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COMPOSITIONAL VARIATION OF PEROVSKITE-GROUP MINERALS FROM THE CARBONATITE COMPLEXES OF THE KOLA ALKALINE PROVINCE, RUSSIA

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ABSTRACT

Perovskite-group minerals from the carbonatite complexes of the Kola Alkaline Province, Russia, are in most instances members of the perovskite – lueshite – loparite-(Ce) – latrappite solid-solution series. From early ultramafic rocks to late calcite carbonatite, the composition of primary perovskite evolves by enrichment in Na, Nb and Fe, and represents a combination of evolutionary trends toward lueshite and latrappite. These trends culminate with the appearance of lueshite and cerian lueshite in late-stage dolomite carbonatite, and Nb–Fe-rich perovskite in some examples of calcite carbonatite. The enrichment of perovskite in the lueshite and latrappite components results in an increase in the unit-cell parameter and tilt angle of the $(Ti,Fe,Nb)O_6$ octahedra. Secondary perovskite and loparite occur as a replacement and overgrowth mantle on primary perovskite in ultramafic rocks, foidolite and carbonatite. These compositions define a loparite evolutionary trend, represented by increases in Na and *LREE*, that is commonly accompanied by an increase in Nb and Th contents. The crystallization of secondary cerian perovskite and loparite results from either deuteric or metasomatic processes, and involves the interaction of primary perovskite with fluids derived from a cognate alkaline or carbonatitic source.

Keywords: perovskite, lueshite, loparite, latrappite, carbonatite complexes, Kola Peninsula, Russia.

SOMMAIRE

Les minéraux du groupe de la pérovskite des complexes à dominance carbonatitique de la province alcaline de Kola, en Russie, sont dans la plupart des cas membres de la solution solide pérovskite – lueshite – loparite-(Ce) – latrappite. Des membres ultramafiques précoces aux venues carbonatitiques à calcite tardives, la composition de la pérovskite primaire montre un enrichissement en Na, Nb et Fe, et représente une combinaison de lignées évolutives vers les pôles lueshite et latrappite. Ces vecteurs d'enrichissement mènent à la formation de lueshite et de lueshite cérique dans les venues de carbonatite à dolomite tardives, et de pérovskite riche en Nb–Fe dans certains exemples de carbonatite à calcite. L'augmentation de la teneur en lueshite et latrappite de la pérovskite mène à un agrandissement de la maille élémentaire et de l'angle d'inclinaison des octaèdres $(Ti,Fe,Nb)O_6$. La pérovskite secondaire et la loparite se présentent comme surcroissance ou remplacement de la pérovskite primaire dans les roches ultramafiques, les foïdolites et les carbonatites. Ces compositions définissent une lignée évolutive vers la loparite, que représente des augmentations dans le niveau des terres rares et du sodium, et dans plusieurs cas aussi en Nb et en Th. La cristallisation de pérovskite cérique et de loparite secondaires résulterait soit de processus deutériques et métasomatiques, et impliquerait l'interaction de pérovskite primaire avec une phase fluide issue d'un assemblage alcalin ou bien carbonatitique.

(Traduit par la Rédaction)

Mots-clés: pérovskite, lueshite, loparite, latrappite, complexes carbonatitiques, péninsule de Kola, Russie.

INTRODUCTION

The carbonatite complexes of the Kola Alkaline Province, Russia, are of tremendous scientific importance, as they represent the products of crystallization of highly differentiated alkaline ultramafic magmas. The complexes comprise an extended series of rocks, ranging from early alkaline ultramafic members to late carbonatites and phonolites (Kukharenko *et al.* 1965, 1971, Kogarko *et al.* 1995). The composition of the parental alkaline ultramafic magmas approached that of olivine melanephelinite, and was enriched in Ca, Ti,

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and Fe, and depleted in SiO_2 (Kukharenko *et al.* 1965, Bulakh & Ivanikov 1996). Hence, perovskite and titaniferous magnetite are among the most common accessory minerals in the major rock-series throughout the complexes.

Owing to the tolerance of the perovskite structure to cation substitutions, perovskite-group minerals from alkaline complexes exhibit a wide range of composition, and thus may serve as sensitive indicators of evolutionary trends (Mitchell 1996). An initial detailed study of perovskite compositions from rocks of the Kola carbonatite complexes was undertaken by Kukharenko & Bagdasarov (1961). Subsequently, Frank-Kamenetskiy & Vesel'skiy (1961a, b) utilized the compositional data of Kukharenko & Bagdasarov (1961), in conjunction with measurement of unit-cell parameters, to create a modified scheme of isomorphic substitutions in perovskite. However, the compositional data used in these initial studies were determined by bulk wet-chemical methods, and may be in error owing to the presence of mineral inclusions in many samples. Recent studies of perovskite from the Kola Peninsula that are based on electron-microprobe data are limited to a study of the distribution of rare-earth elements (*REE*) in perovskite from the Afrikanda complex (Bagdasarov 1980) and a short review of Nb-bearing phases in metasomatic rocks of the Vuorijarvi complex (Subbotina *et al.* 1991).

The current study was undertaken to establish evolutionary trends in the composition of perovskite in the carbonatite complexes of the Kola Alkaline Province, and to determine the relationship between isomorphic substitution and crystal chemistry in perovskite. A third objective was to compare our data with those for perovskite-group minerals from other carbonatite complexes. Some of the samples of perovskite-bearing rocks examined in this study were collected by the authors. Others were supplied by our colleagues from St. Petersburg State University, Moscow State University and the Kola Scientific Center at Apatity, Russia.

GEOLOGICAL SETTING

The Kola Alkaline Province includes 14 carbonatite complexes which, with the exception of the Early Proterozoic Tiksheozero pluton, were emplaced during the middle to late Devonian re-activation of ancient deep-seated faults (rift systems) developed within the Baltic (Fennoscandinavian) Shield (Kogarko *et al.* 1995, Kramm *et al.* 1993, Orlova 1993). The Paleozoic carbonatite plutons are concentric, differentiated bodies ranging in area from 1 to 55 km² at the current level of erosion. The concentric structure of the plutons is a result of successive emplacement of separate magma-batches. These may correspond to distinct stages in the evolution of a parental alkaline ultramafic melt (Kukharenko *et al.* 1965, Bulakh & Ivanikov 1984) or to intrusion of different parental magmas (Zaitsev & Bell 1995).

The earliest intrusive series consists of ultramafic rocks that usually occupy the central parts of the complexes or occur as xenoliths in the later-emplaced rock-types. This series includes olivinite, clinopyroxenite and modally transitional olivine–clinopyroxene rock (wehrlite). Melilite olivinite has been found only in the Afrikanda complex (Kukharenko *et al.* 1965, 1971). We use the term "olivinite", not dunite, to emphasize the presence of titaniferous magnetite plus perovskite, not chromite, as the major opaque phases in this rock. At the contact with alkaline rocks and carbonatites, the ultramafic rocks are commonly transformed into a variety of mica-, apatite- and amphibole-bearing rocks, *e.g.*, phlogopite-bearing pyroxenite or amphibole-bearing olivinite. Modally diverse melilitic plutonic rocks (uncompahgrite, melilitolite, turjaite, okaite) and foidolite (melteigite–urtite) normally form the peripheral parts of the complexes. In this paper, melilitolite is used to refer to a plutonic rock with more than 9ù0 modal % melilite (or products of its alteration) rather than as a general descriptive term (Le Maitre 1989). The old names (*e.g.*, turjaite) are applied to other melilitic plutonic rocks, as these cannot be precisely defined using the existing classification based on modal abundances of melilite, olivine and clinopyroxene (Le Maitre 1989). Age relationships between the melilitic rocks and foidolites are not always unequivocal. Kukharenko *et al.* (1965, 1971) interpreted the former as a product of the interaction between the early ultramafic rocks and an alkaline melt. Egorov (1984) suggested that the melilitic rocks were formed prior to the foidolites. On the example of the Turiy Mys complex, Bulakh & Ivanikov (1984, 1996) proposed that foidolite was emplaced in two stages, separated by the crystallization of melilitic rocks. Such contradictory observations may indicate that melilitic rocks in the carbonatite intrusions at Kola originated by more than one mechanism. These may include the metasomatic scheme proposed by Le Bas (1977) for the Kisingiri melilitolites, the one-lineage evolutionary scheme (Onuma & Yagi 1967), or the two-lineage scheme suggested by Nielsen (1994) for the Gardiner complex. Further discussion of this problem is beyond the scope of this work.

