

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233707657>

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

Article in *Mineralogical Magazine* · June 1998

DOI: 10.1180/002646198547738

---

CITATIONS

25

---

READS

72

2 authors:



Roger H. Mitchell

Lakehead University Thunder Bay Campus

325 PUBLICATIONS 9,283 CITATIONS

SEE PROFILE



Anton Chakhmouradian

University of Manitoba

143 PUBLICATIONS 3,240 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



REE mineralization associated with nepheline syenites and carbonatites [View project](#)



Too many projects to list [View project](#)

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

ROGER H. MITCHELL

AND

ANTON R. CHAKHMOURADIAN

Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada

## ABSTRACT

Th-rich (up to 18.4 wt.% ThO<sub>2</sub>) 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<sub>0.39</sub>LREE<sub>0.19</sub>Th<sub>0.12</sub>Ca<sub>0.05</sub>Sr<sub>0.02</sub>) $\Sigma$ 0.77(Ti<sub>0.76</sub>Nb<sub>0.27</sub>) $\Sigma$ 1.03O<sub>3</sub>. The mineral is partly or completely metamict and after annealing gives an X-ray diffraction powder pattern similar to that of synthetic NaLaTi<sub>2</sub>O<sub>6</sub> 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<sub>2</sub>O<sub>3</sub> and ThO<sub>2</sub> contents. Both 'ceriobetafite' and belyankinite were formed due to metasomatic alteration of loparite.

**KEYWORDS:** loparite, betafite, belyankinite, nepheline-syenite pegmatite, Khibina alkaline complex, Kola Peninsula, Russia.

## Introduction

PEROVSKITE-GROUP minerals from alkaline rocks exhibit wide ranges in composition and may serve as sensitive indicators of evolutionary trends (Kukhareno and Bagdasarov, 1961; Mitchell, 1996; Mitchell and Chakhmouradian, 1996; Tikhonenkova *et al.*, 1982). Comprehensive studies of isomorphous 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 tetravalent actinides and Ce<sup>4+</sup>. 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<sub>1-x</sub>BO<sub>3-x</sub>(OH)<sub>x</sub> (*x* = 0–0.5). Borodin and Kazakova (1954) reported the occurrence of Th-rich

(13.0 wt.% ThO<sub>2</sub>) loparite (termed 'irinite') with minor amounts of Fe<sub>2</sub>O<sub>3</sub> 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<sup>2-</sup> ⇌ (OH)<sup>-</sup> 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<sub>2</sub> 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<sub>2</sub>O, Nb<sub>2</sub>O<sub>5</sub>, LREE<sub>2</sub>O<sub>3</sub> and ThO<sub>2</sub> (up to 6.2 wt.%) contents (Mitchell, 1996).

Initial synthesis of Th-bearing perovskite-type oxides produced compounds of the type AThO<sub>3</sub> (*A* = Ca, Sr, Ba, Pb), in which Th<sup>4+</sup> 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<sup>4+</sup> at twelve-coordinated A-sites in the perovskite structure. These compounds were highly cation-deficient relative to ideal ABX<sub>3</sub> perovskite, having the general formula A<sub>1/4</sub>BO<sub>3</sub> (*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<sub>1/4</sub>WO<sub>3</sub> to Th<sub>1/30</sub>WO<sub>3</sub>. Other synthetic perovskites with *A*-site Th include CaThV<sub>2</sub>O<sub>6</sub> and SrThV<sub>2</sub>O<sub>6</sub> (Vidiasagar and Gopalakrishnan, 1982), Na<sub>2/3</sub>Th<sub>1/3</sub>TiO<sub>3</sub> (Zhu and Hor, 1995) and the solid solution series NaNbO<sub>3</sub>-Th<sub>0.25</sub>NbO<sub>3</sub> (Labeau and Joubert, 1978). The above examples demonstrate that: (i) Th<sup>4+</sup> 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), manganian fayalite (Mn), synthetic SrTiO<sub>3</sub> (Sr), BaSiO<sub>3</sub> (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-Scherrer 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<sub>2</sub>O vapour apparently present in the spectrometer.

## Occurrence

Until recently, loparite with the ThO<sub>2</sub> 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.* (1978*a,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 intergrowths 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.*, 1978*a*). The aegirine-astrophyllite aggregate encloses numerous irregular- or lens-shaped polygranular segregations of analcite, phillipsite, natrolite and gibbsite plus Fe-hydroxides. 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.

