Lueshite, pyrochlore and monazite-(Ce) from apatite-dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula, Russia

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ABSTRACT

Apatite-dolomite carbonatite at Lesnaya Varaka, Kola Peninsula, Russia, hosts intricate mineral intergrowths composed of lueshite in the core and pyrochlore-group minerals in the rim. Lueshite is a primary Nb-bearing phase in the carbonatite and ranges in composition from cerian lueshite to almost pure $NaNbO_3$. For comparison, the compositional variation of lueshite from the Kovdor and Sallanlatvi carbonatites is described. At Lesnaya Varaka, lueshite is replaced by nearly stoichiometric Na-Ca pyrochlore due to late-stage re-equilibration in the carbonatite system. X-ray powder diffraction data for both minerals are presented. Barian strontiopyrochlore, occurring as replacement mantles on Na-Ca pyrochlore, contains up to 43% Sr and 8–18% Ba at the A-site, and shows a high degree of hydration and strong ionic deficiency at the A- and Y-sites. This mineral is metamict and, upon heating, recrystallises to an aeschynite-type structure. Monazite-(Ce) found as minute crystals in fractures, represents the solid solution between monazite-(Ce) $CePO_4$, brabantite $CaTh(PO_4)_2$ and $SrTh(PO_4)_2$. Our data indicate the high capacity of the monazite structure for Th and accompanying divalent cations at low temperatures and pressures that has a direct relevance to solving the problem of long-term conservation of radioactive wastes. Monazite-(Ce) and barian strontiopyrochlore are products of low-temperature hydrothermal or secondary (hypergene) alteration of the primary mineral assemblage of the carbonatite.

KEYWORDS: lueshite, pyrochlore, strontiopyrochlore, monazite-(Ce), apatite-dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula.

Introduction

APATITE-dolomite carbonatite at Lesnaya Varaka hosts a number of niobium minerals, including natroniobite, for which it is a type locality (Bulakh *et al.*, 1960; Kukharenko *et al.*, 1965). The present work was undertaken to re-examine relationships between niobium-bearing accessory phases in apatite-dolomite carbonatite, and determine the compositional variation of most of these minerals for the first time. Given that there is some confusion regarding the definition of natroniobite in the literature, we also wished to re-investigate this mineral. Unfortunately, we were unable to locate the holotype specimen of natroniobite discovered by A.A. Kukharenko (Bulakh *et al.*, 1960). Hence we investigated

material from the Mineralogical Museum of St. Petersburg State University, Russia, labelled as 'natroniobite' in the Museum archives.

In addition to Lesnaya Varaka, natroniobite has also been described from the Sallanlatvi carbonatite, Kola Peninsula (Kukharenko *et al.*, 1965), the Elet'ozero alkaline intrusion, Karelia (Kukharenko *et al.*, 1969), and a vermiculite rock at the Gem Park Complex, Colorado (Parker and Sharp, 1970). In all these occurrences, natroniobite is an alteration product of primary Nb-rich minerals, mainly lueshite or pyrochlore. In most non-Russian mineralogical glossaries and reference-books, natroniobite is considered as a monoclinic polymorph of $NaNbO_3$, dimorphous with orthorhombic lueshite (Safiannikoff, 1959) and cubic isolueshite (Chakhmouradian *et al.*,

1997); both of which belong to the perovskite mineral group. However, the original structural formula of natroniobite, given as $NaNb_2O_5(OH)$ (Kukharenko *et al.*, 1965), rules out any links to the perovskite group, and suggests a relationship to AB_2O_6-type oxides. XRD studies of natroniobite suggest that this mineral represents a Na-analogue of either fersmite (Kukharenko *et al.*, 1965) or aeschynite (Gorzhevskaya *et al.*, 1974).

Lueshite is a common accessory phase in the carbonatite occurrences at the Kola Peninsula, including Lesnaya Varaka (Kirillov and Burova, 1967; Orlova *et al.*, 1963; Rimskaya-Korsakova *et al.*, 1963), and elsewhere (Bagdasarov *et al.*, 1962; Parker and Sharp, 1970; Safiannikoff, 1959). However, only a few microprobe analyses are available for lueshite from the Sebljavr complex, Kola Peninsula (Subbotin and Men'shikov, 1987) and Lueshe, Zaire (Mitchell, 1996). Most other descriptions either lack compositional data or include bulk, mostly wet-chemical, analyses. This is reflected in the poor recalculation of the analyses into structural formulae and unrealistically high contents of such components as Al_2O_3, SiO_2 and MgO. During this study, lueshite was identified as one of the major Nb-bearing accessories in the Lesnaya Varaka carbonatite. Accordingly, we have concentrated on the compositional variation of this mineral and also examined samples of lueshite from other carbonatite occurrences, including the Kovdor and Sallanlatvi complexes, Kola Peninsula.

Occurrence and phase relationships

The Lesnaya Varaka complex was intensively studied in the 1950s and 1960s by a group of scientists, headed by A.A. Kukharenko, from the Russian Geological Institute (St. Petersburg) and St. Petersburg State University. The geology, petrology and mineralogy of this, and other Middle-Palaeozoic carbonatite complexes of the Kola Peninsula, were described by Kukharenko *et al.* (1965). During the following three decades, olivinites from the Lesnaya Varaka pluton were investigated as a possible source of refractory raw material and platinum-group metals. The mineralogy of carbonatites and other minor lithologies exposed at Lesnaya Varaka has, as yet, not been examined in detail.

The complex is situated in the western part of Kola Peninsula, Russia (67°23′ N, 33°04′ E), in the vicinity of Khabozero village. The complex is expressed topographically as a ridge surrounded by lowlands, and from the east and north-east, by the Segozero Lake. The ridge is forested and exposures are typically lacking, except for a few prospecting trenches and pits in the central and eastern parts of the pluton. The geological description given below is according to Kukharenko *et al.* (1965).

The intrusion covers an area of about 9 sq. km, and is composed predominantly of olivinites, including varieties enriched in titaniferrous magnetite and perovskite. At the southern contact, the olivinites grade into clinopyroxenite through a modally transitional olivine-clino-pyroxene rock. In the central part of the complex, the olivinites are cut by dikes of alkaline rocks (foidolites and phonolites) and dolomite carbonatites, including 'pure' dolomite and apatite-dolomite varieties. Nb-*REE* mineralization is confined to the latter. The apatite-dolomite carbonatite occurs as veins rimmed at their selvages by tremolite-dolomite aggregate. The rock commonly shows flow texture due to the alignment of apatite prisms along contacts.