Carbonatites are developed as plugs, pipes, dikes and stockworks within the complexes or in the fenitized country-rocks. In the most evolved complexes, there were several cycles of carbonatite magmatic activity, each starting with the formation of silicate-rich rocks (phoscorite or camaforite), then carbonatite, and culminating with explosive events producing carbonatite breccia (Balaganskaya 1994). The earliest and most abundant rock-types are calcite carbonatites and their precursor phoscorites. Calcite–dolomite, dolomite and ankerite carbonatites are less common. As shown by field observations, petrological, mineralogical and isotopic data, the formation of carbonatites in the Kola Alkaline Province involved both primary magmatic and late-stage hydrothermal metasomatic phenomena (Bulakh & Ivanikov 1996, Kapustin 1984, Zaitsev & Bell 1995). In particular, the metasomatic interaction of intrusive carbonatites with previously emplaced alkaline rocks produced modally diverse rocks composed of calcite, hastingsite, vesuvianite, monticellite and calcic garnet (Kukharenko *et al.* 1965, Bulakh & Ivanikov 1996). In Russian geological literature, these assemblages are referred to as "autoskarns". The calcite – amphibole – diopside rocks developed as veins in clinopyroxenite of the Afrikanda complex are enigmatic in origin. Kukharenko *et al.* (1965) have proposed that these rocks were formed by deuteric ("autometasomatic") alteration of the host ultramafic rocks by CO_2-rich residual fluids prior to the formation of the foidolite series. However, the modal composition of these rocks and the occurrence in them of such minerals as pyrochlore, zirconolite, calzirtite and baddeleyite indicate their close affinity with carbonatites. The youngest intrusive rocks encountered in the carbonatite complexes of the Kola Alkaline Province are nepheline and cancrinite syenites; these are found mostly as thin dikes intruding the alkaline ultramafic series and carbonatites (Kukharenko *et al.* 1965).

Experimental studies (Kjarsgaard & Hamilton 1988, Platt & Edgar 1972, Onuma & Yagi 1967, Wilkinson & Stolz 1983) and petrological modeling (Bulakh & Ivanikov 1996, Le Bas 1977, Nielsen 1994) suggest that all rock types found in carbonatite complexes, including the carbonatites and small volumes of feldspathoid syenites, were derived from the same parental magma by a combination of crystal fractionation and liquid immiscibility. Depending on the composition and depth of formation of the parental melt, the carbonatite plutons may include some or all members of the differentiation path. Missing members (*e.g.*, melilitic rocks, carbonatites or feldspathoid syenites) may not have been produced in sufficient quantities or may have been removed by erosion (Kukharenko *et al.* 1965, 1971). Isotopic studies (Zaitsev & Bell 1995) demonstrate that at least in some complexes, the formation of carbonatites cannot be explained by closed-system differentiation of a single parental magma.

DISTRIBUTION OF PEROVSKITE

In the carbonatite complexes of the Kola Alkaline Province, perovskite occurs in most intrusive and metasomatic mineral assemblages. The highest concentrations of the mineral are found in ultramafic rocks, where it may comprise up to 30 vol.% of the rock (Kukharenko *et al.* 1965). In olivinite, melilite olivinite and clinopyroxenite, perovskite and titaniferous magnetite are the latest phases to form, and they fill the interstices between euhedral crystals of the silicate minerals. The perovskite grains range in size from 0.05–0.2 mm in fine-grained ultramafic rocks to >5 mm in the coarse-grained (pegmatitic) clinopyroxenite. In some ultramafic rocks, a second generation of perovskite forms a thin rim (less than 100 μm) enveloping titaniferous magnetite. Perovskite and titaniferous magnetite are two major minerals in so-called ore schlieren developed within the ultramafic rocks. Here, the ore minerals occur as a fine-grained aggregate, here called a granulopolyhedral texture. This texture morphologically resembles that exhibited by styrofoam and results from the face-sharing of subhedral or euhedral crystals of perovskite and titaniferous magnetite. The schlieren are believed to have crystallized from an extremely Ca–Ti–Fe-enriched liquid fractionated from the ultramafic magma and squeezed into fractures (Kukharenko *et al.* 1965). Perovskite from the olivinite and melilite olivinite of the Afrikanda complex encloses ovoid melt inclusions of silicate and silico-carbonate composition. Inclusions of similar morphology have been found in perovskite from olivinite from the Mata da Corda Formation, Brazil (F.E. Lloyd, pers. commun.), and jacupirangite from Iron Hill, Colorado (this work). Textural features involving perovskite and rock-forming silicates, and the intimate association of these minerals with titaniferous magnetite and melt inclusions, indicate that most of the primary perovskite in the ultramafic rocks crystallized after olivine and clinopyroxene from a residual melt enriched in Ca, Ti and Fe.

Back-scattered electron imagery reveals late-stage corrosion and overgrowths on primary perovskite from some ultramafic rocks. These overgrowths are developed mostly on margins of crystals and along fractures, and range from 10 to 60 μm in thickness. The composition of the overgrowths ranges from perovskite (hereafter termed secondary perovskite) to loparite (see below). Both minerals occur with titanite and diverse Ca–*REE* silicates. In typical carbonatite complexes, loparite was first found by Subbotina *et al.* (1991) at Vuorijarvi, Kola Peninsula. Platt (1994) described loparite from melnoite [ultramafic lamprophyre: Mitchell (1994)] of the Schryburt Lake carbonatite complex, Ontario. In these occurrences, loparite forms an overgrowth, possibly a corrosion-related mantle, on primary perovskite. These authors attributed the loparite to the interaction between the primary perovskite and a *REE*-enriched fluid that probably fractionated from a carbonatitic source (Platt 1994, Subbotina *et al.* 1991). In the current study, we characterize the loparite in the ore schlieren of the Afrikanda and Sebljavr complexes, and present the data in conjunction with data on secondary perovskite and loparite from melilite olivinite of the Afrikanda complex obtained by Mitchell (1996).

Among the foidolites, perovskite is found principally in ijolite pegmatite in "comb"-structured veins of variable thickness emplaced in the ultramafic suite. In these rocks, perovskite forms pseudo-octahedral to pseudocubic crystals located primarily at the selvages of the veins. Associated minerals are diopside, altered nepheline, magnetite, schorlomite, titanite and calcite. At Afrikanda, perovskite also occurs in so-called "hybrid" alkaline pegmatites, which may result from small-volume injections of alkaline melt into the ultramafic rocks (Bagdasarov 1959). In these rocks, perovskite may be a relict phase assimilated from the wall-rock ultramafic rocks.

Secondary perovskite and loparite morphologically analogous to those described above in the ultramafic rocks were found in ijolite pegmatite and "hybrid" pegmatite from the Afrikanda complex. In both occurences, these minerals are associated with calcite, thomsonite and other late-stage products of nepheline alteration.