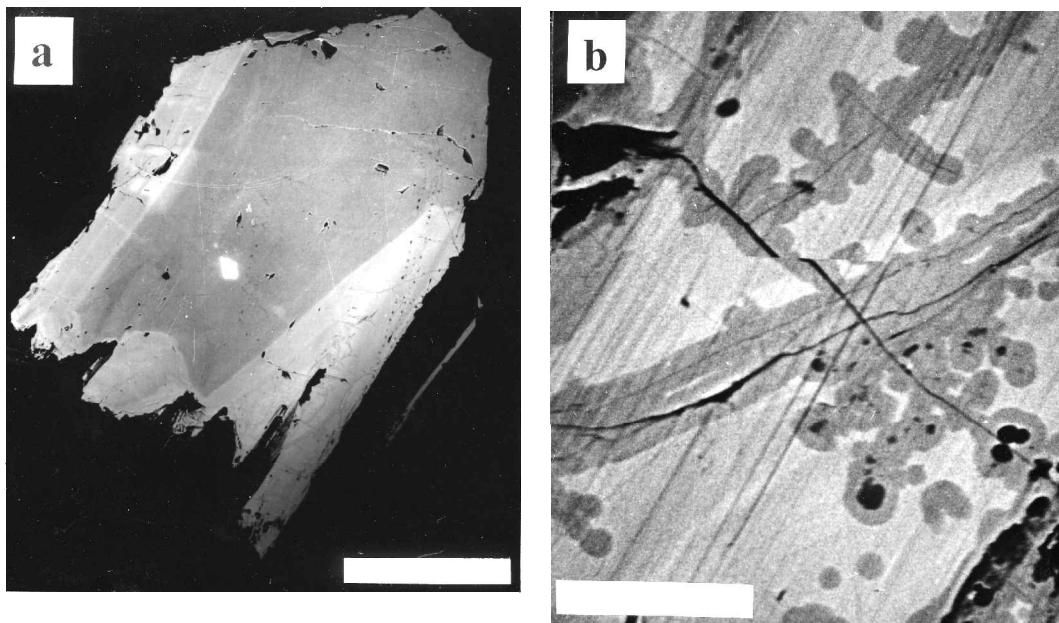


FIG. 1. Back-scattered electron images of a zoned Th-rich loparite crystal. (a) rim of thorian niobian and niobian thorian loparite (light grey) on niobian loparite (dark grey), scale bar is 400 µm; (b) 'ceriobetafite' (dark grey) developed along fractures and margins of thorian niobian loparite (light 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  $\text{ThO}_2$  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  $\mu\text{m}$ ) zones decorating margins of the crystals and fractures within phase 2 (Fig. 1b). Composition determinations show that both phases have comparable CaO, SrO,  $\text{LREE}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$  (Ti > Nb) contents. However, phase 1 gives low analysis totals (93.6–97.0 wt.%) and contains considerably less  $\text{Na}_2\text{O}$  (0.3–1.0 wt.%) and generally more  $\text{ThO}_2$  (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  $\text{cm}^{-1}$ . This band corresponds to bond vibrations in the octahedral complexes  $(\text{Ti,Nb})\text{O}_6$  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  $(\text{Ti,Nb})\text{O}_6$  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  $(\text{Ti,Nb})\text{O}_6$  absorption band, the infrared spectrum of the rim (Fig. 2b) contains bands at 1650, 2330, 3300–3320 and 3530  $\text{cm}^{-1}$ , the latter two partially overlapping each other. The OH stretching bands at 3300–3320 and 3530  $\text{cm}^{-1}$  and Nb–OH band at 1650  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ .

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  $\mu\text{m}$ ) 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  $\text{ThO}_2$  and depletion in  $\text{Na}_2\text{O}$ ,  $\text{LREE}_2\text{O}_3$  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

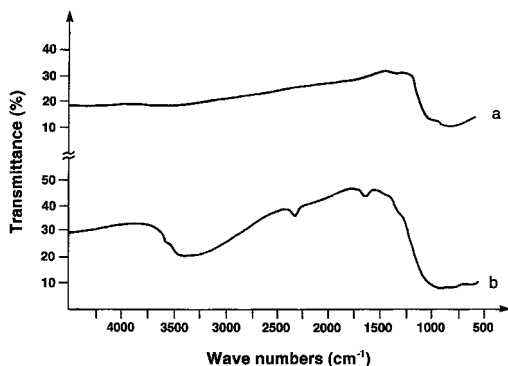


FIG. 2. Infra-red transmission spectra of Th-rich loparite. (a) core sample; (b) rim sample.

TH-RICH LOPARITE

TABLE 1. Representative compositions of major and accessory silicate minerals

Wt.%	1*	2*	3	4	5	6	7	8	9	10	11*	12*
Na <sub>2</sub> O	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 <sub>2</sub> O	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>5</sub>	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 <sup>2+</sup>	0.020	0.047	3.583	3.486	1.575	1.340	–	–	–	–	1.742	1.693
Fe <sup>3+</sup>	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	–	–

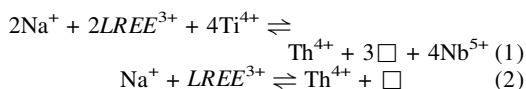
Compositions: 1 and 2 aegirine; 3 and 4 astrophyllite; 5 and 6 eudialyte; 7 and 8 lamprophyllite; 9 and 10 lorenzenite; 11 and 12 magnesio-arfvedsonite.