Apatite-dolomite carbonatite examined in this study is fresh, yellowish-white in colour, fine-grained and composed mainly of dolomite (80−85 vol.%) and fluorapatite (less than 20 vol.%). Dolomite is close to its ideal composition and contains 4−8 mol.% ankerite. Fluorapatite is enriched in SrO and $LREE_2O_3$ (up to 12.8 and 1.8 wt.%, respectively). Accessory phases include biotite, strontianite and complex intergrowths of minerals. The latter are referred to as natroniobite in the Museum archives, and are composed of a black core and a thick (1−2.5 mm) honey-yellow replacement rim. In thin sections, the core is pinkish-brown, birefrigent and shows polysynthetic twinning typical of low-symmetry members of the perovskite group. The replacement rim is pale yellow, optically isotropic or turbid, and shows no pleochroism. Back-scattered electron (BSE) imagery, compositional data and X-ray powder diffractometry (see below), show that the intergrowths are composed of lueshite in the core and pyrochlore-group minerals in the rim (Fig. 1). Lueshite commonly encloses irregular dolomite inclusions containing minute crystals of fluorapatite, anatase and ilmenite. The latter two minerals were not observed in the dolomite matrix outside of the lueshite crystals. Late fractures in both core and rim of the intergrowths host irregular grains of monazite-(Ce) up to 20 μm in size.
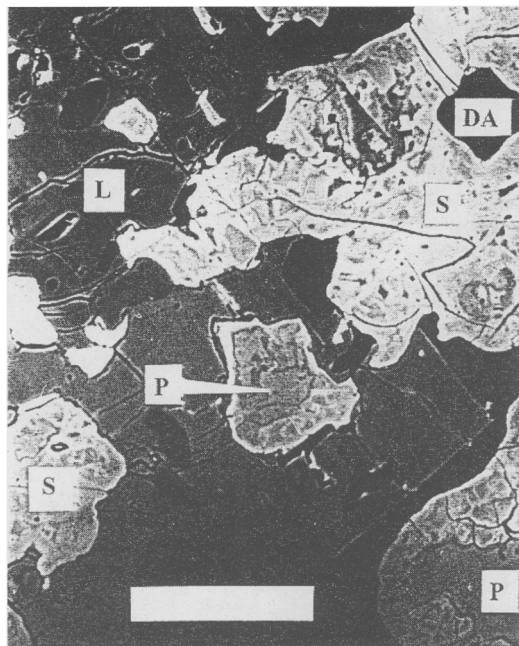
FIG. 1. BSE image of the lueshite-pyrochlore aggregate from apatite-dolomite carbonatite of the Lesnaya Varaka complex. L - lueshite, P - Na-Ca pyrochlore, S - barian strontiopyrochlore, DA - dolomite + fluorapatite. Scale bar is 50 μm.

Mineral chemistry

Compositions of the minerals described in the present work were determined by X-ray energy-dispersive spectrometry (EDS) using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector, located at Lakehead University, Ontario. EDS spectra were acquired at 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 (*LREE*), Lueshe lueshite (Na, Nb), Magnet Cove perovskite (Ca, Ti, Fe), apatite (P), jeppeite (Ba), synthetic $SrTiO_3$ (Sr), metallic Ta and Th. The accuracy of the method was cross-checked by wave-length-dispersive electron microprobe analysis using an automated CAMECA SX-50 microprobe located at the University of Manitoba, following techniques described by Mitchell and Vladykin (1993).

Lueshite

BSE imagery reveals complex zonation of the lueshite crystals. The crystals typically exhibit irregular *LREE*-enriched cores and Ca- and Ti-enriched rims (Fig. 1). A series of thin irregular zones between the core and rim, which cover the core-to-rim compositional range, are collectively described here as an intermediate zone. The irregular outline of separate zones, presumably indicates repeated dissolution and growth of the crystals. Crystals of lueshite from Kovdor (dolomite carbonatite) and Sallanlatvi (calcite carbonatite) also show irregular zonation reflecting a very complex crystallization history of the mineral. Representative compositions of lueshite from Lesnaya Varaka and these other localities are given in Table 1. Data were re-calculated into perovskite-type end-members following the methods described by Mitchell (1996). Most of the compositions can be adequately characterized using only three end-member components: lueshite $NaNbO_3$, loparite-(Ce) $NaCeTi_2O_6$ and perovskite $CaTiO_3$ (Fig. 2). The contents of $SrTiO_3$, $CaThO_3$ and other end-members are negligible (Table 1). As demonstrated in Fig. 2, lueshite from Lesnaya Varaka compositionally evolves from cerian lueshite to lueshite *sensu stricto*. Samples of lueshite from the Kovdor and Sallanlatvi carbonatites differ significantly from Lesnaya Varaka lueshite in their compositional ranges and evolutionary trends. Our data (Table 1) and those available from the literature (Bagdasarov *et al.*, 1962; Subbotin and Men'shikov, 1987) demonstrate that lueshite from dolomite carbonatites is generally richer in $LREE_2O_3$, compared with that from calcite carbonatites. Among the latter, the highest $LREE_2O_3$ content was reported in lueshite from Sebljavr (2.6 wt.%: Subbotin and Men'shikov, 1987).

Pyrochlore

Pyrochlore developed on lueshite shows a wide compositional range from 'normal' almost stoichiometric Na-Ca pyrochlore to Na-poor Sr- and Ba-rich pyrochlore. Using the pyrochlore-group nomenclature suggested by Hogarth (1989), the latter should be classified as barian strontiopyrochlore (Sr > 20% Σ A-cations; Ba > 8% Σ A-cations).

Representative compositions of Na-Ca pyrochlore are given in Table 2. Structural formulae of this mineral, recalculated on the basis of two B-cations (Nb + Ti + Fe^{3+}), are close to the ideal

