-stage zones of fibrous aegirine in nepheline-syenite pegmatites are commonly interpreted as being of deuteric ('autometasomatic') origin (Kostyleva-Labuntsova et al., 1978a). The aegirine-astro-phyllite aggregate encloses numerous irregular- or lens-shaped polygranular segregations of analcite, phillipsite, natrolite and gibbsite plus Fe-hydr-oxides. These segregations commonly contain relics of nepheline and undoubtedly, represent alteration products of the latter. Accessory minerals developed in the aegirine-astrophyllite aggregate are eudialyte, loparite, lamprophyllite, lorenzenite and rare magnesio-arfvedsonite. Representative compositions of the major and accessory silicates from the aegirine-astrophyllite rock are given in Table 1.

In the aegirine-astrophyllite aggregate, loparite occurs as 'fluorite'-type interpenetration twins ranging from 3−7 mm across. The mineral is deep reddish-brown in thin sections and commonly has a yellow-coloured rim up to 0.3 mm in thickness. Some loparite crystals poikilitically enclose fine (less than 10 µm) needles of aegirine. In this study, we examined zoned crystals of loparite from two pegmatite veins: KHB-44 and KHB-70.
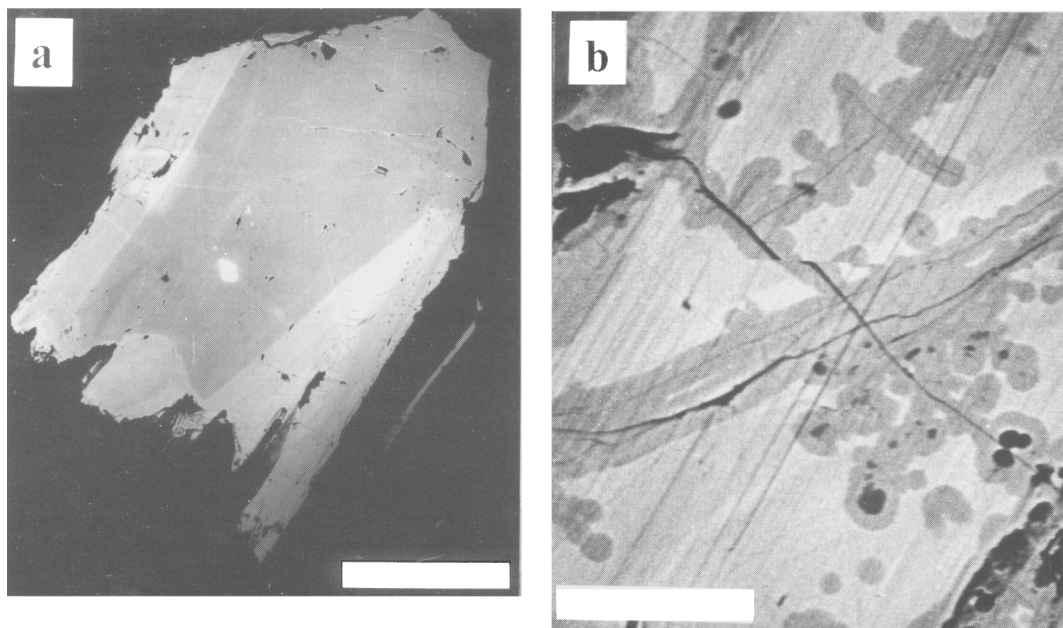

FIG. 1. Back-scattered electron images of a zoned Th-rich loparite crystal. (a) rim of thorian niobian and niobian thorian loparite (light grey) on niobian loparite (dark grey), scale bar is 400 µm; (b) 'ceriobetafite' (dark grey) developed along fractures and margins of thorian niobian loparite (light grey), scale bar is 30 µm.

Phase relationships

Back-scattered electron (BSE) imagery combined with line scanning reveals that loparite crystals exhibit strong compositional zonation reflecting enrichment in ThO_2 from the core towards the rim (Fig. 1a). The Th-rich rims of the crystals are heterogeneous and consist of two phases. Phase 1 having a lower average atomic number, is developed as dendrite-like narrow (3–30 μm) zones decorating margins of the crystals and fractures within phase 2 (Fig. 1b). Composition determinations show that both phases have comparable CaO, SrO, $LREE_2O_3$, TiO_2 and Nb_2O_5 (Ti > Nb) contents. However, phase 1 gives low analysis totals (93.6-97.0 wt.%) and contains considerably less Na_2O (0.3–1.0 wt.%) and generally more ThO_2 (17.8–22.0 wt.%) than phase 2. X-ray diffraction study (see below) demonstrates that phase 1 comprising the bulk of the sample extracted from the rim of the crystal is loparite. Three 'additional' weak diffraction lines observed on the XRD film could not be assigned to loparite or any structure derived from the perovskite parent, but corresponded well with the three strongest diffraction lines of betafite (ASTM 13-197: Hogarth, 1961).