All data this work.

\* Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio calculated using Droop's (1987) method;

deficiency (Fig. 3g), it is deduced that Th<sup>4+</sup> 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<sub>4</sub>O<sub>12</sub> and ThTi<sub>2</sub>O<sub>6</sub> (Fig. 3). The solid solution series between loparite

NaLREETi<sub>2</sub>O<sub>6</sub> and Na<sub>2/3</sub>Th<sub>1/3</sub>TiO<sub>3</sub>, believed to be present, is not present as the A- and B-sites occupancy remains constant. The isomorphic substitutions are as follows:



ThNb<sub>4</sub>O<sub>12</sub> (= Th<sub>0.25</sub>NbO<sub>3</sub>) 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 <sub>2</sub> O	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 <sub>2</sub> O <sub>3</sub>	9.72	8.88	6.47	6.46	5.41	11.42	9.37	8.24	5.79
Ce <sub>2</sub> O <sub>3</sub>	14.77	14.21	11.19	10.27	8.91	16.91	14.64	13.37	9.87
Pr <sub>2</sub> O <sub>3</sub>	1.86	1.72	1.56	n.d.	1.14	1.03	2.20	2.54	1.38
Nd <sub>2</sub> O <sub>3</sub>	2.04	2.02	1.56	1.96	1.86	1.61	2.47	1.98	1.95
ThO <sub>2</sub>	3.46	7.38	10.29	15.40	18.45	2.34	3.66	8.69	17.28
TiO <sub>2</sub>	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 <sub>2</sub> O <sub>5</sub>	21.38	21.98	27.16	22.10	20.18	18.72	22.13	20.34	19.62
Ta <sub>2</sub> O <sub>5</sub>	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 <sub>2</sub> O <sub>6</sub>	60.10	57.99	45.93	43.06	40.47	65.80	61.03	58.33	43.68
NaNbO <sub>3</sub>	28.20	20.62	27.06	23.68	21.20	21.60	21.18	16.09	18.50
ThNb <sub>4</sub> O <sub>12</sub>	0.00	8.68	10.17	7.75	7.92	2.90	7.93	11.94	9.36
ThTi <sub>2</sub> O <sub>6</sub>	4.56	5.46	8.97	18.08	22.81	1.55	0.43	6.07	20.06
CaTiO <sub>3</sub>	4.76	5.00	5.56	5.06	5.57	5.60	6.42	5.29	6.25
SrTiO <sub>3</sub>	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<sub>2</sub>O<sub>6</sub>) 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<sub>6</sub> 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<sub>2</sub>O<sub>6</sub> is possible.

The compositions of Th-rich loparite were recalculated into major perovskite-group end-members (Mitchell, 1996) plus the two thorium compounds ThNb<sub>4</sub>O<sub>12</sub> and ThTi<sub>2</sub>O<sub>6</sub> (Table 2, Fig. 4). The loparite composition evolves by becoming enriched in the thorium end-members