TABLE 1. Representative compositions of lueshite

Wt.%	1	2	3	4	5	6	7	8	9	10	11
Na_2O	15.27	16.42	16.53	16.27	15.62	15.78	15.49	15.49	15.69	14.91	15.63
CaO	1.19	1.42	2.04	2.04	2.93	0.86	2.63	2.27	1.80	3.07	1.79
SrO	0.47	0.35	0.52	0.23	0.24	0.45	0.46	0.44	0.25	n.d	n.d
La_2O_3	1.05	0.80	n.d	0.04	0.24	1.15	0.42	0.97	0.33	0.06	n.d
Ce_2O_3	2.70	1.99	1.20	1.53	1.34	2.48	0.96	2.76	0.63	0.43	0.33
Pr_2O_3	n.d	n.d	n.d	0.14	n.d	n.d	n.d	n.d	0.31	n.d	n.d
Nd_2O_3	0.65	0.36	0.19	0.27	0.08	0.10	0.27	0.35	n.d	n.d	0.29
ThO_2	0.71	2.28	1.30	1.71	0.31	0.15	0.24	n.d	n.d	0.13	n.d
TiO_2	3.41	5.18	3.78	5.61	5.39	2.98	5.97	5.36	3.61	4.24	3.16
Fe_2O_3	0.34	0.22	0.30	0.10	n.d	0.10	n.d	0.09	0.08	0.45	0.63
Nb_2O_5	73.96	71.24	74.33	72.20	72.41	76.00	71.82	70.95	78.07	74.68	76.52
Ta_2O_5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2.15	n.d
Total	99.75	100.26	100.19	100.14	98.56	100.05	98.26	98.68	100.77	100.12	98.35
Structural formulae (O = 3)											
Na	0.821	0.877	0.876	0.860	0.830	0.841	0.824	0.832	0.817	0.783	0.831
Ca	0.035	0.042	0.060	0.060	0.086	0.025	0.077	0.067	0.052	0.089	0.053
Sr	0.007	0.006	0.008	0.004	0.004	0.007	0.007	0.007	0.004	0.000	0.000
La	0.011	0.008	0.000	0.000	0.002	0.012	0.004	0.010	0.003	0.001	0.000
Ce	0.027	0.020	0.012	0.015	0.013	0.025	0.010	0.028	0.006	0.004	0.003
Pr	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.003	0.000	0.000
Nd	0.006	0.004	0.002	0.003	0.001	0.001	0.003	0.004	0.000	0.000	0.003
Th	0.004	0.014	0.008	0.011	0.002	0.001	0.002	0.000	0.000	0.001	0.000
Ti	0.071	0.107	0.078	0.115	0.111	0.062	0.077	0.067	0.073	0.086	0.065
Fe	0.007	0.004	0.006	0.002	0.000	0.002	0.000	0.002	0.002	0.009	0.013
Nb	0.927	0.887	0.918	0.890	0.898	0.945	0.891	0.889	0.948	0.914	0.949
Ta	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.000
Mol.% end-members											
$NaNbO_3$	85.46	88.39	90.01	89.12	86.85	88.18	87.28	83.42	90.89	88.73	92.71
$CaTiO_3$	3.40	2.89	5.39	5.19	8.98	2.68	8.19	7.11	5.85	10.07	5.91
$NaCeTi_2O_6$	9.82	6.64	2.90	4.18	3.56	8.25	3.58	8.73	2.82	1.11	1.38
$SrTiO_3$	0.83	0.58	0.86	0.39	0.41	0.79	0.79	0.75	0.44	0.00	0.00
$CaThO_3$	0.49	1.50	0.84	1.12	0.21	0.10	0.16	0.00	0.00	0.09	0.00

Compositions: 1 core, 2–3 intermediate zone and 4 rim of a zoned lueshite crystal, Lesnaya Varaka; 5 core, 6–7 intermediate zone and 8 rim of a zoned lueshite crystal, Kovdor; 9–11 core, intermediate zone and rim of a zoned lueshite crystal, Sallanlatvi. Total Fe expressed as Fe_2O_3; n.d = not detected.

formula $NaCaNb_2O_6(F, OH)$. This pyrochlore contains moderate $LREE_2O_3$, SrO and TiO_2 and shows a low cation deficiency at the A-site (0.05–0.39 apfu). In places, Na-Ca pyrochlore is enriched in ThO_2 (up to 5.7–5.8 wt.%). The ThO_2 content correlates negatively with CaO (Fig. 3) and shows no correlation with other major and minor components. This suggests that Th is accommodated in this mineral according to the following isomorphic scheme:

$$2Ca^{2+} \leftarrow Th^{4+} + \square.$$

Barian strontiopyrochlore (Ba-strontiopyrochlore hereafter) is developed in peripheral zones and along fractures within the primary 'normal' pyrochlore. This mineral exhibits strong compositional variation with respect to CaO, SrO, BaO and Nb_2O_5 (Table 3). Ba-strontiopyrochlore compositionally evolves by becoming depleted in Ca and enriched in Sr plus Ba at essentially constant $LREE$ and Th (Fig. 4A,C,D). The depletion in Na and Ca is accompanied by increasing cation deficiency at the A-site (Fig. 4B). Recalculation of the analyses of this mineral gives approximately 6 atoms of
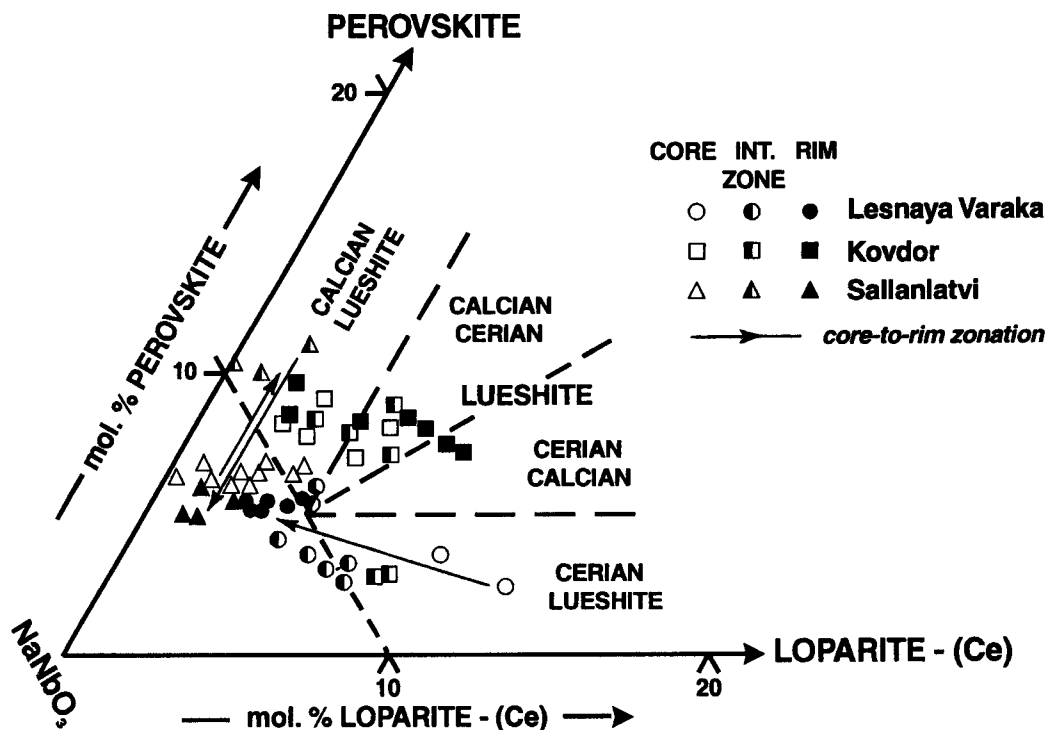
FIG. 2. Compositions (mol.%) of lueshite from the Lesnaya Varaka, Kovdor and Sallanlatvi carbonatites in the ternary system lueshite $NaNbO_3$–perovskite $CaTiO_3$–loparite-(Ce) $NaCeTi_2O_6$.