In the melilitic rocks, perovskite commonly occurs as euhedral or anhedral crystals ranging in size from 100–200 μm to 2–3 cm (in pegmatitic varieties). In some instances of melilitolite and melilite – pyroxene – nepheline rocks, termed pyroxene turjaite, early perovskite is accompanied by a second generation of the mineral, forming a thin (<100 μm) rim on magnetite. Similarly, two generations of perovskite have been recognized in melilitolite of the Gardiner complex, Greenland (Nielsen 1980) and in uncompahgrite of the Rangwa complex, East Africa (Le Bas 1977). In melilitic rocks, perovskite is commonly rimmed, or partly replaced, by titanian andradite or titanite (or both). It is characteristic that a rim of perovskite on magnetite is never found in association with a rim of titanite (or garnet) on perovskite. This observation indicates that the melilitic plutonic rocks show a Ca-enrichment trend and depletion in SiO_2 and, perhaps, FeO_T (perovskite rim on magnetite) or a trend toward SiO_2-saturated compositions (replacement of perovskite by silicates).

The occurrence of perovskite in the carbonatites and allied rocks of the Kola complexes seems to be restricted to early members, where calcite is the only carbonate phase. Here, perovskite invariably forms euhedral crystals of pseudocubic, pseudocubo-octahedral or, less commonly, pseudo-octahedral habit. The crystals range in size from 0.3–0.5 mm in phoscorite to 5–6 mm in carbonatite. In phoscorite, perovskite is accompanied by calcite, apatite, magnetite, forsterite, pyrochlore, baddeleyite and titanite. Perovskite crystals in the carbonatites commonly decorate the margins of calcite grains; the associated minerals are apatite, phlogopite, magnetite, pyrrhotite, chalcopyrite and less abundant ilmenite, zirconolite, titanian andradite and titanite. In the calcite – amphibole – diopside rock of the Afrikanda complex, perovskite occurs as exceptionally large (up to 4 cm) crystals of diverse morphology. Both elongate pseudocubic and pseudocubo-octahedral crystals are commonly found in the same hand-specimen and in the same paragenesis. Thus, their age relationships are not clear.

Secondary perovskite and loparite mantles on primary perovskite are common in calcite – amphibole – diopside rock of the Afrikanda complex and in calcite carbonatite of the Vuorijarvi complex. In both occurrences, the mantles are morphologically similar to those described above for perovskite from the ultramafic rocks and foidolites.

Late dolomite–calcite, dolomite and ankerite carbonatites have not been reported to contain perovskite. Instead, lueshite ($NaNbO_3$) is a common accessory constituent of these rocks (Rimskaya-Korsakova *et al.* 1963, Orlova *et al.* 1963, Kirillov & Burova 1967). In some complexes (Sebljavr and Sallanlatvi), lueshite also occurs in calcite carbonatites (Subbotin & Men'shikov 1987, Subbotina & Subbotin 1990). In this study, we examined samples of lueshite from dolomite carbonatite of the Kovdor and Lesnaya Varaka complexes. An X-ray-diffraction study showed that in both cases, the mineral is orthorhombic, and thus is lueshite *sensu stricto.*

Perovskite is a very rare phase in the country-rock fenites because the association of perovskite with feldspar is thermodynamically unstable (Ghiorso & Carmichael 1987). Perovskite has been encountered only in the late-stage nepheline-bearing fenites of the Turiy complex (M.D. Evdokimov, pers. comm.).

ANALYTICAL METHODS

All mineral compositions were determined by X-ray energy-dispersion spectrometry (EDS) using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn*K*) at Lakehead University. EDS spectra of perovskite and lueshite were acquired for 120 seconds, those of loparite for 300 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86 nA. X-ray spectra were collected and processed with the LINK ISIS–SEMQUANT software package. Full ZAF corrections were applied to the raw X-ray data. The following standards were employed for the determination of mineral compositions: Khibina loparite (Na, La, Ce, Pr, Nd, Nb), Magnet Cove perovskite (Ca, Fe, Ti), synthetic $SrTiO_3$ (Sr), metallic Th and Ta. A multi-element standard for the *REE* was used, as experience has shown that this gives more accurate data than single-*REE* standards when using EDS spectrum-stripping techniques. However, peak profiles used for the analytical X-ray lines were obtained using single-*REE* fluoride standards. The accuracy of the method was cross-checked by wavelength-dispersion electron-microprobe analysis of some samples using an automated CAMECA SX–50 microprobe located at the University of Manitoba, using methods described by Mitchell & Vladykin (1993).

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

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12
CaO	39.94	39.69	38.85	38.92	26.15	5.55	38.52	38.92	35.21	36.98	38.17	40.04
SrO	n.d	0.31	0.35	0.29	0.15	0.09	0.42	0.44	0.38	0.33	0.55	0.30
Na_2O	0.18	0.11	n.d	0.05	2.94	7.76	0.31	0.39	0.60	0.65	0.65	0.26
La_2O_3	n.d	0.08	2.37	1.62	2.35	8.04	0.51	n.d	1.32	1.25	0.57	n.d
Ce_2O_3	1.29	1.34	1.96	1.52	8.71	21.38	1.55	0.96	2.40	2.57	2.85	0.87
Pr_2O_3	n.d	n.d	n.d	n.d	0.87	1.73	n.d	n.d	1.09	n.d	0.21	n.d
Nd_2O_3	n.d	0.50	0.35	0.54	2.85	4.67	0.25	0.18	0.68	0.66	0.25	0.26
ThO_2	n.d	0.16	0.06	0.02	2.07	2.12	n.d	n.d	0.27	0.27	0.21	0.26
TiO_2	56.55	55.88	54.28	54.78	50.17	41.65	55.32	55.89	54.72	53.31	53.20	55.50
Fe_2O_3	1.12	1.91	1.10	1.19	0.88	0.26	1.10	1.21	1.31	1.78	1.54	1.12
Nb_2O_5	n.d	0.45	0.72	0.32	2.41	7.55	1.09	1.07	1.40	1.67	2.01	0.39
Ta_2O_5	n.d	0.05	0.13	0.06	n.d	0.33	0.37	0.33	0.22	0.27	0.03	0.05
Total	99.08	100.48	100.17	99.31	99.55	101.13	99.44	99.39	99.60	99.74	100.24	99.05
Structural formulae calculated on the basis of 3 atoms of oxygen												
Ca	0.99	0.98	0.97	0.98	0.71	0.17	0.96	0.96	0.89	0.93	0.96	1.00
Sr	-	-	-	-	-	-	0.01	0.01	-	-	0.01	-
Na	0.01	-	-	-	0.14	0.43	0.01	0.02	0.03	0.03	0.03	0.01
La	-	-	0.02	0.01	0.02	0.08	-	-	0.01	0.01	-	-
Ce	0.01	0.01	0.02	0.01	0.08	0.22	0.01	0.01	0.02	0.02	0.02	0.01
Pr	-	-	-	-	0.01	0.02	-	-	0.01	-	-	-
Nd	-	-	-	-	0.03	0.05	-	-	0.01	0.01	-	-
Th	-	-	-	-	0.01	0.01	-	-	-	-	-	-
Ti	0.98	0.96	0.96	0.96	0.95	0.89	0.97	0.97	0.97	0.94	0.94	0.97
Fe	0.02	0.03	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.03	0.03	0.02
Nb	-	-	0.01	-	0.03	0.10	0.01	0.01	0.01	0.02	0.02	-
Ta	-	-	-	-	-	-	-	-	-	-	-	-
Mol.% end-members												
$CaTiO_3$	98.39	98.51	99.48	99.13	70.27	20.77	96.59	96.69	93.52	93.32	92.99	97.31
$SrTiO_3$	-	0.42	0.49	0.40	0.22	0.20	0.57	0.59	0.55	0.46	0.77	0.41
$CaThO_3$	-	0.08	0.03	0.01	1.20	1.83	-	-	0.15	0.15	0.12	0.14
Loparite	1.61	0.99	-	0.46	27.52	65.81	2.83	1.93	5.78	6.08	6.12	1.92
$NaNbO_3$	-	-	-	-	0.79	6.66	-	0.79	-	-	-	0.22
$Ce_2Ti_2O_7$	-	-	-	-	-	4.73	-	-	-	-	-	-

Compositions: 1 olivinite, Lesnaya Varaka, 2 olivinite, Afrikanda, 3 & 4 core and rim of a crystal, melilite olivinite, Afrikanda, 5 & 6 secondary perovskite and loparite, melilite olivinite, Afrikanda, 7 & 8 core and rim of a crystal, clinopyroxenite, Afrikanda, 9 phlogopitized olivinite, Kovdor, 10 phlogopite rock, Kovdor, 11 & 12 core and rim of a zoned crystal, clinopyroxenite, Turiy. n.d = not detected.