Infrared transmission spectra recorded from the core and rim of a loparite crystal are compared in Fig. 2(a,b). Both spectra show a broad absorption band at 650–900 cm^{-1}. This band corresponds to bond vibrations in the octahedral complexes $(Ti,Nb)O_6$ and is typical of various perovskite- and pyrochlore-group minerals (Kostyleva-Labuntsova et al., 1978b; Pilipenko et al., 1971) and their synthetic analogues (Nyquist and Kagel,

1971; Sych et al., 1973). The relative position of this absorption band in the spectrum depends on the Ti vs. Nb ratio of the mineral. Splitting of the $(Ti,Nb)O_6$ band commonly observed in the infrared spectra of low-symmetry perovskite-type compounds (Pilipenko et al., 1971; Sych et al., 1973) is not observed in our spectra (Fig. 2a,b). Similar coalescence of several absorption lines into one broad band has been observed in metamict pyrochlore (Krivokoneva and Sidorenko, 1971). In addition to the $(Ti,Nb)O_6$ absorption band, the infrared spectrum of the rim (Fig. 2b) contains bands at 1650, 2330, 3300–3320 and 3530 cm^{-1}, the latter two partially overlapping each other. The OH stretching bands at 3300–3320 and 3530 cm^{-1} and Nb–OH band at 1650 cm^{-1} are characteristic of pyrochlore-group minerals (Voloshin et al., 1989) and most probably result from micro-intergrowths of ceriobetafite in the studied samples. In the current study, we could not assign the absorption band at 2330 cm^{-1}.

As evidenced by back-scattered electron imagery, loparite from the vein KHB-70 has undergone further alteration giving rise to the complex Ti hydroxide belyankinite. The mineral occurs as thin (20–30 μm) replacement mantles on loparite. Its Nb-dominant analogue gerasimovskite forms rare rectangular plates enclosed in fibrous aegirine. Both minerals have been insufficiently studied and were originally described in peralkaline pegmatites of the Lovozero alkaline complex, Kola Peninsula, where they occur predominantly as pseudomorphs after titanium-silicates (Gerasimovskii and Kazakova, 1950; Semenov, 1957).

Composition

Loparite

Representative compositions of zoned loparite crystals are given in Table 2. From core to rim, loparite compositionally evolves by enrichment in ThO_2 and depletion in Na_2O, $LREE_2O_3$ and SrO (Table 2). In order to reveal possible end-member compositions which may account for the accommodation of Th in the structure of loparite, relationships between the amounts of Th (apfu) and other major elements (Fig. 3) were analysed. With strongly decreasing Na, LREE and to a lesser degree Sr, and increasing Th (Fig. 3a,b,d), the occupancy of the B sites remains relatively unchanged (Fig. 3e,f). As the most Th-rich compositions also exhibit the greatest cation
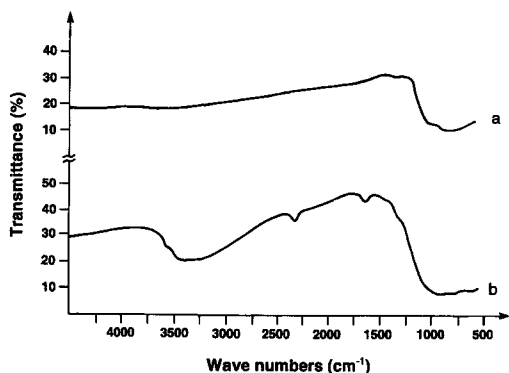
FIG. 2. Infra-red transmission spectra of Th-rich loparite. (a) core sample; (b) rim sample.

TABLE 1. Representative compositions of major and accessory silicate minerals

Wt.%	1*	2*	3	4	5	6	7	8	9	10	11*	12*
Na_2O	12.81	12.20	2.27	2.16	11.24	10.94	10.66	11.04	17.07	16.96	8.89	8.71
K_2O	0.04	0.08	6.02	6.06	0.41	0.35	0.64	0.61	n.d	n.d	2.04	2.18
CaO	2.25	2.67	1.41	1.55	9.29	8.79	0.45	0.40	0.05	0.08	0.56	0.67
SrO	n.a	n.a	n.d	n.d	1.49	1.18	13.06	11.62	n.d	n.d	n.a	n.a
BaO	n.a	n.a	n.d	n.d	n.d	n.d	0.85	3.22	n.d	n.d	n.a	n.a
MgO	1.02	1.03	1.89	1.91	0.09	0.37	0.43	0.45	0.35	0.23	8.20	8.08
MnO	0.37	0.39	12.92	13.29	3.83	4.52	5.58	5.26	n.d	0.12	3.73	3.83
FeO	0.60	1.36	19.04	18.50	3.92	3.24	n.a	n.a	n.a	n.a	13.93	13.51
Fe_2O_3	26.70	25.35	n.a	n.a	n.a	n.a	2.93	2.50	0.80	0.69	5.92	6.62
La_2O_3	n.a	n.a	n.d	n.d	0.67	1.06	0.60	0.42	n.a	n.a	n.a	n.a
Ce_2O_3	n.a	n.a	n.d	n.d	1.40	1.31	0.52	0.26	n.a	n.a	n.a	n.a
Al_2O_3	1.65	1.17	0.86	1.04	n.d	n.d	0.29	0.02	n.d	n.d	1.01	1.30
SiO_2	53.26	51.96	35.55	35.50	49.95	48.52	31.00	30.35	33.31	33.82	53.20	52.36
TiO_2	1.81	1.97	11.60	11.57	0.40	0.23	29.59	29.91	44.79	45.16	0.98	1.25
ZrO_2	n.a	n.a	0.65	0.49	13.26	12.20	n.d	n.d	n.d	n.d	n.a	n.a
Nb_2O_5	n.a	n.a	0.65	0.77	2.90	3.31	0.09	0.41	2.12	1.88	n.a	n.a
Total	100.52	98.18	92.86	92.84	98.85	96.02	96.69	96.47	98.49	98.94	98.46	98.51