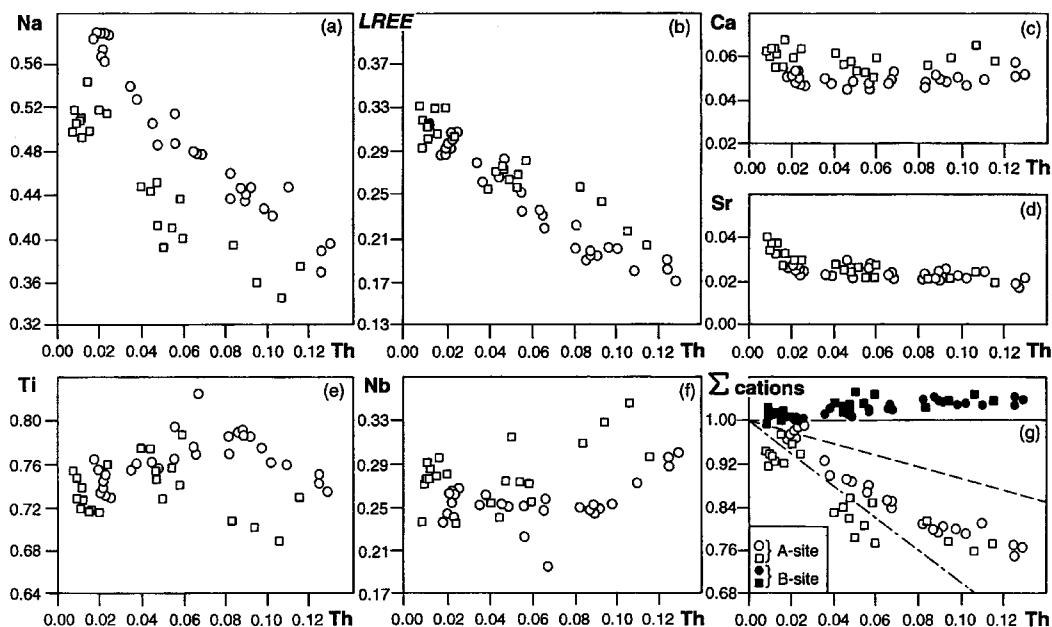


FIG. 3. Variations (apfu) of: (a) Na, (b) *LREE*, (c) Ca, (d) Sr, (e) Ti, (f) Nb and (g) cation totals at the A and B sites, with respect to Th for Th-rich loparite. Circles correspond to loparite KHB-44, squares to KHB-70. Variation of A-cation totals in the solid solution series  $\text{NaLREETi}_2\text{O}_6\text{-Na}_2\text{ThTi}_3\text{O}_9$  is shown by solid line, in the series  $\text{NaLREETi}_2\text{O}_6\text{-ThTi}_2\text{O}_6$  by dashed line, and in the series  $\text{NaLREETi}_2\text{O}_6\text{-ThNb}_4\text{O}_{12}$  by dash-dotted line (g).

at essentially constant lueshite content. Using nomenclature principles suggested for the pyrochlore-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 ( $LREE > \text{Th} > 20\%$  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 Commission 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