TABLE 2. Representative compositions of Na-Ca pyrochlore

	1	2	3	4	5		1	2	3	4	5
Wt.%						Structural formulae (ΣB-cations = 2)					
Na_2O	7.24	7.27	6.87	4.91	6.06	Na	0.864	0.877	0.844	0.590	0.735
CaO	13.68	12.77	12.57	12.16	11.27	Ca	0.902	0.851	0.853	0.808	0.756
SrO	1.15	1.14	1.07	1.06	0.81	Sr	0.041	0.041	0.039	0.038	0.029
La_2O_3	0.11	0.42	n.d.	1.20	1.01	La	0.002	0.010	0.000	0.027	0.023
Ce_2O_3	1.85	2.07	1.94	3.12	2.55	Ce	0.042	0.047	0.045	0.071	0.058
Nd_2O_3	0.40	1.03	0.94	0.16	0.37	Nd	0.009	0.023	0.021	0.004	0.008
ThO_2	2.43	3.42	3.88	4.86	5.69	Th	0.034	0.048	0.056	0.069	0.081
						ΣA	1.894	1.897	1.858	1.607	1.690
TiO_2	2.62	3.00	2.72	3.31	3.01	Ti	0.121	0.140	0.130	0.154	0.142
Fe_2O_3	0.11	0.11	0.21	0.15	0.10	Fe	0.005	0.005	0.010	0.007	0.005
Nb_2O_5	67.35	65.93	64.97	65.58	65.52	Nb	1.874	1.854	1.860	1.839	1.854
Total	96.94	97.16	95.17	96.51	96.39						

Total Fe expressed as Fe_2O_3;
F was detected on EDS spectra, but not analysed.
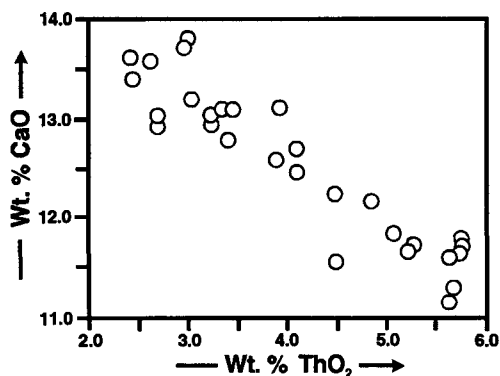n.d = not detected.

FIG. 3. Correlation between CaO and ThO_2 contents in Na-Ca pyrochlore, Lesnaya Varaka.

oxygen per 2 *B*-cations, indicating strong anion deficiency at the *Y*-site. Most compositions approach the generalized formula $(Ca,Sr,Ba)Nb_2O_6 \cdot nH_2O$ or $(Ca,Sr,Ba)_{2-x}Nb_2O_6(OH)_{1-y} \cdot nH_2O$ ($x \sim 1$, $y \sim 1$, n ~ 1.5). The maximum amount of H_2O which can be accommodated in the structure of pyrochlore, is given as $1 + 3/8x$ where *x* is cation deficiency at the *A*-site (Ercit *et al.*, 1994). For Ba-strontiopyrochlore, this value (~ 1.4) is in a good agreement with the amount of H_2O estimated by difference of analysis totals to 100% (~ 1.5). This implies that cation deficiency at the *A*-site and

anion deficiency at the *Y*-site are compensated by molecular H_2O entering the structure.

At present, evolutionary trends of pyrochlore compositions in the carbonatite rock series are not completely understood. Pyrochlore close to the ideal composition $NaCaNb_2O_6(F, OH)$ with low-to-moderate *LREE*, Sr, Ti and Th occurs in a broad variety of carbonatites and related metaso-matic rocks ('second' and 'third' pyrochlore generations: Kapustin, 1980; 'ideal' pyrochlore: Mariano *et al.*, 1997; pyrochlore C: Petruk and Owens, 1975; Wall *et al.*, 1996). Th-rich ($ThO_2 > 4$ wt.%) pyrochlore is not characteristic of carbonatites and has been encountered only in a few localities (Vuorijarvi, Kola: Epshtein *et al.*, 1991; Guli, Siberia: Williams and Kogarko, 1996). Data available from the literature (Kapustin, 1980; Williams, 1996; Williams and Kogarko, 1996) suggest that pyrochlore ('hatch-ettolite') from early calcite carbonatites and phoscorites is enriched in Ta_2O_5 (up to 25.6 wt.%), TiO_2 (up to 11.4 wt.%) and UO_2 (up to 20.4 wt.%) relative to pyrochlore from late-stage carbonatites. This is in a good agreement with relatively low TiO_2 and not detectable Ta_2O_5 and UO_2 contents in pyrochlore from apatite-dolomite carbonatite of the Lesnaya Varaka complex.

Pyrochlores enriched in Sr, Ba, *LREE* and, less commonly, K are typical for weathered carbona-tites and related rocks and, in most cases, form

TABLE 3. Representative compositions of barian strontiopyrochlore

	1	2	3	4		1	2	3	4
Wt.%					Structural formulae (ΣB-cations = 2)				
Na_2O	0.91	0.66	0.45	0.31	Na	0.117	0.084	0.061	0.043
CaO	6.27	5.54	4.50	3.89	Ca	0.445	0.392	0.336	0.297
SrO	6.28	7.90	8.24	8.91	Sr	0.241	0.303	0.333	0.369
BaO	3.38	3.18	5.16	6.28	Ba	0.088	0.082	0.141	0.176
La_2O_3	n.d	0.69	0.33	0.97	La	0.000	0.017	0.008	0.026
Ce_2O_3	1.35	2.47	1.86	2.08	Ce	0.033	0.060	0.047	0.054
Nd_2O_3	0.25	0.23	n.d	0.10	Nd	0.006	0.005	0.000	0.002
ThO_2	3.80	4.32	3.48	3.35	Th	0.057	0.065	0.056	0.054
					ΣA	0.987	1.008	0.982	0.971
TiO_2	4.40	4.60	3.41	4.08	Ti	0.219	0.228	0.178	0.219
Fe_2O_3	1.30	1.28	1.75	1.56	Fe	0.065	0.064	0.092	0.084
Nb_2O_5	57.26	57.17	54.91	52.60	Nb	1.716	1.708	1.730	1.697
Total	85.20	88.04	84.09	84.13					