Back-scattered electron (BSE) imagery revealed that many samples exhibit complex compositional zonation. Samples were analyzed at several points to determine the compositional range within and between zones. Grains with no obvious BSE zonation also were analyzed at several points to test for possible zoning at constant average atomic number.

Mitchell (1996) demonstrated that the compositions of naturally occurring perovskite-group minerals can be expressed in terms of the following end-member compositions: $CaTiO_3$ (perovskite), $Na\mathit{REE}Ti_2O_6$ (loparite), $NaNbO_3$ (lueshite), $SrTiO_3$ (tausonite), $PbTiO_3$ (macedonite), $Ca_2Fe^{3+}NbO_6$ (latrappite), $Ca_2Nb_2O_7$, $\mathit{REE}_2Ti_2O_7$, $CaThO_3$, $CaZrO_3$, $KNbO_3$ and $BaTiO_3$. Compositional data obtained in this work were recalculated into these end-members using an APL program for PC following methods suggested by Mitchell (1996).

X-ray diffraction (XRD) powder patterns ($CuK\alpha$ radiation) were obtained using a DRON–2.0 diffractometer located at the Department of Crystallography, St. Petersburg University. The diffractometer was operated at 35 kV and 20 mA in the scanning mode at a goniometer rate of 0.5°/min. Metallic germanium was used as an internal standard. Unit-cell parameters were calculated from the diffraction patterns using the least-squares method.

COMPOSITIONAL VARIATION

Ultramafic rocks

Primary perovskite from olivinite contains very low levels of *REE* (0.3–5.2 wt.% REE_2O_3), Fe (0.5–2.3 wt.% Fe_2O_3), Nb (0–0.7 wt.% Nb_2O_5), Na (0–0.4 wt.% Na_2O) and other minor components. In comparison, primary

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM ULTRAMAFIC ROCKS

Wt.%	1	2	3	4	5	6	7	8	9	10	11
CaO	41.62	37.97	35.82	7.41	36.85	35.95	35.74	10.73	36.81	37.61	36.46
SrO	0.13	0.44	0.49	0.71	0.58	0.30	0.39	0.46	0.36	0.36	0.42
Na_2O	n.d	0.29	0.70	8.70	0.58	0.74	0.66	6.65	0.61	0.61	0.90
La_2O_3	n.d	1.11	0.63	7.01	1.20	2.60	2.97	6.36	1.80	1.28	1.56
Ce_2O_3	0.43	1.38	2.67	17.47	2.46	3.65	3.82	17.74	3.07	2.84	2.81
Pr_2O_3	n.d	n.d	0.55	0.17	n.d	0.60	0.54	1.44	0.34	0.11	n.d
Nd_2O_3	n.d	0.24	0.94	3.48	0.70	0.90	1.00	4.13	0.69	0.64	0.79
ThO_2	n.d	0.13	0.05	3.93	0.09	n.d	0.13	2.08	n.d	0.01	0.33
TiO_2	57.44	54.76	53.43	40.11	54.75	53.26	53.63	44.96	54.41	54.11	53.10
Fe_2O_3	0.80	0.90	1.28	0.06	1.23	1.20	1.04	0.51	1.24	1.54	1.08
Nb_2O_5	n.d	0.85	1.60	10.71	1.38	1.51	1.52	3.75	1.27	1.46	1.76
Ta_2O_5	n.d	0.64	0.48	0.22	0.42	n.d	n.d	0.32	n.d	0.22	0.20
Total	100.42	98.71	98.64	99.98	100.24	100.71	101.44	99.13	100.60	100.79	99.41
Structural formulae calculated on the basis of 3 atoms of oxygen											
Ca	1.01	0.96	0.91	0.22	0.92	0.91	0.90	0.32	0.92	0.94	0.93
Sr	-	0.01	0.01	0.01	0.01	-	0.01	0.01	-	-	0.01
Na	-	0.01	0.03	0.47	0.03	0.03	0.03	0.36	0.03	0.03	0.04
La	-	0.01	0.01	0.07	0.01	0.02	0.03	0.07	0.02	0.01	0.01
Ce	-	0.01	0.02	0.18	0.02	0.03	0.03	0.18	0.03	0.02	0.02
Pr	-	-	-	-	-	0.01	-	0.01	-	-	-
Nd	-	-	0.01	0.03	0.01	0.01	0.01	0.04	0.01	0.01	0.01
Th	-	-	-	0.03	-	-	-	0.01	-	-	-
Ti	0.98	0.97	0.96	0.85	0.96	0.95	0.95	0.94	0.96	0.95	0.95
Fe	0.01	0.02	0.02	-	0.02	0.02	0.02	0.01	0.02	0.02	0.02
Nb	-	0.01	0.02	0.14	0.01	0.02	0.02	0.05	0.01	0.02	0.02
Ta	-	-	-	-	-	-	-	-	-	-	-
Mol.% end-members											
$CaTiO_3$	99.37	96.64	92.68	20.83	93.80	92.59	93.15	31.29	93.85	93.84	90.67
$SrTiO_3$	0.63	0.61	0.69	1.22	0.80	0.42	0.55	0.76	0.50	0.50	0.60
$CaThO_3$	-	0.07	0.03	2.64	0.05	-	0.07	1.34	-	0.05	0.18
Loparite	-	2.68	6.60	60.82	5.35	6.99	6.23	61.55	5.65	5.65	8.55
$NaNbO_3$	-	-	-	14.49	-	-	-	5.06	-	-	-

Compositions: 1 perovskite rim on magnetite, clinopyroxenite, Turiy, 2 & 3 core and rim of a zoned perovskite crystal, ore schlieren, Afrikanda, 4 loparite, ore schlieren, Afrikanda, 5 unzoned perovskite crystal, pegmatoid clinopyroxenite, Afrikanda, 6 & 7 core and rim of a zoned perovskite crystal, ore schlieren, Sebljavr, 8 loparite, ore schlieren, Sebljavr, 9 unzoned perovskite crystal, pegmatoid clinopyroxenite, Sebljavr, 10 & 11 core and rim of a zoned perovskite crystal, apatite nest in micaceous clinopyroxenite, Afrikanda. n.d = not detected.

perovskite from clinopyroxenite and ore schlieren is somewhat enriched in *REE* (up to 8.5 wt.% REE_2O_3), Nb (up to 2.4 wt.% Nb_2O_5) and Na (up to 1.0 wt.% Na_2O) (Tables 1–2, Figs. 1a, b). With few exceptions, primary perovskite does not exhibit any intragranular compositional zonation. Where zoned, it may compositionally evolve by enrichment in Na, *REE* and Nb (ore schlieren, Afrikanda and Sebljavr complexes) or by depletion in these elements (clinopyroxenite, Turiy complex) toward the rim. Compositions of primary perovskite from the ultramafic rocks are similar to those of perovskite from olivinite and jacupirangite in other alkaline provinces (Fig. 1d: Chernysheva *et al.* 1991, Dawson *et al.* 1995, Treiman & Essene 1985, this work).