Structural formulae:

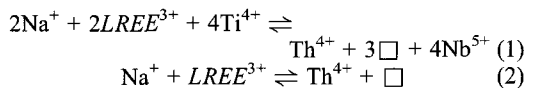|	O = 6		Si = 8		Si = 24		Si = 4		O = 9		O = 23	
Na	0.934	0.913	0.990	0.944	10.471	10.492	2.667	2.821	1.929	1.904	2.576	2.530
K	0.002	0.004	1.728	1.742	0.251	0.221	0.105	0.103	–	–	0.389	0.417
Ca	0.091	0.111	0.340	0.374	4.782	4.658	0.062	0.056	0.003	0.005	0.090	0.107
Sr	–	–	–	–	0.415	0.338	0.977	0.888	–	–	–	–
Ba	–	–	–	–	–	–	0.043	0.166	–	–	–	–
Mg	0.057	0.059	0.634	0.642	0.064	0.273	0.083	0.088	0.030	0.020	1.827	1.804
Mn	0.012	0.013	2.463	2.537	1.559	1.894	0.610	0.587	–	0.006	0.472	0.486
Fe^{2+}	0.020	0.047	3.583	3.486	1.575	1.340	–	–	–	–	1.742	1.693
Fe^{3+}	0.756	0.735	–	–	–	–	0.284	0.248	0.035	0.0300	0.666	0.747
La	–	–	–	–	0.119	0.193	0.029	0.020	–	–	–	–
Ce	–	–	–	–	0.246	0.237	0.025	0.013	–	–	–	–
Al	0.073	0.054	0.228	0.276	–	–	0.044	0.003	–	–	0.178	0.229
Si	2.003	2.007	8.000	8.000	24.000	24.000	4.000	4.000	1.942	1.958	7.951	7.845
Ti	0.052	0.057	1.963	1.961	0.145	0.086	2.871	2.964	1.963	1.966	0.110	0.141
Zr	–	–	0.071	0.054	3.107	2.943	–	–	–	–	–	–
Nb	–	–	0.066	0.078	0.630	0.740	0.005	0.024	0.056	0.049	–	–

Compositions: 1 and 2 aegirine; 3 and 4 astrophyllite; 5 and 6 eudialyte; 7 and 8 lamprophyllite; 9 and 10 lorenzenite; 11 and 12 magnesio-arfvedsonite.
All data this work.
* Fe^{2+}/Fe^{3+} ratio calculated using Droop's (1987) method;

deficiency (Fig. 3g), it is deduced that Th^{4+} cations are accommodated at the A site of loparite, and that the corresponding substitution scheme involves the appearance of vacancies at these sites. Calculations show that the observed relationship between Th content and number of vacancies at the A-site most closely corresponds to the solid solution series between loparite and two hypothetical end-members: $ThNb_4O_{12}$ and $ThTi_2O_6$ (Fig. 3). The solid solution series between loparite

$NaLREETi_2O_6$ and $Na_{2/3}Th_{1/3}TiO_3$, believed to be present, is not present as the A- and B-sites occupancy remains constant. The isomorphic substitutions are as follows:

$$2Na^+ + 2LREE^{3+} + 4Ti^{4+} \rightleftharpoons$$
$$Th^{4+} + 3\square + 4Nb^{5+} \quad (1)$$
$$Na^+ + LREE^{3+} \rightleftharpoons Th^{4+} + \square \quad (2)$$

$ThNb_4O_{12}$ (= $Th_{0.25}NbO_3$) has been synthesized and shown to have a perovskite-type

TABLE 2. Representative compositions of loparite

Wt.%	1	2	3	4	5	6	7	8	9
Na_2O	10.43	8.68	8.50	7.42	6.69	9.71	9.18	7.66	6.62
CaO	1.53	1.59	1.71	1.50	1.63	1.82	2.08	1.62	1.86
SrO	1.40	1.33	1.29	1.33	1.09	1.65	1.77	1.31	1.20
La_2O_3	9.72	8.88	6.47	6.46	5.41	11.42	9.37	8.24	5.79
Ce_2O_3	14.77	14.21	11.19	10.27	8.91	16.91	14.64	13.37	9.87
Pr_2O_3	1.86	1.72	1.56	n.d	1.14	1.03	2.20	2.54	1.38
Nd_2O_3	2.04	2.02	1.56	1.96	1.86	1.61	2.47	1.98	1.95
ThO_2	3.46	7.38	10.29	15.40	18.45	2.34	3.66	8.69	17.28
TiO_2	32.39	33.08	30.46	33.65	33.72	34.37	32.41	33.55	34.80
FeO	0.12	0.07	0.07	n.d.	0.11	0.07	n.d.	0.11	0.48
Nb_2O_5	21.38	21.98	27.16	22.10	20.18	18.72	22.13	20.34	19.62
Ta_2O_5	0.37	0.22	0.32	0.43	0.30	0.33	0.49	0.59	0.58
Total	99.47	101.16	100.58	100.52	99.49	99.98	100.40	100.00	101.43