Total Fe expressed as Fe_2O_3;
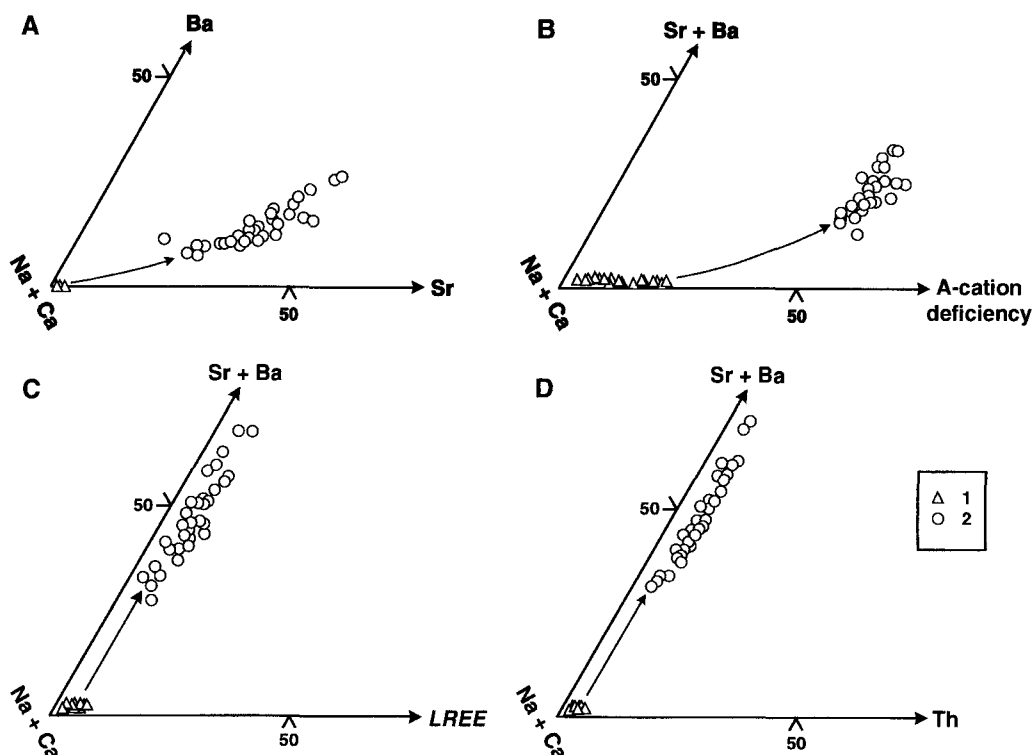F was not detected on EDS spectra.
n.d. = not detected.

FIG. 4. Compositional variation of pyrochlore-group minerals from the Lesnaya Varaka carbonatite. 1 Na-Ca pyrochlore, 2 barian strontiopyrochlore. For discussion see text.

due to secondary alteration of primary Na-Ca pyrochlore (Lapin and Kulikova, 1989; Lottermoser and England, 1988; Lumpkin and Ewing, 1995; Mariano *et al.*, 1997; Van Wambeke, 1978; Wall *et al.*, 1996). The secondary alteration involves cation and anion leaching, cation exchange and hydration of primary pyrochlore, but does not affect the actinide elements (Lumpkin and Ewing, 1995). Primary alteration of carbonatitic pyrochlore by late-stage hydrothermal fluids also involves loss of cations at the *A*-site and anions at the *Y*-site, as well as an increase in Sr content, but proceeds to a lesser extent in terms of anion and cation deficiency (Lumpkin and Ewing, 1995). Secondary strontiopyrochlore compositionally similar to that described in this study, has been previously observed in a number of carbonatite localities including the Lueshe complex, Zaire (Wall *et al.*, 1996), Mt. Weld, Australia (Lottermoser and England, 1988) and some Siberian complexes (Lapin *et al.*, 1988; Lapin
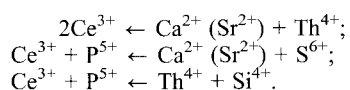
and Kulikova, 1989). The only known occurence of primary strontiopyrochlore is Mt. Vavnbed, Lovozero complex, Kola Peninsula. At this locality, strontiopyrochlore (up to 84 % A-site occupied by Sr) occurs as inclusions in a hydrothermal albite-aegirine paragenesis (Voloshin *et al.*, 1989). This mineral differs from the secondary strontiopyrochlore in showing regular zonation patterns with outer zones commonly enriched in Na and Ca, and depleted in Ba (Voloshin *et al.*, 1989).

Monazite-(Ce).

This mineral shows significant intergranular variation in composition. Individual grains may or may not exhibit irregular, 'patchy' zonation. Apart from the *LREE*, dominated by Ce, this mineral contains significant Ca, Sr and Th (Table 4). Previous studies (Bowie and Horne, 1953; Kukharenko *et al.*, 1965) demonstrate that these cations may be accommodated in monazite according to the following substitution schemes:

TABLE 4. Representative compositions of monazite-(Ce)

	1	2	3	4		1	2	3	4
Wt.%					Structural formulae ($\Sigma O = 4$)				
CaO	0.92	1.55	4.00	2.81	Ca	0.039	0.067	0.171	0.122
SrO	5.17	6.03	7.54	8.33	Sr	0.119	0.141	0.174	0.197
La_2O_3	15.14	10.80	0.46	0.62	La	0.221	0.161	0.007	0.009
Ce_2O_3	29.18	25.08	22.33	14.78	Ce	0.423	0.370	0.326	0.220
Pr_2O_3	3.85	4.64	3.29	2.96	Pr	0.056	0.068	0.048	0.044
Nd_2O_3	8.77	9.02	5.16	5.50	Nd	0.124	0.130	0.073	0.080
ThO_2	9.74	14.96	26.53	34.94	Th	0.088	0.137	0.240	0.324
P_2O_5	29.00	28.38	29.58	29.06	P	0.972	0.969	0.998	1.001
Total	101.77	100.46	98.89	99.00					

$$2Ce^{3+} \leftarrow Ca^{2+} (Sr^{2+}) + Th^{4+};$$
$$Ce^{3+} + P^{5+} \leftarrow Ca^{2+} (Sr^{2+}) + S^{6+};$$
$$Ce^{3+} + P^{5+} \leftarrow Th^{4+} + Si^{4+}.$$