Secondary perovskite and loparite occurring as a mantle on primary perovskite are essentially members of the perovskite–loparite solid-solution series (Fig. 1c). In some instances, loparite mantles are enriched in Nb (up to 10.7 wt.% Nb_2O_5) and Th (up to 3.9 wt.% ThO_2; Tables 1–2).

Foidolites

Compared to primary perovskite from the ultramafic rocks, that from the foidolites is generally richer in *REE* (2.9–9.2 wt.% REE_2O_3) and Na (0.4–1.2 wt.% Na_2O) and contains comparable amounts of Fe, Nb, Th and other minor components (Table 3, Fig. 2). Perovskite of similar composition occurs in rocks of the foidolite series of other carbonatite complexes: Nizhnesayanskiy (Lower Sayan), East Sayan Alkaline Province, Siberia (Chernysheva *et al.* 1991), Magnet Cove, Arkansas (Flohr & Ross 1989), and Oldoinyo Lengai, Tanzania (Dawson *et al.* 1995). Perovskite from ijolite of the Oka complex, Quebec, is considerably enriched in Na, Fe and Nb (Treiman & Essene 1985), *i.e.*, in the lueshite and latrappite components.

Secondary perovskite and loparite found as a mantle on primary perovskite in the ijolite pegmatite vein are essentially members of the perovskite–loparite series, *i.e.*, cerian perovskite and calcian loparite sporadically enriched in Nb (up to 4.7 wt.% Nb_2O_5) and Th (up to 4.6 wt.% ThO_2; Table 3, Fig. 2b). Most of the loparite from the "hybrid" pegmatite is niobian calcian loparite with high Ta contents (up to 1.9 wt.% Ta_2O_5). This difference in composition suggests that there were at least two processes responsible for the formation of loparite in the alkaline pegmatites of the Afrikanda complex.

Melilitic rocks

Perovskite from different melilitic rocks examined in this study (melilitolite, pegmatitic melilitolite, turjaite, melilite – diopside – nepheline rock) is similar in composition to the primary perovskite from the ultramafic rocks and foidolites of the Kola carbonatite complexes (compare Figs. 1, 2 and 3). It has relatively low contents of *REE* (up to 8.1 wt.% REE_2O_3), Na (up to 1.0 wt.% Na_2O), Fe (up to 1.9 wt.% Fe_2O_3) and Nb (up to 2.6 wt.% Nb_2O_5) (Table 4). Large euhedral crystals of perovskite are typically zoned. Relative to the core of the crystals, the rim is depleted in Na, *REE* and Nb. The rim compositions are similar to reaction rims of perovskite on magnetite (Table 4). Na-, *REE*- and Nb-poor perovskite occurs in okaite of the Nizhnesayanskiy carbonatite complex, Siberia (Chernysheva *et al.* 1991) (Fig. 3b). At Oka, perovskite from okaite is enriched in *REE* (8.1–9.6 wt.% REE_2O_3), Fe (5.2–5.7 wt.% Fe_2O_3) and Nb (10.2–11.3 wt.% Nb_2O_5), *i.e.*, in the loparite and latrappite components (this work).

Carbonatites and kindred rocks

Perovskite from phoscorite of the Kovdor complex is unzoned and compositionally corresponds to cerian perovskite with low Na, Fe and Nb contents (Table 5). At Kugda, Siberia (Maimecha-Kotuy alkaline province), and Gardiner, Greenland, phoscorite also contains perovskite or cerian perovskite (or both) with variable Na (0.9–1.4 and 0.2–0.7 wt.% Na_2O), Fe (1.4–2.1 and 1.0–1.5 wt.% Fe_2O_3), and Nb (2.2–4.0 and 0.5–0.9 wt.% Nb_2O_5, respectively (Fig. 4).

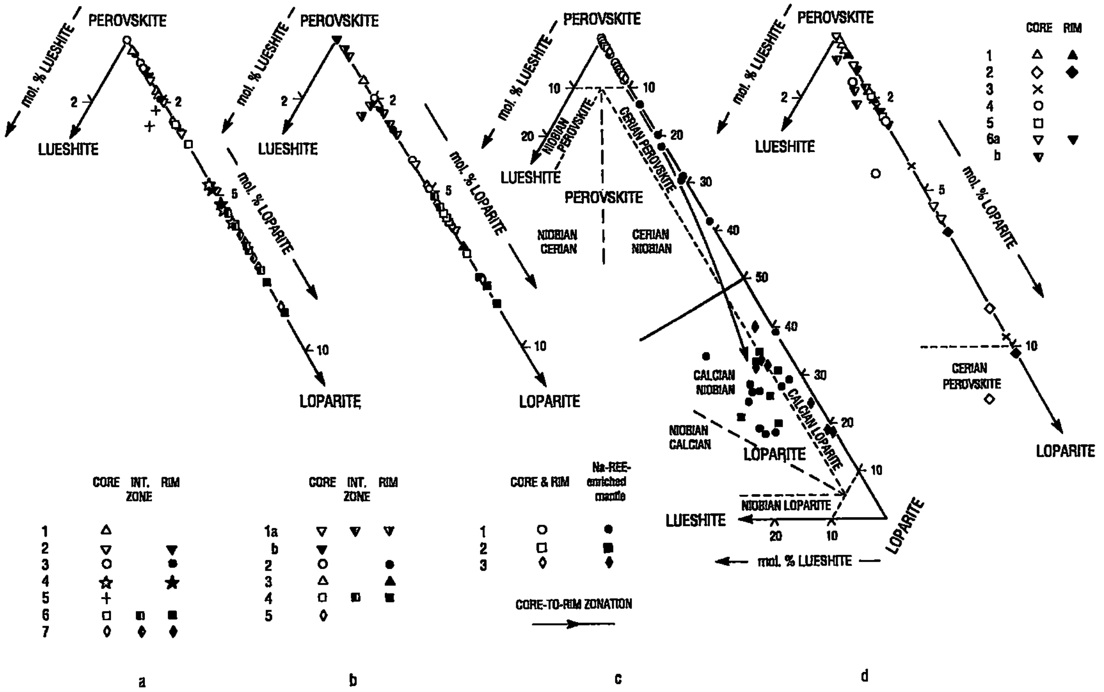

FIG. 1. Composition (mol.%) of perovskite and loparite from ultramafic rocks: (a) 1 olivinite, Lesnaya Varaka, 2 olivinite, Afrikanda, 3 melilite olivinite, Afrikanda, 4 phlogopitized olivinite, Kovdor, 5 clinopyroxenite, Afrikanda, 6 ore schlieren, Afrikanda, 7 ore schlieren, Sebljavr; (b) 1 clinopyroxenite, Turiy (a euhedral crystals, b rims on magnetite), 2 pegmatitic clinopyroxenite, Sebljavr, 3 pegmatitic clinopyroxenite, Afrikanda, 4 apatite nest in micaceous clinopyroxenite, Afrikanda, 5 phlogopite rock, Kovdor; (c) 1 melilite olivinite, Afrikanda, 2 ore schlieren, Afrikanda, 3 ore schlieren, Sebljavr; (d) 1 olivinite, Mata da Korda, Brasil, 2–6 jacupirangite: 2 Jacupiranga, Brazil, 3 Oldoinyo Lengai, Tanzania (Dawson *et al.* 1995), 4 Nizhnesayanskiy, Siberia (Chernysheva *et al.* 1991), 5 Oka, Quebec (Treiman & Essene 1985), 6 Iron Hill, Colorado (a euhedral crystals, b rims on magnetite).