Structural formulae (O = 3)
Na	0.589	0.486	0.477	0.420	0.387	0.545	0.515	0.436	0.375
Ca	0.048	0.049	0.053	0.047	0.052	0.056	0.064	0.051	0.058
Sr	0.024	0.022	0.022	0.022	0.019	0.028	0.030	0.022	0.020
La	0.104	0.095	0.069	0.070	0.060	0.122	0.100	0.089	0.062
Ce	0.158	0.150	0.118	0.110	0.097	0.179	0.155	0.144	0.106
Pr	0.020	0.018	0.016	0.000	0.012	0.011	0.023	0.027	0.015
Nd	0.021	0.021	0.016	0.020	0.020	0.017	0.026	0.021	0.020
Th	0.023	0.048	0.067	0.102	0.125	0.015	0.024	0.058	0.115
Ti	0.710	0.719	0.663	0.739	0.756	0.749	0.705	0.741	0.764
Fe	0.003	0.002	0.002	0.000	0.003	0.002	0.000	0.002	0.012
Nb	0.282	0.287	0.355	0.292	0.272	0.245	0.290	0.270	0.259
Ta	0.003	0.002	0.002	0.003	0.002	0.003	0.004	0.005	0.005

Mol.% end-members
$NaCeTi_2O_6$	60.10	57.99	45.93	43.06	40.47	65.80	61.03	58.33	43.68
$NaNbO_3$	28.20	20.62	27.06	23.68	21.20	21.60	21.18	16.09	18.50
$ThNb_4O_{12}$	0.00	8.68	10.17	7.75	7.92	2.90	7.93	11.94	9.36
$ThTi_2O_6$	4.56	5.46	8.97	18.08	22.81	1.55	0.43	6.07	20.06
$CaTiO_3$	4.76	5.00	5.56	5.06	5.57	5.60	6.42	5.29	6.25
$SrTiO_3$	2.38	2.25	2.31	2.37	2.03	2.55	3.01	2.28	2.15

Compositions: 1−2 core and 3−5 rim of a zoned loparite crystal KHB-44, 6−7 core and 8−9 rim of a zoned loparite crystal KHB-70.
All data this work.
Total Fe expressed as FeO; n.d. = not detected.

structure (Keller, 1965; Kovba and Trunov, 1963). Thorium dititanate ($ThTi_2O_6$) occurs in two polymorphs of monoclinic symmetry. Structures of both polymorphs differ from that of perovskite in being built of sheets of edge-sharing TiO_6 octahedra bound by Th atoms in either six-fold or eight-fold coordination (Balić Žunić *et al.*, 1984; Ruh and Wadsley, 1966). Given the considerable structural difference, loparite and thorium dititanate apparently should not form a continuous solid solution series; however, limits of the solubility between these two end-members are unknown. Our data suggest at least 23 mol.% $ThTi_2O_6$ is possible.