All compositions obtained in this study are pure phosphates and, therefore, the latter two schemes have to be ruled out. The first substitution scheme represents a solid solution series between monazite-(Ce) $CePO_4$, brabantite $CaTh(PO_4)_2$ and $SrTh(PO_4)_2$. Brabantite is a rare mineral, previously encountered only in granite pegmatites at Brabant, Namibia (Rose, 1980) and two localities in Travancore, India (Bowie and Horne, 1953). The samples from Travancore have significant monazite and huttonite ($ThSiO_4$) contents and have been classified by Bowie and Horne (1953) as 'cheralite', a mineral inter-mediate between $CePO_4$ and $CaTh(PO_4)_2$. Although the name 'cheralite' used by Bowie and Horne (1953) to describe this mineral has chronological priority, we favour the term 'brabantite' as most closely corresponding to the end-member composition $CaTh(PO_4)_2$ (Rose, 1980). Experimental studies by Podor and Cuney (1997) prove complete solubility between $CePO_4$ and $CaTh(PO_4)_2$ at geological conditions. $SrTh(PO_4)_2$ is not known as a distinct mineral species, but has been synthesized by solid-state reaction and shown to be monoclinic and isostructural with monazite (Rose, 1980).

The compositions of LREE-phosphate from Lesnaya Varaka plot mostly into the monazite-(Ce) part of the ternary system $CePO_4$–$CaTh(PO_4)_2$–$SrTh(PO_4)_2$, but show strong enrich-ment in $SrTh(PO_4)_2$ (Fig. 5). Only a few compositions represent a distinct mineral species with the general formula $SrTh(PO_4)_2$. The variational trend demonstrates that the enrichment in $SrTh(PO_4)_2$ is combined with an increase in the brabantite component (Fig. 5). It is noteworthy that the most Th-enriched monazite compositions are systematically depleted in La (Table 4, anals. 3 and 4). This feature cannot be explained unequivocally due to the lack of structural data. We suggest that incorporation of Th results in the contraction of the monazite lattice, and makes the cation site unsuitable for the relatively large La^{3+}.

Although monazite is an ubiquitous accessory phase in carbonatites and sometimes form commercially viable deposits (Mariano, 1989), there is no modern systematic study of its composition. Scarce data available from the literature show that monazite from carbonatites is compositionally close to that of its ideal formula (Kapustin, 1980). At different carbonatite localities, the abundance of different LREE varies, but Ce is always dominant. The only other known occurrence of Ca-Th-rich (4.6 wt.% CaO and 5.8 wt.% ThO_2) monazite-(Ce) in carbonatite is the Vuorijarvi complex, Kola Peninsula (Kukharenko et al., 1965). However, this mineral initially described as sulphate-monazite, differs from the Lesnaya Varaka samples in containing significant $CaSO_4$ and $ThSiO_4$ and being depleted in Sr (Kukharenko et al., 1965).

Compositional data on secondary monazite found in the laterite crusts covering carbonatite deposits, are limited to a few microprobe analyses (Lottermoser, 1990). This mineral is poor in SrO and ThO_2 and sporadically-enriched in CaO (up to 4.7 wt.%; Lottermoser, 1990). However, the presence of hexagonal brockite $CaTh(PO_4)_2 \cdot nH_2O$ in some carbonatite laterites
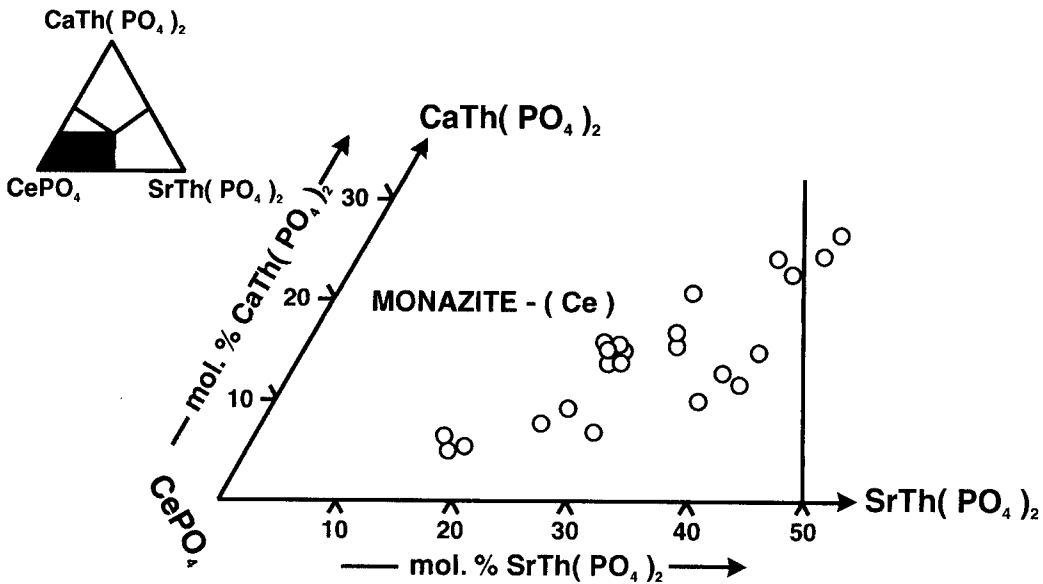
FIG. 5. Compositions (mol.%) of phosphates from the Lesnaya Varaka carbonatite in the ternary system monazite-(Ce) $CePO_4$–brabantite $CaTh(PO_4)_2$–$SrTh(PO_4)_2$.

(Mariano, 1989), suggests that Ca- and Th-enriched monazite-(Ce) or brabantite may also be found in this type of *LREE* deposits.

X-ray powder diffractometry

X-ray diffraction (XRD) powder patterns were obtained with a Philips 3710 diffractometer (Cu radiation) at Lakehead University, Ontario, using a Philips Debye-Scherer type camera with a diameter of 114.6 mm. The diffractometer was operated at 40 kV and 20 mA. Relative intensities of the diffraction lines were estimated visually from the films.

The mineral developed as black cores of the intergrowths, gives an XRD pattern typical of perovskite-type compounds (Table 5). Splitting of the most intense diffraction line, the presence of several 'extra' lines on the pattern and optical properties of the mineral (see above), suggest that it is lueshite, the orthorhombic $NaNbO_3$ polymorph from the perovskite group (Safiannikoff, 1959), rather than cubic isolueshite (Chakhmouradian *et al.*, 1997).