The two morphological varieties of primary perovskite from calcite – amphibole – diopside rock (Afrikanda) differ in composition. Pseudocubo-octahedral crystals are richer in Na (1.3–1.8 wt.% Na_2O) and *REE* (7.6–13.1 wt.% REE_2O_3), compared to those having a hexahedral habit (0.7–1.2 and 5.8–8.0 wt.%, respectively) (Table 5). Both varieties became enriched in loparite. This trend culminates in secondary cerian perovskite and calcian loparite as a narrow mantle on the primary perovskite (Fig. 4).

In most cases, the primary perovskite from calcite carbonatite is enriched in Na (up to 4.3 wt.% Na_2O), Fe (up to 4.3 wt.% Fe_2O_3), Nb (up to 14.2 wt.% Nb_2O_5) and Th (up to 3.0 wt.% ThO_2) (Tables 6–7). With few exceptions, the crystals are complexly zoned. Separate zones may be parallel to each other, reflecting relatively stable growth-conditions (*e.g.*, Sebljavr complex), or be irregularly embayed owing to repeated dissolution and growth (*e.g.*, Kovdor complex). Relative to the core of the crystals, the rim is enriched in Na and Nb, *i.e.*, in the lueshite component (Fig. 5). The compositional evolution occurs at an essentially constant latrappite end-member content, and may be accompanied by changes in *REE* and Th contents. In perovskite from the Kovdor calcite carbonatite, two evolutionary trends were established: toward cerian niobian perovskite (Fig. 5: trend A) and toward niobian cerian perovskite (trend B). The latter reflects core-to-rim zonation in crystals, whereas the former is pronounced only in small "patches" bordering apatite and calcite inclusions. Trend A may be a result of intragranular re-equilibration between perovskite and the inclusions. A trend of strongly increasing Na, Nb and *REE* contents, culminating in the appearance of calcian niobian loparite, is characteristic of perovskite from the Vuorijarvi carbonatite (Fig. 4).

Perovskite of similar composition occurs in calcite carbonatites of the Magnet Cove (Arkansas),

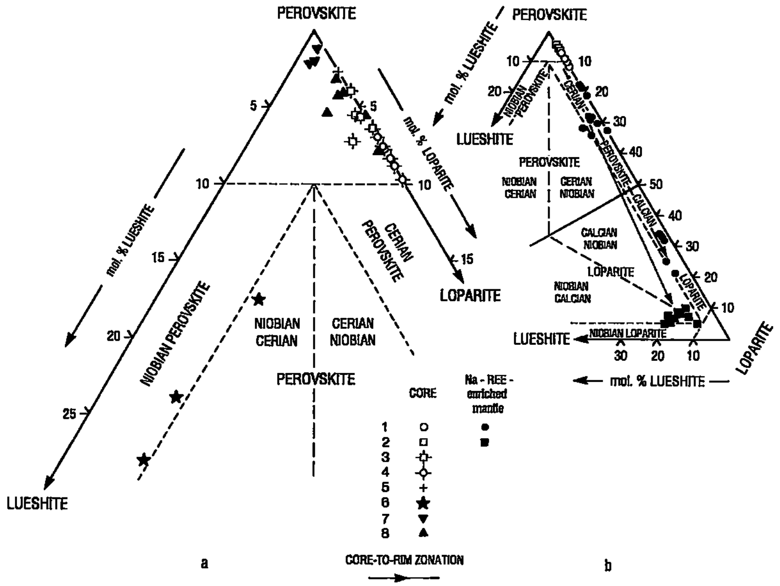

FIG. 2. Composition (mol.%) of perovskite and loparite from foidolites: (a) and (b) 1 ijolite pegmatite, Afrikanda, 2 "hybrid" pegmatite, Afrikanda, 3 urtite, Afrikanda, 4 ijolite, Kovdor, 5 melteigite, Nizhnesayanskiy, Siberia (Chernysheva *et al.* 1991), 6–8 ijolite: 6 Oka, Quebec (Treiman & Essene 1985), 7 Magnet Cove, Arkansas (Flohr & Ross 1989), 8 Oldoinyo Lengai, Tanzania (Dawson *et al.* 1995).

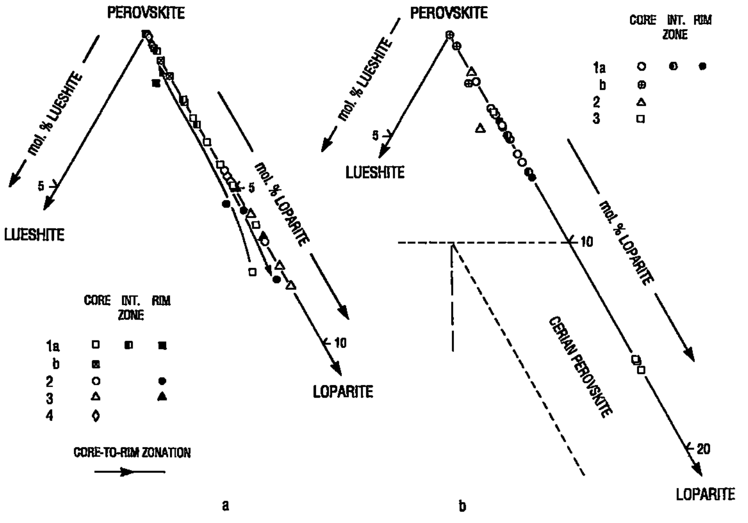

FIG. 3. Composition (mol.%) of perovskite from melilitic rocks: (a) 1 melilitolite, Turiy (a euhedral crystals, b rims on magnetite), 2 pegmatitic melilitolite, Turiy, 3 turjaite, Turiy, 4 turjaite, Kovdor; (b) 1 melilite – pyroxene – nepheline rock, Kovdor (a euhedral crystals, b rims on magnetite), 2–3 okaite: 2 Oka, Quebec, 3 Nizhnesayanskiy, Siberia (Chernysheva *et al.* 1991).

TABLE 3. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM FOIDOLITES

Wt.%	1	2	3	4	5	6	7	8
CaO	36.59	1.69	36.97	35.49	36.48	25.68	5.12	34.04
SrO	0.31	0.64	0.47	0.39	0.33	0.46	0.80	0.50
Na_2O	0.50	9.56	0.70	0.96	0.81	3.24	7.41	0.77
La_2O_3	1.46	10.20	1.06	1.27	0.54	3.11	10.22	2.10
Ce_2O_3	2.33	19.68	2.63	3.72	2.88	6.70	20.55	4.77
Pr_2O_3	n.d	2.49	n.d	0.42	0.10	0.61	1.16	0.72
Nd_2O_3	0.55	4.15	0.34	1.42	1.40	2.98	4.43	1.31
ThO_2	n.d	0.77	0.29	0.14	0.14	1.99	1.20	0.45
TiO_2	55.19	38.24	55.17	52.64	54.20	50.52	42.99	52.03
Fe_2O_3	1.36	0.01	1.18	1.53	1.60	1.18	0.06	2.36
Nb_2O_5	1.14	10.19	1.41	1.96	1.73	1.79	4.39	1.58
Ta_2O_5	0.22	1.94	0.54	0.52	0.83	0.81	0.45	0.20
Total	99.65	99.56	100.76	100.46	101.04	99.07	98.78	100.83
	Structural formulae calculated on the basis of 3 atoms of oxygen							
Ca	0.92	0.05	0.92	0.90	0.91	0.69	0.16	0.87
Sr	-	0.01	0.01	0.01	-	0.01	0.01	0.01
Na	0.02	0.54	0.03	0.04	0.04	0.16	0.42	0.04
La	0.01	0.11	0.01	0.01	-	0.03	0.11	0.02
Ce	0.02	0.21	0.02	0.03	0.02	0.08	0.22	0.04
Pr	-	0.03	-	-	-	0.01	0.01	0.01
Nd	-	0.04	-	0.01	0.01	0.03	0.05	0.01
Th	-	0.01	-	-	-	0.01	0.01	-
Ti	0.97	0.84	0.96	0.94	0.95	0.95	0.94	0.94
Fe	0.02	-	0.02	0.03	0.03	0.02	-	0.04
Nb	0.01	0.14	0.01	0.02	0.02	0.02	0.06	0.02
Ta	-	0.02	-	-	0.01	0.01	-	-
	Mol.% end-members							
$CaTiO_3$	94.87	4.81	92.80	90.24	92.00	68.20	19.92	91.50
$SrTiO_3$	0.44	1.09	0.64	0.56	0.46	0.67	1.77	0.73
$CaThO_3$	-	0.51	0.16	0.08	0.08	1.14	1.04	0.26
Loparite	4.69	78.50	6.40	9.12	7.48	28.32	70.27	7.51
$NaNbO_3$	-	15.09	-	-	-	1.67	4.03	-
$Ce_2Ti_2O_7$	-	-	-	-	-	-	2.97	-