The compositions of Th-rich loparite were recalculated into major perovskite-group end-members (Mitchell, 1996) plus the two thorium compounds $ThNb_4O_{12}$ and $ThTi_2O_6$ (Table 2, Fig. 4). The loparite composition evolves by becoming enriched in the thorium end-members
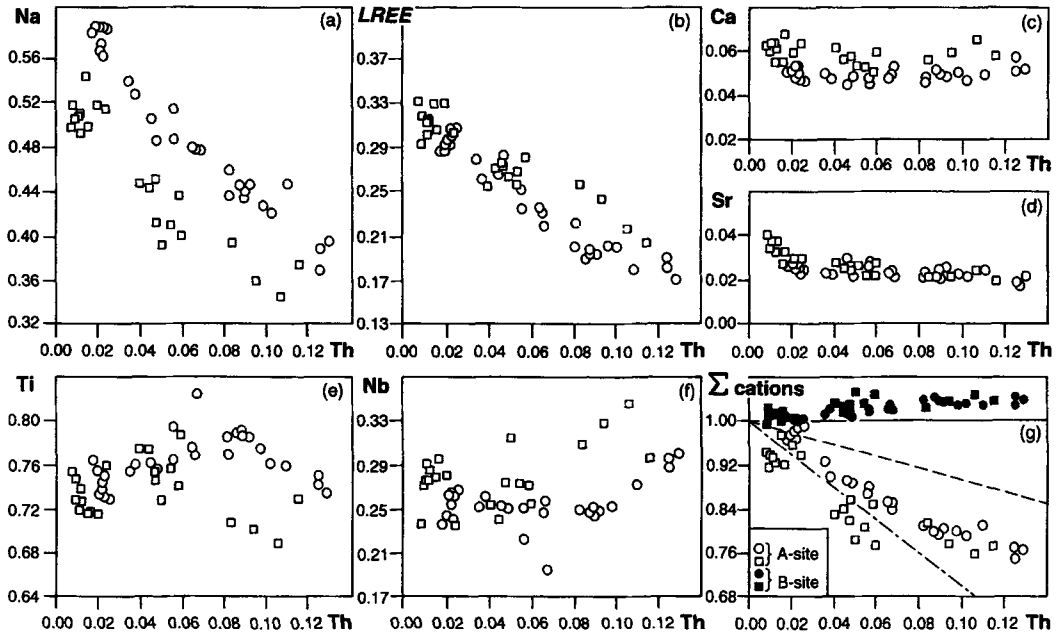
FIG. 3. Variations (apfu) of: (a) Na, (b) LREE, (c) Ca, (d) Sr, (e) Ti, (f) Nb and (g) cation totals at the A and B sites, with respect to Th for Th-rich loparite. Circles correspond to loparite KHB-44, squares to KHB-70. Variation of A-cation totals in the solid solution series $NaLREETi_2O_6-Na_2ThTi_3O_9$ is shown by solid line, in the series $NaLREETi_2O_6-ThTi_2O_6$ by dashed line, and in the series $NaLREETi_2O_6-ThNb_4O_{12}$ by dash-dotted line (g).

at essentially constant lueshite content. Using nomenclature principles suggested for the perovskite-group minerals by Mitchell (1996), the examined samples compositionally evolve from niobian loparite toward niobian thorian and thorian niobian loparite.

Betafite

Representative analyses of betafite developed in thorian loparite, are given in Table 3. LREE dominated by Ce, and Th are the major A-cations. According to the classification scheme proposed by Hogarth (1989) for the pyrochlore-group minerals, this mineral should be regarded as ceriobetafite or thorium ceriobetafite (LREE > Th> 20 % cation sum at the A sites). In this study, we prefer to refer to the mineral using quotation marks, as 'ceriobetafite' is not approved as a distinct mineral species by the Comission on New Minerals and Mineral Names of the IMA.

At the Khibina complex, pyrochlore-group minerals were previously described as accessory constituents of aegirine-feldspar veins (Kozyreva,

1990) and peralkaline pegmatites (Kapustin, 1989; Shilin et al., 1966). These minerals correspond to pyrochlore sensu stricto that may be somewhat enriched in SrO (Shilin et al., 1966) or LREE (Kapustin, 1989). Ti-dominant species, i.e. members of the betafite subgroup have not been previously recognized in the Khibina alkaline complex.