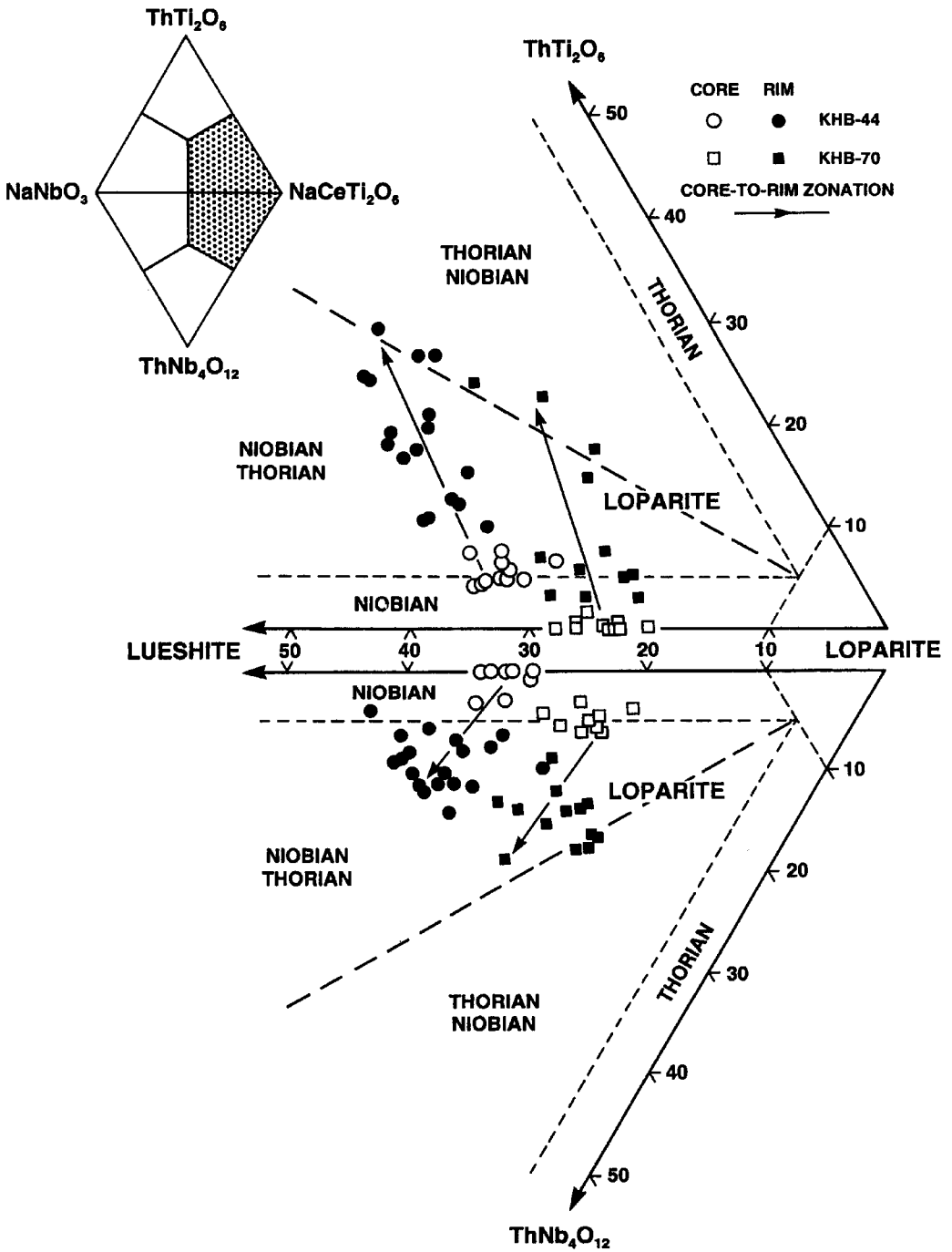


FIG. 4. Compositions (mol.%) of Th-rich loparite in the system loparite ( $\text{NaCeTi}_2\text{O}_6$ )-lueshite ( $\text{NaNbO}_3$ )- $\text{ThTi}_2\text{O}_6$ - $\text{ThNb}_4\text{O}_{12}$

Th-RICH LOPARITE

TABLE 3. Representative compositions of 'ceriobetafite'

	1	2	3		1	2	3
Wt. %					Structural formulae ( $\Sigma$ B-cations = 2)		
Na <sub>2</sub> O	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 <sub>2</sub> O <sub>3</sub>	5.79	4.81	5.10	La	0.121	0.101	0.103
Ce <sub>2</sub> O <sub>3</sub>	9.01	8.65	8.46	Ce	0.186	0.180	0.169
Nd <sub>2</sub> O <sub>3</sub>	1.52	2.62	1.14	Nd	0.034	0.053	0.022
ThO <sub>2</sub>	19.65	20.88	20.41	Th	0.244	0.270	0.253
TiO <sub>2</sub>	33.82	35.06	37.50	Ti	1.438	1.499	1.539
Fe <sub>2</sub> O <sub>3</sub>	n.d.	0.03	0.47	Fe	0.000	0.001	0.017
Nb <sub>2</sub> O <sub>5</sub>	21.77	19.26	17.76	Nb	0.556	0.495	0.438
Ta <sub>2</sub> O <sub>5</sub>	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<sub>2</sub>O<sub>3</sub>; n.d. = not detected.

(Ca,Th,LREE)<sub>1.3</sub>(Ti,Nb,Si,Fe)<sub>5</sub>O<sub>12</sub>·nH<sub>2</sub>O (average of 18 determinations) and approaches that deduced by Fleischer from Semenov's analytical data (see reference to Semenov, 1957): Ca<sub>0.9</sub>(Ti,Zr,Nb,Si)<sub>5.5</sub>O<sub>12</sub>·10H<sub>2</sub>O.

However, the mineral from Khibina differs from Lovozero belyankinite in having much higher ThO<sub>2</sub> (up to 24.17 wt.%) and LREE<sub>2</sub>O<sub>3</sub> (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 <sub>2</sub> O	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 <sub>2</sub> O <sub>3</sub>	2.08	2.00	La	0.179	0.169
Ce <sub>2</sub> O <sub>3</sub>	8.62	2.21	Ce	0.733	0.186
Nd <sub>2</sub> O <sub>3</sub>	0.81	0.76	Nd	0.067	0.062
ThO <sub>2</sub>	12.42	24.17	Th	0.657	1.264
SiO <sub>2</sub>	13.03	12.21	Si	3.033	2.805
TiO <sub>2</sub>	22.81	24.73	Ti	3.991	4.273
Al <sub>2</sub> O <sub>3</sub>	1.21	1.66	Al	0.331	0.450
Fe <sub>2</sub> O <sub>3</sub>	6.16	5.07	Fe	1.078	0.877
Nb <sub>2</sub> O <sub>5</sub>	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<sub>2</sub>O<sub>3</sub>; ZrO<sub>2</sub> 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<sub>2</sub>O<sub>6</sub> 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<sub>2</sub>O<sub>6</sub> 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<sub>2</sub>O<sub>5</sub>, CaO, Na<sub>2</sub>O, TiO<sub>2</sub> and SrO contents (Haggerty and Mariano, 1983; Kostyleva-Labuntsova *et al.*, 1978*b*; Mitchell *et al.*, 1996). Given a significant difference in ionic radius between Th<sup>4+</sup>, Na<sup>+</sup> and Ce<sup>3+</sup> (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<sup>4+</sup> 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<sub>0.6–0.8</sub>Th<sub>0.1–0.2</sub>NbO<sub>3</sub> range of the NaNbO<sub>3</sub>–Th<sub>0.25</sub>NbO<sub>3</sub> 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