Compositions: 1 unzoned perovskite crystal, "hybrid"pegmatite, Afrikanda, 2 loparite, "hybrid"pegmatite, Afrikanda, 3 unzoned perovskite crystal, urtite, Afrikanda, 4 & 5 core and rim of a perovskite crystal, ijolite pegmatite, Afrikanda, 6 & 7 secondary perovskite and loparite, ijolite pegmatite, Afrikanda, 8 unzoned perovskite crystal, ijolite, Kovdor. n.d = not detected.

Nizhnesayanskiy, Guli and Gornoozerskiy complexes (all in Siberia: East Sayan, Maimecha-Kotuy and Sette-Daban alkaline provinces, respectively) (Fig. 5: Chernysheva *et al.* 1991, Mitchell *et al.* 1998, Williams & Kogarko 1996, this work). Nb-enrichment also has been noted in perovskite from calcite carbonatite in complexes in the Sette-Daban and East Sayan provinces (Gaidukova & Zdorik 1962, Pozharitskaya & Samoylov 1972). Calcite carbonatite at Kaiserstuhl, Germany, and Oka, Quebec, contains perovskite-group minerals with a much wider compositional range (Fig. 5, and references therein). The trend is from ferrian niobian perovskite to niobian ferrian perovskite in the Kaiserstuhl carbonatite, and to latrappite in the Oka carbonatite. Perovskite of very unusual composition, with high levels of Zr and Fe (up to 3.3 wt.% ZrO_2 and 6.1% Fe_2O_3, respectively) at very low Nb and Na contents, occurs in carbonatite at Polino, Italy (Lupini *et al.* 1992).

Lueshite from dolomite carbonatite of the Kovdor and Lesnaya Varaka complexes contains considerable amounts of Ca (up to 2.8 wt.% CaO), Ti (up to 6.8 wt.% TiO_2) and *REE* (up to 6.3 wt.% REE_2O_3: Table 8). In the Lesnaya Varaka carbonatite, the mineral is distinctly zoned from cerian lueshite in the core to lueshite *sensu stricto* in the rim (Fig. 6). Enrichment in Na and Nb is accompanied by an increase in Th content (up to 3.2 wt.% ThO_2). Our data and those from the literature (Bagdasarov *et al.* 1962, Subbotin & Men'shikov 1987, Subbotina & Subbotin 1990) show that lueshite from calcite carbonatites is richer in Ca and Ti than that in dolomite or dolomite–calcite carbonatites (Fig. 6). Lueshite described by Lapin & Kazakova (1966), from an aegirine–zeolite rock at Kovdor, is strongly enriched in Ca, Ti and Th (Fig. 6). High Mg, K and Al contents reported in this mineral by these authors most likely result from analytical errors.

Evolutionary trends

Data from this study show that perovskite in carbonatite complexes of the Kola alkaline province evolves along three distinct evolutionary trends. These are as follows (Fig. 7, empty arrows):

(1) *The lueshite trend.* Primary perovskite from ultramafic rocks, foidolites and melilitic rocks is poor in Na, *REE*, Fe, and Nb, and contains negligible amounts of other minor elements (Sr, Th and Ta). In

TABLE 4. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE FROM MELILITIC ROCKS

Wt.%	1	2	3	4	5	6	7	8	9	10	11
CaO	38.19	37.28	35.72	36.80	37.59	40.10	40.20	35.75	40.14	40.49	37.15
SrO	0.49	0.22	0.25	0.43	0.14	0.16	0.32	0.47	0.35	0.17	0.17
Na_2O	0.67	0.38	0.60	0.52	0.45	0.07	0.05	0.51	n.d	0.06	0.71
La_2O_3	0.53	1.03	1.51	0.97	1.15	1.11	1.06	1.33	n.d	n.d	1.46
Ce_2O_3	1.62	2.40	3.17	2.60	2.07	0.99	0.87	3.24	0.29	0.37	1.64
Pr_2O_3	n.d	n.d	0.97	0.46	0.19	0.29	0.38	0.81	n.d	n.d	1.04
Nd_2O_3	0.83	0.73	0.84	0.87	0.52	n.d	n.d	1.15	n.d	n.d	0.84
ThO_2	0.03	0.47	0.63	0.28	0.28	0.02	n.d	0.18	0.19	n.d	0.25
TiO_2	56.30	53.42	52.32	53.33	54.86	56.82	56.29	53.23	57.42	56.63	54.72
Fe_2O_3	1.39	1.74	1.86	1.66	1.32	0.92	0.61	1.64	0.56	0.86	1.06
Nb_2O_5	1.23	1.67	1.74	1.20	1.63	n.d	0.03	0.81	n.d	n.d	1.75
Ta_2O_5	0.33	0.30	0.46	0.26	0.48	0.09	0.14	0.19	0.22	0.18	0.01
Total	101.61	99.64	100.07	99.38	100.68	100.57	99.95	99.31	99.17	98.76	100.80
	Structural formulae calculated on the basis of 3 atoms of oxygen										
Ca	0.93	0.94	0.91	0.93	0.93	0.98	0.99	0.91	0.99	1.00	0.93
Sr	0.01	-	-	0.01	-	-	-	0.01	-	-	-
Na	0.03	0.02	0.03	0.02	0.02	-	-	0.02	-	-	0.03
La	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	0.01
Ce	0.01	0.02	0.03	0.02	0.02	0.01	0.01	0.03	-	-	0.01
Pr	-	-	0.01	-	-	-	-	0.01	-	-	0.01
Nd	0.01	0.01	0.01	0.01	-	-	-	0.01	-	-	0.01
Th	-	-	-	-	-	-	-	-	-	-	-
Ti	0.97	0.95	0.94	0.95	0.96	0.98	0.98	0.96	0.99	0.98	0.96
Fe	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.03	0.01	0.01	0.02
Nb	0.01	0.02	0.02	0.01	0.02	-	-	0.01	-	-	0.02
Ta	-	-	-	-	-	-	-	-	-	-	-
	Mol.% end-members										
$CaTiO_3$	93.86	95.89	93.58	94.38	95.52	99.15	99.11	94.35	99.53	99.23	93.08
$SrTiO_3$	0.65	0.31	0.36	0.60	0.19	0.21	0.43	0.67	0.47	0.23	0.24
$CaThO_3$	0.02	0.26	0.35	0.15	0.15	0.01	-	0.10	-	-	0.14
Loparite	4.98	3.54	5.71	4.87	4.14	0.63	0.45	4.88	-	0.54	6.55
$NaNbO_3$	0.49	-	-	-	-	-	-	-	-	-	-