Belyankinite

Compositional data on belyankinite and related Ti-Nb hydroxides available from literature are limited to a few bulk wet-chemical analyses (Gerasimovskii and Kazakova, 1950; Semenov, 1957; Vlasov et al., 1966). Semenov (1957) has suggested that Ti-dominant belyankinite forms solid solution series with its Mn-analogue manganbelyankinite and Nb-dominant gerasimovskite. The mineral examined in the present study is a member of the belyankinite-gerasimovskite series with negligible content of manganbelyankinite (Table 4). A generalized structural formula of belyankinite calculated on the basis of 12 atoms of oxygen, is
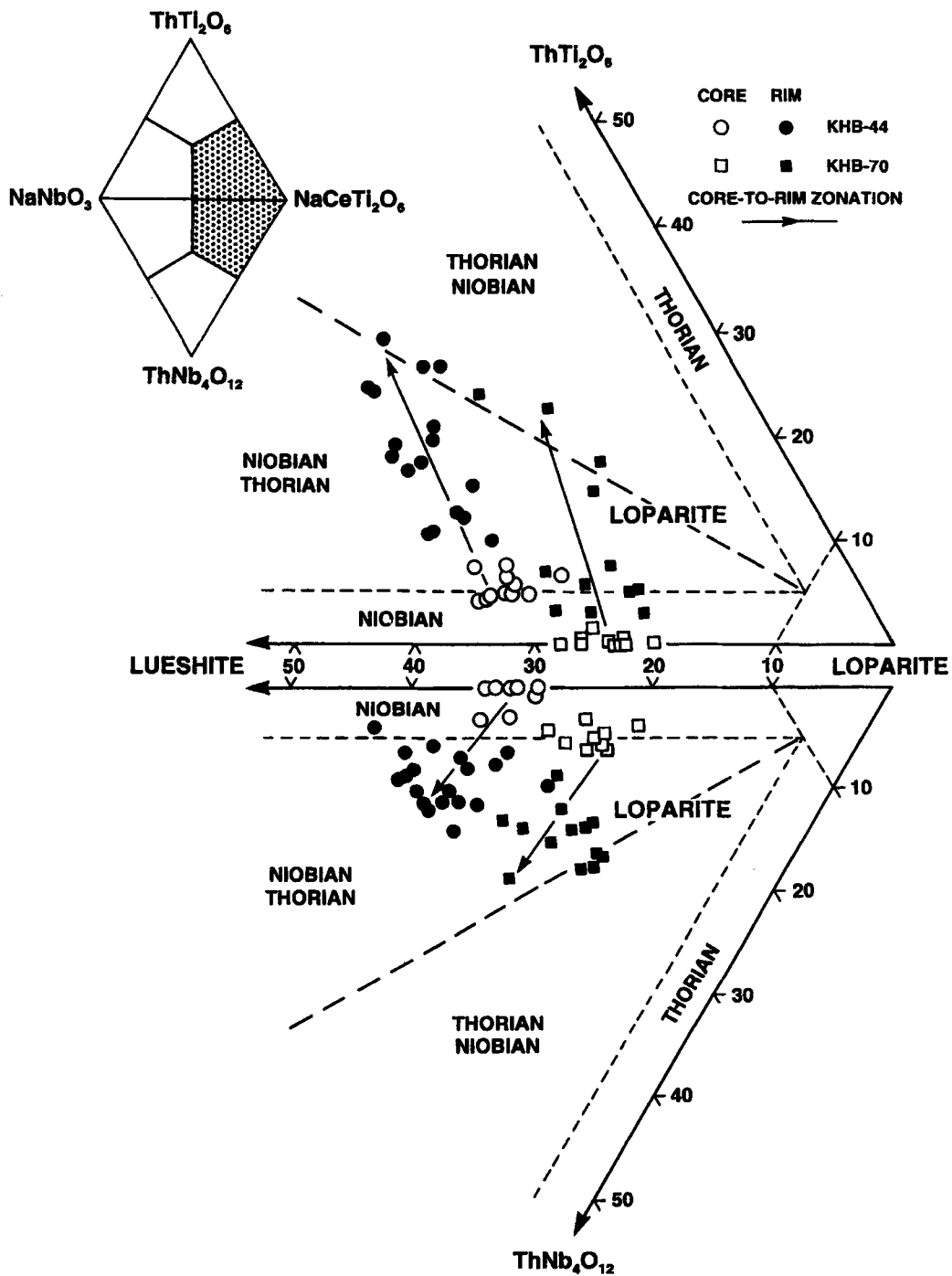
FIG. 4. Compositions (mol.%) of Th-rich loparite in the system loparite $(NaCeTi_2O_6)$–lueshite $(NaNbO_3)$–$ThTi_2O_6$–$ThNb_4O_{12}$.

TABLE 3. Representative compositions of 'ceriobetafite'

	1	2	3		1	2	3
Wt.%					Structural formulae (ΣB-cations = 2)		
Na_2O	1.01	0.54	0.34	Na	0.111	0.060	0.036
CaO	1.79	1.67	1.76	Ca	0.108	0.102	0.103
SrO	1.17	1.15	1.30	Sr	0.038	0.038	0.041
La_2O_3	5.79	4.81	5.10	La	0.121	0.101	0.103
Ce_2O_3	9.01	8.65	8.46	Ce	0.186	0.180	0.169
Nd_2O_3	1.52	2.62	1.14	Nd	0.034	0.053	0.022
ThO_2	19.65	20.88	20.41	Th	0.244	0.270	0.253
TiO_2	33.82	35.06	37.50	Ti	1.438	1.499	1.539
Fe_2O_3	n.d.	0.03	0.47	Fe	0.000	0.001	0.017
Nb_2O_5	21.77	19.26	17.76	Nb	0.556	0.495	0.438
Ta_2O_5	0.37	0.34	0.39	Ta	0.006	0.005	0.006
Total	95.40	95.01	94.63				

Compositions: 1 and 2 KHB-44, 3 KHB-70.
All data this work.
Total Fe expressed as Fe_2O_3; n.d. = not detected.

$(Ca,Th,LREE)_{1.3}(Ti,Nb,Si,Fe)_5O_{12} \cdot nH_2O$ (average of 18 determinations) and approaches that deduced by Fleischer from Semenov's analytical data (see reference to Semenov, 1957): $Ca_{0.9}(Ti,Zr,Nb,Si)_{5.5}O_{12} \cdot 10H_2O$.

However, the mineral from Khibina differs from Lovozero belyankinite in having much higher ThO_2 (up to 24.17 wt.%) and $LREE_2O_3$ (up to 11.6 wt.%) contents, both of which are undoubtedly 'inherited' from the loparite parent.