<i>hkl</i>	1		2		3		4		5	
	<i>d</i>	<i>I/I<sub>o</sub></i>	<i>d</i>	<i>I/I<sub>o</sub></i>	<i>d</i>	<i>I/I<sub>o</sub></i>	<i>d</i>	<i>I/I<sub>o</sub></i>	<i>d</i>	<i>I/I<sub>o</sub></i>
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<sub>2</sub>O<sub>6</sub>;  $a = 3.873$  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 referred to as stabilized polymorphism (Smirnova and Belov, 1969) is well-known for  $\text{TiO}_2$  and  $\text{ZrO}_2$  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  $\text{Na}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  and depletion in  $\text{LREE}_2\text{O}_3$  and  $\text{TiO}_2$  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  $\text{ThO}_2$  contents (up to 6.2 wt.%), accompanied by enrichment in  $\text{Na}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  (lueshite), and depletion in SrO and  $\text{TiO}_2$  (tausonite) (Mitchell, 1996, Table 3.6). Th-enrichment (up to 4.9 wt.%  $\text{ThO}_2$ ) in the composition of perovskite from the carbonatite complexes of the Kola Peninsula is

coupled with increasing  $\text{LREE}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$ , i.e. loparite and lueshite components (Chakhmouradian and Mitchell, 1997). In the Polino carbonatite, Th-bearing (1.5–1.7 wt.%  $\text{ThO}_2$ ) perovskite has high  $\text{Fe}_2\text{O}_3$  and  $\text{ZrO}_2$  contents (Lupini *et al.*, 1992).

The limits of solubility between loparite ( $\text{NaLREETi}_2\text{O}_6$ ) and the thorium end-member compositions,  $\text{ThNb}_4\text{O}_{12}$ ,  $\text{Na}_{2/3}\text{Th}_{1/3}\text{TiO}_3$  and  $\text{ThTi}_2\text{O}_6$  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  $\text{ThTi}_2\text{O}_6$ . Experimental studies of the  $\text{NaLaTi}_2\text{O}_6$ - $\text{ThNb}_4\text{O}_{12}$ ,  $\text{NaLaTi}_2\text{O}_6$ - $\text{Na}_2\text{ThTi}_3\text{O}_9$  and  $\text{NaLaTi}_2\text{O}_6$ - $\text{ThTi}_2\text{O}_6$  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,  $\text{Th}^{4+}$  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 ( $\text{NaLREETi}_2\text{O}_6$ )–lueshite ( $\text{NaNbO}_3$ )– $\text{ThTi}_2\text{O}_6$ – $\text{ThNb}_4\text{O}_{12}$  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<sub>2</sub> content. Thorian loparite is metamict or partly metamict and upon heating, regains a structure close to that of synthetic loparite NaLaTi<sub>2</sub>O<sub>6</sub>.

### Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada and Lakehead University, Ontario (RHM, ARC). ARC also acknowledges support from St. Petersburg State University, Russia (grant *Evolution of framework niobium-titanium oxides in carbonate-bearing nepheline-syenite complexes*). Alan MacKenzie and Keith Pringnitz are thanked for their assistance with the analytical work. Ann Hammond and Sam Spivak are thanked for thin section preparation and drafting services, respectively.