The pyrochlore-group minerals which form the honey-yellow rim are metamict, but may be restored to crystallinity after heating to 800°C for 1 hour. Upon heating, Na-Ca pyrochlore restores a pyrochlore-type structure (Table 5), while Ba-strontiopyrochlore gives an XRD pattern similar

to that of aeschynite-group minerals (Table 6, vigezzite is given as an example). The XRD pattern of Ba-strontiopyrochlore also includes a few faint diffraction lines corresponding to the strongest peaks of pyrochlore (d = 5.95, 1.84, 1.56). The aeshynite group includes a series of complex oxides with the general formula AB_2X_6 (A = *REE*, Ca, Th, Na; B = Nb, Ta, Ti, Fe; X = O, OH). As noted above, Ba-strontiopyrochlore from Lesnaya Varaka approaches the formula (Ca, Sr, Ba)Nb_2O_6·nH_2O. Compositionally similar niobate hydrates ANb_2O6·nH_2O (A = Ca, Sr, Ba) were synthesized from aqueous solutions by Krylov and Alekseev (1954; 1955). Upon heating, these polyhydrates first transform to monohydrates at 110–300°C, and then to anhydrous salts at 250–480°C (Krylov and Alekseev, 1954; 1955). It is important to note that the niobate hydrates of alkali-earth elements have a structure similar to that of CaF_2 (or pyrochlore) and accommodate the water molecules in the large 'cages' within the lattice (Krylov and Alekseev, 1955). Therefore, we may propose that upon heating, metamict Ba-strontiopyrochlore became dehydrated and recrystallised to an aeschynite-type structure. Apparently, the latter is the most stable structural state of anhydrous Sr-rich $CaNb_2O_6$. The commonest naturally-occurring form of pure Ca niobate ($CaNb_2O_6$) is fersmite; its structure is orthorhombic (Table 6) and similar to that of columbite

TABLE 5. X-ray diffraction patterns of lueshite and Na-Ca pyrochlore

| | 1 | | | 2 | |
hkl	d	I/I_o	hkl	d	I/I_o
101	3.91	80	111	5.95	30
200	2.88	20	311	3.13	20
141, 002	2.76	100	222	2.98	100
161	2.18	<10	400	2.59	20
202	1.947	50	333, 511	1.99	10
023, 162	1.795	10	440	1.835	70
371, 282	1.382	40	622	1.564	50
381	1.303	30	444	1.502	10
343, 412	1.236	40	553, 731	1.353	10
442, 244	1.180	10	800	1.301	10
			662	1.196	20
			840	1.166	10
			844	1.062	10
			10.22, 666	1.001	10
a, Å	5.76(2)			10.396(5)	
b, Å	15.62(8)				
c, Å	5.30(2)				

1 lueshite, Lesnaya Varaka;
2 Na-Ca pyrochlore heated to 800°C for 1 h, Lesnaya Varaka.

(Aleksandrov, 1960; Cummings and Simonsen, 1970; Shabalin, 1981). The other mineral with the general formula $CaNb_2O_6$ is vigezzite. It is isostructural with aeschynite, occurs only at a few localities (Graeser et al., 1979; Subbotin and Men'shikov, 1987), and is not known to exist in a synthetic form. As suggested by Graeser et al. (1979) the aeschynite structure of vigezzite may be stabilized by REE and Ti cations. The $(LREE)_2O_3$ content in Ba-strontiopyrochlore examined in this study is low, but SrO is very high, suggesting that Sr may play a stabilizing role in the aeschynite-type lattice. Indeed, one of the $SrNb_2O_6$ polymorphs is isostructural with aeschynite and has either orthorhombic (Whiston and Smith, 1967) or monoclinic (Brusset et al., 1971) symmetry (Table 6). Further discussion on structural relationships between pyrochlore and related Ca-Sr niobates is beyond the scope of this work.

Discussion

The genesis of carbonate-bearing rocks associated with the alkaline ultramafic complexes, is a subject of extensive petrological discussion. Recent studies demonstrate that the formation of carbonatites (sensu lato) at Kola Peninsula was a multi-stage process involving magmatic as well as late-stage re-equilibration and metasomatic phenomena (Bulakh and Ivanikov, 1996; Subbotin and Mikhaelis, 1986; Zaitsev and Bell, 1995; Zaitsev and Polezhaeva, 1994). In the Kola intrusions, dolomite carbonatites are relatively rare, compared with the calcite-dominated varieties. Textural features suggest that some dolomite in the Kola carbonatites is exsolved from early magnesian calcite or is a product of late-stage dolomitization by Mg-rich fluids (Kapustin, 1984; Zaitsev and Polezhaeva, 1994). Kukharenko et al. (1965, pp. 733–4) note that, although some dolomite carbonatites occur in the form of intrusive bodies, the evidence for their magmatic origin is inadequate. These authors interpret the geological setting of Lesnaya Varaka carbonatite and its textural features (see above) to be a result of metasomatic replacement of the wall-rock ultramafites in a tectonically active environment. Kapustin (1984) also suggests a metasomatic origin for the Lesnaya Varaka carbonatite. However, as demonstrated by Harmer and Gittins (1997), intrusive dolomite carbonatites are fairly common in a number of alkaline provinces and primary magnesian carbonatite melts may be a source of calciocarbonatites, but not vice versa. Further isotopic and experimental studies are required to reveal the nature of

TABLE 6. X-ray diffraction patterns of heated barian strontiopyrochlore, vigezzite, $SrNb_2O_6$ and fersmite