TABLE 4. Representative compositions of belyankinite

	1	2		1	2
Wt.%				Structural formulae (O = 24)	
Na_2O	0.03	0.28	Na	0.014	0.122
CaO	4.12	1.62	Ca	1.027	0.402
MgO	0.16	0.17	Mg	0.055	0.060
MnO	0.11	0.28	Mn	0.022	0.053
La_2O_3	2.08	2.00	La	0.179	0.169
Ce_2O_3	8.62	2.21	Ce	0.733	0.186
Nd_2O_3	0.81	0.76	Nd	0.067	0.062
ThO_2	12.42	24.17	Th	0.657	1.264
SiO_2	13.03	12.21	Si	3.033	2.805
TiO_2	22.81	24.73	Ti	3.991	4.273
Al_2O_3	1.21	1.66	Al	0.331	0.450
Fe_2O_3	6.16	5.07	Fe	1.078	0.877
Nb_2O_5	15.02	15.87	Nb	1.578	1.649
Total	86.58	91.03			

Compositions: 1 and 2 replacement mantles on thorian loparite KHB-70.
Total Fe expressed as Fe_2O_3; ZrO_2 was sought, but not found.

X-ray powder diffractometry

An XRD powder pattern of a sample of the core of a thorian loparite showed only a few faint diffraction lines with relatively high d-spacings, whereas a rim sample appeared to be completely metamict. After heating to 700°C for 1 hour, the core and rim samples gave XRD powder patterns (Table 5) similar to those of La-dominant synthetic loparite $NaLaTi_2O_6$ and 'irinite' as described by Borodin and Kazakova (1954). The former has been proposed to have the undistorted cubic lattice (ASTM 39-65: Belous et al., 1985). However, Rietveld refinement of an XRD powder pattern of $NaLaTi_2O_6$ suggests that this compound is orthorhombic (space group $Pnma$) rather than cubic (Mitchell and Chakhmouradian, in preparation). The pattern of the rim sample of thorian loparite also includes three diffraction lines with d-spacings of 2.95, 1.795 and 1.535 Å, that cannot be produced by the perovskite-type structure. These are characteristic of pyrochlore-type phases and correspond to the most intense lines 222, 440 and 622, respectively (ASTM 13-197; ASTM 17-746).

Data available from the literature show that XRD powder patterns similar to those obtained in this study are produced by naturally occurring loparite of various Nb_2O_5, CaO, Na_2O, TiO_2 and SrO contents (Haggerty and Mariano, 1983; Kostyleva-Labuntsova et al., 1978b; Mitchell et al., 1996). Given a significant difference in ionic radius between Th^{4+}, Na^+ and Ce^{3+} (1.21, 1.39 and 1.34 Å, respectively: Shannon, 1976), it is expected that Th-rich loparite should have a strongly distorted perovskite-type structure. However, the obtained patterns (Table 5) do not exhibit 'extra' diffraction lines reflecting cation ordering or geometric distortion of the ideal cubic perovskite-type lattice. Such diffraction lines, e.g. 7.69−7.90, 3.44−3.50, 2.57−2.60, 1.87−1.89 Å, are present in patterns of most synthetic perovskite-type titanates and niobates with Th^{4+} localized at the A sites (Keller, 1965; Kovba and Trunov, 1963; Labeau and Joubert, 1978; Zhu and Hor, 1995). The only known exceptions so far are compounds from the $Na_{0.6-0.8}Th_{0.1-0.2}NbO_3$ range of the $NaNbO_3-Th_{0.25}NbO_3$ solid solution series (ASTM-34-1068; Labeau and Joubert, 1978, Table III).

TABLE 5. X-ray diffraction patterns of loparite, 'irinite' and Th-rich loparite

hkl	1 d	1 I/I_o	2 d	2 I/I_o	3 d	3 I/I_o	4 d	4 I/I_o	5 d	5 I/I_o
100	3.870	2								
110	2.730	100	2.71	100	2.76	100	2.64	100	2.72	100
111	2.225	50								
200	1.933	92	1.919	90	1.950	10	1.905	30	1.925	40
			1.860	20b						
211	1.578	95	1.569	80	1.598	30	1.562	60	1.575	60
			1.503	10						
220	1.367	70	1.360	40	1.383	20	1.355	30	1.368	30
300	1.290	4								
310	1.225	25	1.216	30	1.233	15	1.214	20	1.222	20
311	1.168	8	1.197	10						
222	1.117	13					1.111	5	1.118	5
320	1.075	3								
321	1.035	38	1.028	60	1.042	20	1.029	10	1.034	10
400	0.9680	5								
411							0.908	10	0.912	5
420							0.864	10	0.865	5
332							0.8245	5	0.8260	3
422							0.7910	3		

1 synthetic $NaLaTi_2O_6$: $a = 3.873$ Å (ASTM 39-65); 2 'irinite' (heated): $a = 3.83$ Å (Borodin and Kazakova, 1954); 3 thorian loparite KHB-70, core (unheated): $a = 3.902(2)$ Å; 4 thorian loparite KHB-70, core (heated): $a = 3.841(1)$ Å; 5 thorian loparite KHB-70, rim (heated): $a = 3.867(2)$ Å + 3 weak lines with $d = 2.95$; 1.795, 1.535 Å (3-5 this work). b = broad line.

The absence of superstructure reflections in the patterns of thorian loparite may result from its metamict state prior to heating, i.e. from failure to restore an initial apparently distorted structure of the mineral. Alternatively, stabilization of the cubic structure may result from the presence of minor cations in thorian loparite, e.g. Ca or Sr. This phenomenon refered to as stabilized polymorphism (Smirnova and Belov, 1969) is well-known for TiO_2 and ZrO_2 polymorphs (Filatov and Frank-Kamenetskii, 1969; Grunin et al., 1983). To select between the two above alternatives, experimental studies of the solid solution series between loparite and Th-bearing end-members are being undertaken by us.