### References

- Balić Žunić, T., Šćavničar, S. and Grobanski, Z. (1984) The structure of thorium (IV) dititanium (IV) oxide, ThTi<sub>2</sub>O<sub>6</sub>. *Croat. Chem. Acta*, **57**, 645–51.
- Belous, A.G., Novitskaya, G.N., Gavrilova, L.G., Polyanetskaya, S.V. and Makarova, Z.Ya. (1985) Lanthanum titanate-zirconates with the perovskite structure. *Sov. Prog. Chem.*, **51**, 13–15.
- Borodin, L.S. (1954) On accommodation of water in the crystal lattice of perovskite-group minerals. *Doklady AN SSSR*, **95**, (in Russian), 873–5.
- Borodin, L.S. and Kazakova M.E. (1954) Irinite – a new mineral from the perovskite group. *Doklady AN SSSR*, **97**, (in Russian), 725–8.
- Chakhmouradian, A.R. and Mitchell, R.H. (1997) Compositional variation of perovskite-group minerals from the carbonatite complexes of the Kola Alkaline Province, Russia. *Canad. Mineral.*, **35**, 1293–310.
- Chakhmouradian, A.R. and Mitchell, R.H. (1998) Compositional variation of perovskite-group minerals from the Khibina alkaline complex, Kola Peninsula. *Canad. Mineral.*, **36**, (in press).
- Filatov, S.K. and Frank-Kamenetskii, V.A. (1969) Structural characteristics of cubic ZrO<sub>2</sub> stabilized by calcium. *Sov. Phys. Cryst.*, **14**, 414–5.
- Galakhov, A.V. (1975) *The petrology of the Khibina Alkaline Massif*. Nauka Press, Leningrad, (in Russian), 256 pp.
- Gerasimovskii, V.I. and Kazakova, M.E. (1950) Belyankinite – a new mineral. *Doklady AN SSSR*, **71**, (in Russian), 925–7.
- Grunin, V.S., Razumenko, M.V., Patrina I.V., Filatov, S.K. and Alekseyeva, T.V. (1983) Mode of existence and abundance of TiO<sub>2</sub>-rutile, anatase and brookite. *Doklady Earth Sci. Sect.*, **268**, 149–50.
- Haggerty, S.E. and Mariano, A.N. (1983) Strontian-lopaprite and strontio-chevkinite: two new minerals in rheomorphic fenites from the Parana Basin carbonatites, South America. *Contrib. Mineral. Petrol.*, **84**, 365–81.
- Hogarth, D.D. (1961) A study of pyrochlore and betafite. *Canad. Mineral.*, **6**, 610–33.
- Hogarth, D.D. (1989) Pyrochlore, apatite and amphibole: distinctive minerals in carbonatites. In: *Carbonatites* (K. Bell, ed), Unwyn Hyman, London, 105–48.
- Kapustin, Yu.L. (1989) Rare earth-bearing pyrochlore from peralkaline pegmatites of the Khibina massif. *New data on minerals (Trudy Mineral. Muz. AN SSSR)*, **36**, (in Russian), 155–61.
- Keller, C. (1965) Die Reaktion der Dioxide der Elemente Thorium bis Americium mit Niob- und Tantalpentoxid (The reaction of dioxides of the elements from thorium to americium with niobium and tantalum pentoxides). *J. Inorg. Nucl. Chem.*, **27**, 1233–46.
- Kogarko, L.N., Kononova, V.A., Orlova, M.P. and Woolley, A.R. (1995) *Alkaline Rocks and Carbonatites of the World. Part 2: Former USSR*. Chapman & Hall, London, U.K., 226 pp.
- Kostyleva-Labuntsova, E.E., Borutskii, B.E., Sokolova, M.N., Shliukova, Z.V., Dorfman, M.D., Dudkin, O.B., Kozyreva, L.V. and Ikorskii, S.V. (1978a) *The Mineralogy of the Khibina Massif. Vol. 1*. Nauka Press, Moscow, (in Russian), 228 p.
- Kostyleva-Labuntsova, E.E., Borutskii, B.E., Sokolova, M.N., Shliukova, Z.V., Dorfman, M.D., Dudkin, O.B., Kozyreva, L.V. and Ikorskii, S.V. (1978b) *The Mineralogy of the Khibina Massif. Vol. 2*. Nauka Press, Moscow, (in Russian), 588 p.
- Kovba, L.M. and Trunov, V.K. (1962) Double oxides containing tungsten, tantalum, or niobium. *Doklady AN SSSR*, **147**, (in Russian), 622–4.
- Kozyreva, L.V. (1990) Aegirine-feldspar veins in the north-eastern part of the Khibina massif. In: *Alkaline Magmatism in the North-eastern Part of the Baltic Shield*, Kola Sci. Centre Press, Apatity, (in Russian), 42–56.
- Kozyreva, L.V., Men'shikov, Yu.P. and Lednev, A.I. (1991) Loparite mineralization of the Khibina massif. In: *New Data on the Rare-metal Mineralogy of the Kola Peninsula*, Kola Sci. Centre Press, Apatity, (in Russian), 37–44.