	1		2			3			4	
hkl	d	I/I_o	d	I/I_o	hkl	d	I/I_o	hkl	d	I/I_o
011			4.821	90	101	4.99	8	020	7.47	40
021	3.86	10	3.854	10	201	3.93	6	110	5.34	20
200			3.784	80	020	3.86	20	130, 111	3.75	60
121	3.43	10						121	3.428	20
220	3.13	20	3.117	10	220	3.158	16	131	3.049	100
031	3.04	60	3.036	100	301	3.065	100	200	2.863	30
211	2.98	100	2.974	100				141, 220	2.681	10
131			2.802	20	311	2.852	5	002	2.606	20
040	2.76	10	2.763	30	002	2.803	20	012	2.564	10
002			2.684	40	221	2.752	6	201	2.510	30
231			2.367	40	031	2.336	6	060	2.489	30
240			2.229	30	420	2.239	6	151	2.368	5
202			2.187	5	122	2.223	5	032	2.306	10
212			2.145	20	222	2.095	12	231	2.242	20
042	1.925	10	1.9226	20	511	1.980	5	132, 042	2.139	10
400	1.876	10	1.8885	30	402	1.964	8	161, 241	2.090	20
341	1.755	20			322	1.928	18	142, 170	2.004	10
242			1.7128	60	103	1.840	6	052	1.962	20
431	1.595	10	1.6018	70	600	1.833	7	202, 251	1.927	30
261	1.590	10			422	1.749	12	212	1.916	5
252			1.5512	40	601	1.742	14	260	1.879	40
071	1.518	10	1.5112	30	123	1.661	16	062, 232	1.799	50
271			1.4028	40	341	1.633	6	330, 311	1.784	30
					313	1.627	11	261	1.768	50
					223	1.607	8	331, 181	1.688	20
					621	1.588	8	113, 072	1.653	10
					700	1.572	5	252, 123	1.622	30
					323	1.528	6	133	1.576	20
					242	1.526	8	351, 312	1.537	70
					033	1.511	12			
System	orthorhombic				orthorhombic (? monoclinic)			orthorhombic		
Sp. gr.	Pmnb				n/a			Pcan		
a, Å	7.53(2)		7.56(1)		11.003			5.73		
b, Å	11.16(3)		11.03(1)		7.714			14.94		
c, Å	5.20(4)		5.360(4)		5.603			5.22		

1 Ba-strontiopyrochlore heated to 800°C for 1 h, Lesnaya Varaka (this work);
2 vigezzite, Valle Vigezzo, Italy (Graeser et al., 1979);
3 $SrNb_2O_6$ (ASTM 28-1243, diffraction lines with $I/I_o < 5$ are omitted);
4 fersmite (ASTM 18-302).
n/a = not available.

apatite-dolomite carbonatite at the Lesnaya Varaka pluton.

In this rock, lueshite is the earliest Nb mineral to crystallize after anatase, ilmenite and the majority of dolomite and fluorapatite. The latter four minerals are commonly found as inclusions in the crystals of lueshite. At late stages of carbonatite evolution, lueshite was partly replaced and overgrown by Na-Ca pyrochlore. Experimental data (Jago and Gittins, 1993) indicate that, compared to pyrochlore, crystallization of lueshite is promoted by a lower F content and higher alkalinity of the carbonatite system. Therefore, the appearance of lueshite at the early stage of carbonatite evolution reflects a relatively high Na/Ca ratio in the residual melt/

fluid after the crystallization of dolomite and fluorapatite, and a depletion of the system in F due to precipitation of fluorapatite. Crystallization of lueshite and loss of Na during metasomatic alteration of the wall rocks brought about gradual decrease in the Na/Ca ratio of the system. This is documented by core-to-rim zonation pattern of lueshite crystals (see above) and appearance of richterite in the tremolite contact zones rimming the carbonatite dikes at Lesnaya Varaka (Kukharenko et al., 1965).

The replacement of Na-Ca pyrochlore by Ba-strontiopyrochlore involved hydration, cation exchange at the A-site and loss of ions at the A- and Y-sites. A general pattern and extent of alteration in terms of ionic deficiency and hydration, suggest that this was a low-temperature hydrothermal or perhaps, secondary process (Lumpkin and Ewing, 1995). In this process, fluorapatite and strontianite were a major source of Sr, while a primary Ba host is unknown. Compositionally similar strontiopyrochlore occurs in a number of weathered carbonatites including the Lueshe complex, Zaire (Lumpkin and Ewing, 1995; Wall et al., 1996), Mt. Weld, Australia (Lottermoser and England, 1988), Enisei Ridge and other occurrences in Siberia (Lapin et al., 1986; Lapin and Kulikova, 1989). Interestingly, secondary pyrochlore from Lesnaya Varaka does not exhibit enrichment in LREE, which suggests that most of LREE leached from fluorapatite and early Nb minerals was precipitated in the form of phosphates. These show an extensive compositional variation, and represent the ternary system monazite-(Ce) $CePO_4$-brabantite $CaTh(PO_4)_2$-$SrTh(PO_4)_2$. This demonstrates a high capacity of secondary monazite-(Ce) toward the actinide elements and accompanying divalent cations, that has a direct implication to the problem of conservation of radioactive wastes. In combination with the experimental data of Podor and Cuney (1997), those obtained in this study show that Th-doped monazite is stable in a broad range of geological conditions.

XRD study showed that, upon heating, Ba-strontiopyrochlore from the Lesnaya Varaka carbonatite produces the aeschynite-type structure. Based on these results, this mineral could be classified as strontian vigezzite, but this name would refer to the heated material rather than to the original phase containing significant molecular H_2O. The latter compositionally approaches synthetic compounds known to crystallize with the pyrochlore structure (Krylov and Alekseev,

1954; 1955). The majority of secondary Sr-, Ba-, LREE- and K-rich pyrochlores described in the literature, are strongly hydrated and exhibit high ionic deficiency. For example, kalipyrochlore from the Lueshe carbonatite (Zaire) has 92–98% cation deficiency at the A-site and contains more than 16 wt.% H_2O, thus compositionally approaching $Nb_2(O,OH)_6 \cdot 1.75H_2O$ (Ercit et al., 1994; Wall et al., 1996). However, even such defect phases as kalipyrochlore retain the pyrochlore structure which is stabilized by H_2O molecules entering partially or completely vacant A- and Y-sites (Ercit et al., 1994). It is obvious that the secondary ion-deficient pyrochlores containing significant Sr, Ba or LREE, may undergo phase transitions during heating and loss of water.

Conclusions

The sample registered as 'natroniobite' in the archives of the Mineralogical Museum of St. Petersburg State University, Russia, is a complex aggregate of lueshite and its replacement products set in a matrix of dolomite and fluorapatite. The occurrence of lueshite, not pyrochlore, as a primary Nb mineral in this apatite-dolomite carbonatite suggests that a parental melt/fluid was enriched in Na and depleted in Ca and F after the crystallization of dolomite plus fluorapatite. The replacement of lueshite by Na-Ca pyrochlore documents evolution of the carbonatite system through the loss of Na. Barian strontiopyrochlore and monazite-(Ce), both showing extensive compositional ranges, are believed to form due to low-temperature hydrothermal or secondary (hypergene) alteration of the early mineral paragenesis including strontianite, fluorapatite, lueshite and Na-Ca pyrochlore.

Finally, we would like to point out that the object of the present paper is not to discredit natroniobite as we have not yet studied the holotype material. Further attempts will be made to obtain samples of this mineral from the type locality, as well as from the other occurrences (Sallanlatvi, Elet'ozero in Russia and Gem Park Complex in Colorado).

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