Discussion

At Khibina, Th-rich loparite occurs only in relation to the foyaite series (Borodin and Kazakova, 1954; Chakhmouradian and Mitchell, 1998; Kozyreva et al., 1991; Tikhonenkova et al., 1982). Zoned Th-rich loparite examined in this study crystallized at a late deuteric stage of the formation of foyaite pegmatites. At this stage, fluids enriched in Ti and incompatible elements (Zr, Nb, Sr, LREE, Th) gave rise to the assemblage of aegirine with loparite, eudialyte and Ti-silicates (astrophyllite, lorenzenite, lamprophyllite). In a similar paragenesis, loparite occurs in the foyaite pegmatites at Mt. Niorkpakhk (east of Mt. Eveslogchorr) and khibinite pegmatites at a number of localities in western Khibina (Chakhmouradian and Mitchell, 1998). In most of these occurrences, loparite is relatively Th-poor and compositionally evolves by enrichment in Na_2O and Nb_2O_5 and depletion in $LREE_2O_3$ and TiO_2 contents toward the rim. This trend coincides with the main magmatic trend of the compositional evolution of loparite in the nepheline-syenite complexes (Chakhmouradian and Mitchell, 1998; Mitchell and Chakhmouradian, 1996). The evolutionary trend from niobian loparite to thorian niobian loparite recognized in the present study has not been previously observed in alkaline rocks. Loparite from fenite-type rocks of the Paraná Basin carbonatite complexes has high ThO_2 contents (up to 6.2 wt.%), accompanied by enrichment in Na_2O and Nb_2O_5 (lueshite), and depletion in SrO and TiO_2 (tausonite) (Mitchell, 1996, Table 3.6). Th-enrichment (up to 4.9 wt.% ThO_2) in the composition of perovskite from the carbonatite complexes of the Kola Peninsula is coupled with increasing $LREE_2O_3$, Na_2O and Nb_2O_5, i.e. loparite and lueshite components (Chakhmouradian and Mitchell, 1997). In the Polino carbonatite, Th-bearing (1.5−1.7 wt.% ThO_2) perovskite has high Fe_2O_3 and ZrO_2 contents (Lupini et al., 1992).

The limits of solubility between loparite (Na$LREE$Ti$_2O_6$) and the thorium end-member compositions, $ThNb_4O_{12}$, $Na_{2/3}Th_{1/3}TiO_3$ and $ThTi_2O_6$ are unknown. From structural data (Balić Žunić et al., 1984; Kovba and Trunov, 1963; Ruh and Wadsley, 1966; Zhu and Hor, 1995), it is expected that loparite forms a complete solid solution series with the former two compounds, and only a limited series with $ThTi_2O_6$. Experimental studies of the $NaLaTi_2O_6$-$ThNb_4O_{12}$, $NaLaTi_2O_6$-$Na_2ThTi_3O_9$ and $NaLaTi_2O_6$-$ThTi_2O_6$ systems are being undertaken by the authors of this paper.

As evidenced by textural relationships and compositional data, the appearance of Na-poor Th-rich 'ceriobetafite' and belyankinite as mantles on thorian loparite was a result of metasomatic processes involving alkali-cation leaching and hydration. Note that the same processes brought about the replacement of nepheline and alkali feldspar present as relics in fibrous aegirine, by zeolites and eventually, by gibbsite. Metasomatites including albitites, albite-aegirine and albite-astrophyllite rocks are very common in the vicinity of pegmatite veins containing thorian loparite at Mt. Eveslogchorr. Hydrothermal solutions responsible for the metasomatic alteration most probably were derived from the phonolitic magma which produced the differentiated intrusion of nepheline syenites including foyaite and its precursor khibinite. An alternative source of such solutions could be a foidolite melt, as some authors suggest that the foidolites were emplaced later than the nepheline syenite intrusion (Kostyleva-Labuntsova et al., 1978a; Sniatkova et al., 1986).

Conclusions

In Na-LREE-Ti-dominant species of the perovskite group, $Th^{4−}$ cations occupy large twelve-coordinated A sites in the structure. The accommodation of Th into the structure is accompanied by appearance of vacancies at the A sites at the expense of Na, LREE and Sr. Thorian loparite is essentially a member of the loparite (Na$LREE$Ti$_2O_6$)–lueshite (NaNbO$_3$)–$ThTi_2O_6$–$ThNb_4O_{12}$ quaternary system with low

or negligible contents of other end-member compositions. The mineral compositionally evolves from niobian loparite to niobian thorian and thorian niobian loparite. Metasomatic alteration of thorian loparite gave rise to 'ceriobetafite' and belyankinite with high ThO_2 content. Thorian loparite is metamict or partly metamict and upon heating, regains a structure close to that of synthetic loparite $NaLaTi_2O_6$.

Acknowledgements

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