- Krivokoneva, G.K. and Sidorenko, G.A. (1971) The essence of the metamict transformation in pyrochlores. *Geochem. Int.*, **1971**, 113–22.
- Kukhareenko, A.A. & Bagdasarov, E.A. (1961) Perovskite from ultramafic-alkaline rocks of the Kola Peninsula. *Trudy VSEGEI*, **45**, (in Russian), 37–66.
- Labeau, M. and Joubert, J.C. (1978) Etude cristallographique des phases de type perovskite du système  $\text{Th}_{0.25}\text{NbO}_3\text{--NaNbO}_3$  (A crystal-chemical study of perovskite-type phases of the system  $\text{Th}_{0.25}\text{NbO}_3\text{--NaNbO}_3$ ). *J. Solid State Chem.*, **25**, 347–53.
- Lupini, L., Williams, C.T. and Woolley, A.R. (1992) Zr-rich garnet and Zr- and Th-rich perovskite from the Polino carbonatite, Italy. *Mineral. Mag.*, **56**, 581–6.
- Mitchell, R.H. (1996) Perovskites: a revised classification scheme for an important rare earth element host in alkaline rocks. In: *Rare Earth Minerals: Chemistry, Origin and Ore Deposits* (A.P. Jones, F. Wall and C.T. Williams, eds), Chapman & Hall, London, 41–76.
- Mitchell, R.H. and Chakhmouradian, A.R. (1996) Compositional variation of loparite from the Lovozero alkaline complex, Russia. *Canad. Mineral.*, **34**, 977–90.
- Mitchell, R.H. and Vladykin, N.V. (1993) Rare earth element-bearing tausonite and potassium barium titanates from the Little Murun potassic alkaline complex, Yakutia, Russia. *Mineral. Mag.*, **57**, 651–64.
- Mitchell, R.H., Chakhmouradian, A.R. and Yakovenchuk, V.N. (1996) "Nioboloparite": a re-investigation and discreditation. *Canad. Mineral.*, **34**, 991–9.
- Náray-Szabó, I. (1947) The perovskite-structure family. *Muegyet. Közlem.*, **1947**, 30–41.
- Nyquist, R.A. and Kagel, R.O. (1971) *Infrared Spectra of Inorganic Compounds (3800–45  $\text{cm}^{-1}$ )*. Academic Press, New York, 495 pp.
- Parker, R.L. and Sharp, W.N. (1970) Mafic-ultramafic igneous rocks and associated carbonatites of the Gem Park Complex, Custer and Fremont Counties, Colorado. *US Geol. Surv. Prof. Paper*, **649**, 24 p.
- Pilipenko, A.T., Shevchenko, L.L. and Patseliuk, V.A. (1971) Infrared spectra of some niobium minerals. *Zh. Prikl. Spekt. (J. Appl. Spectr.)*, **14**, (in Russian), 638–43.
- Ruh, R. and Wadsley, A.D. (1966) The crystal structure of  $\text{ThTi}_2\text{O}_6$  (brannerite). *Acta Cryst.*, **21**, 974–8.
- Semenov, E.I. (1957) Oxides and hydroxides of titanium and niobium in the Lovozero alkaline massif. *Trudy IMGRE*, **1**, (in Russian), 41–59. Abstracted in *Amer. Mineral.* (1958), **43**, 1220–1.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751–67.
- Shilin, L.L., Burova, T.A. and Dmitrieva, M.T. (1966) Accessory pyrochlore in pegmatites of the Khibiny Tundra. In: *Alkaline Rocks of the Kola Peninsula*, Kola Sci. Centre Press, Apatity, (in Russian), 93–8.
- Smirnova, N.L. and Belov, N.V. (1969) Isomorphism and related concepts in the light of crystal chemistry. *Geokhim.*, **1969**, (in Russian), 1291–301.
- Smith, A.J. and Welch, A.J.E. (1960) Some mixed metal oxides of perovskite structure. *Acta Cryst.*, **13**, 653–6.
- Sniatkova, O.L., Proniagin, N.I., Markitakhina, T.M. and Efstaf'ev, A.S. (1986) New data on the structural position of urtite-ijolite-melteigites in nepheline syenites of the Khibina massif. In: *Deposits of Non-metallic Mineral Resources in the Kola Peninsula*, Kola Sci. Centre Press, Apatity, (in Russian), 11–17.
- Sych, A.M., Belokon', A.T., Dem'yanenko, V.P. and Eremenko, L.A. (1973) Vibration spectra of perovskite-structure rare-earth niobates. *Ukrain. Phys. Zh. (Ukrain. J. Phys.)*, **18**, (in Russian), 787–92.
- Tikhononkova, R.P., Kazakova, M.E. and Kataeva Z.T. (1982) Chemistry of accessory loparite from alkaline rocks and its genetic significance. In: *Accessory Minerals of Magmatic and Metamorphic Rocks*, Nauka Press, Moscow, (in Russian), 150–61.
- Trunov, V.K. and Kovba L.M. (1963) X-ray analysis of thorium tungstate and molybdenate. *Vest. Mosk. Univ., Ser. II Khim.*, **18**, (in Russian), 60–3.
- Vidiasagar, K. and Gopalakrishnan, J. (1982) New vanadium oxides with perovskite type structure:  $\text{AThV}_2\text{O}_6$  (A = Ca, Sr). *Indian J. Chem.*, **21A**, 716–7.
- Vlasov, K.A., Kuz'menko, M.Z. and Es'kova, E.M. (1966) *The Lovozero Alkaline Massif*. Oliver & Boyd Ltd., Edinburgh, U.K., 627 pp.
- Voloshin, A.V., Pakhomovskii, Ya.A., Pushcharovskii, D.Yu., Nadezhina, T.N., Bakhchisaraitsev, A.Yu. and Kobiashev, Yu.S. (1989) Strontian pyrochlore: Composition and structure. *New data on minerals (Trudy Mineral. Muz. AN SSSR)*, **36**, (in Russian), 12–24.
- Zak, S.I., Kamenev, E.A., Minakov, F.V., Armand, A.L., Mikheichev, A.S. and Petersil'e, I.A. (1972) *The Khibina Alkaline Massif*. Nedra Press, Leningrad, (in Russian), 175 pp.
- Zhu, W.J. and Hor, H.P. (1995) A new titanium perovskite oxide,  $\text{Na}_{2/3}\text{Th}_{1/3}\text{TiO}_3$ . *J. Solid State Chem.*, **120**, 208–9.

[Manuscript received 6 May 1997;  
revised 9 September 1997]