Compositions: 1 unzoned crystal, pegmatoid melilitolite, Turiy, 2-5 successive zones (from core to rim), euhedral crystal, melilite-pyroxene-nepheline rock, Kovdor, 6 rim on magnetite, melilite-pyroxene-rock, Kovdor, 9 turjaite, Kovdor, 10 & 11 core and rim of a zoned crystal, melilitolite, Turiy, 12 rim on magnetite, melilitolite, Turiy, 13 unzoned crystal, turjaite, Turiy. n.d = not detected.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM PHOSCORITE AND CALCITE-AMPHIBOLE-DIOPSIDE ROCK

Wt.%	1	2	3	4	5	6	7	8	9
CaO	34.28	34.85	34.73	23.87	10.56	31.15	30.92	19.86	6.63
SrO	0.35	0.38	0.40	0.28	0.56	0.56	0.46	0.57	0.81
Na_2O	0.90	0.67	0.76	3.25	5.94	1.71	1.81	4.30	6.73
La_2O_3	2.25	1.81	1.05	3.07	7.94	2.37	2.57	4.16	8.84
Ce_2O_3	4.25	3.07	3.00	9.43	18.06	5.24	5.81	11.84	18.18
Pr_2O_3	0.85	n.d	n.d	n.d	3.36	0.68	1.00	2.69	5.75
Nd_2O_3	1.32	1.45	1.79	5.88	6.02	1.67	2.24	4.73	4.99
ThO_2	n.d	0.40	0.50	1.08	0.56	0.50	1.06	1.23	2.46
TiO_2	51.18	53.04	52.96	50.28	44.87	51.98	51.70	46.83	42.61
Fe_2O_3	1.48	1.23	1.34	0.79	0.49	0.96	0.99	0.76	0.24
Nb_2O_5	1.79	1.63	1.69	2.49	1.56	1.36	1.39	2.15	2.21
Ta_2O_5	0.24	0.42	0.33	0.20	0.17	0.65	0.42	0.73	0.61
Total	98.89	98.95	98.55	100.62	100.09	98.83	100.37	99.85	100.06
Structural formulae calculated on the basis of 3 atoms of oxygen									
Ca	0.89	0.90	0.89	0.65	0.32	0.82	0.81	0.56	0.21
Sr	-	0.01	0.01	-	0.01	0.01	0.01	0.01	0.01
Na	0.04	0.03	0.04	0.16	0.32	0.08	0.09	0.22	0.38
La	0.02	0.02	0.01	0.03	0.08	0.02	0.02	0.04	0.09
Ce	0.04	0.03	0.03	0.09	0.19	0.05	0.05	0.12	0.19
Pr	0.01	-	-	-	0.03	0.01	0.01	0.03	0.06
Nd	0.01	0.01	0.02	0.05	0.06	0.01	0.02	0.04	0.05
Th	-	-	-	0.01	-	-	0.01	0.01	0.02
Ti	0.94	0.96	0.96	0.95	0.95	0.96	0.95	0.93	0.93
Fe	0.03	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01
Nb	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.03
Ta	-	-	-	-	-	-	-	0.01	-
Mol.% end-members									
$CaTiO_3$	90.68	92.75	91.85	66.06	37.57	82.30	81.12	52.08	23.87
$SrTiO_3$	0.51	0.55	0.57	0.42	1.09	0.81	0.67	0.92	1.71
$CaThO_3$	-	0.23	0.28	0.64	0.43	0.28	0.60	0.78	2.04
Loparite	8.81	6.47	7.30	32.88	54.24	16.61	17.61	46.22	65.03
$NaNbO_3$	-	-	-	-	1.26	-	-	-	2.12
$Ce_2Ti_2O_7$	-	-	-	-	5.41	-	-	-	5.22

Compositions: 1 unzoned perovskite crystal, phoscorite, Kovdor, 2 & 3 core and rim of hexahedral perovskite crystal, calcite-amphibole-diopside rock, Afrikanda, 4 & 5 secondary perovskite and loparite mantles on hexahedral perovskite crystal, calcite-amphibole-diopside rock, Afrikanda, 6 & 7 core and rim of cubo-octahedral perovskite crystal, calcite-amphibole-diopside rock, Afrikanda, 8 & 9 secondary perovskite and loparite mantles on cubo-octahedral perovskite crystal, calcite-amphibole-diopside rock, Afrikanda. n.d = not detected.

such perovskite, the total content of loparite, lueshite and other end-members does not exceed 10 mol.% (Tables 1–4). Calcite carbonatite contains primary perovskite with up to 16.8 mol.% $NaNbO_3$, and late-stage calcite and dolomite carbonatites contain lueshite. According to Pozharitskaya & Samoylov (1972) and Chernysheva *et al.* (1991), the lueshite trend is also typical of perovskite-group minerals from the carbonatite complexes of the East Sayan alkaline province. At the Oka and Kaiserstuhl carbonatite complexes (Nickel 1964, Boctor & Yoder 1980, van Wambeke 1980, Treiman & Essene 1985, Chakhmouradian 1996, Mitchell *et al.* 1998), this evolutionary trend is combined with significant enrichment of perovskite in Fe (see below).

(2) *The latrappite trend.* Enrichment of Nb and Fe in perovskite delineates a latrappite evolutionary trend, from perovskite *sensu stricto* in the early silicate rocks to ferrian, ferrian niobian and niobian ferrian perovskite in calcite carbonatite (up to 9.1 mol.% Ca_2FeNbO_6). This trend is more strongly developed in the carbonatite units of the Oka and Kaiserstuhl complexes.

(3) *The loparite trend.* Mantles of Na–*REE*-enriched secondary perovskite and loparite on primary perovskite occur in most rock series of the carbonatite complexes. In most cases, enrichment in Na and *REE* is accompanied by an increase in Nb and Th. Very similar trends have been established for perovskite-group minerals from melnoite of the Schryburt Lake carbonatite complex, Ontario (Platt 1994), and from alkaline ultramafic rocks of the Khibina complex, Kola alkaline province (Chakhmouradian & Mitchell 1998).

X-RAY DIFFRACTION

Synthetic $CaTiO_3$ is an orthorhombic derivative of the cubic perovskite structure (Beran *et al.* 1996). The latter may be viewed as a framework of corner-linked BX_6 octahedra, with the "cavities" occupied by twelve-coordinated *A*-cations. Distortion of the ideal cubic structure is produced by tilting (rotation) of the TiO_6 octahedra about a tetrad axis and a diad axis of the cubic cell (Náray-Szabó 1943), usually referred to as the tilt angles φ and ω (Megaw 1973) or ϕ and θ (Zhao *et al.* 1993). The distortion induced by the independent tilts ϕ and θ is described by a tilt Φ about an appropriate triad axis (O'Keeffe & Hyde 1977). All three tilt angles can be derived from unit-cell dimensions of the orthorhombic structure using

TABLE 6. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM CALCITE CARBONATITES

Wt.%	1	2	3	4	5	6	7	8	9	10
CaO	38.90	41.05	31.87	34.53	33.95	33.38	32.00	34.31	34.22	11.60
SrO	0.18	0.16	0.09	0.29	n.d	0.19	0.15	0.39	0.24	0.82
Na_2O	0.11	0.04	2.15	0.65	0.82	1.01	1.74	0.89	1.01	7.56
La_2O_3	0.75	n.d	0.71	1.24	1.05	0.68	1.21	1.43	1.35	4.85
Ce_2O_3	2.01	n.d	3.67	3.81	3.22	3.74	3.82	3.86	3.80	13.90
Pr_2O_3	n.d	n.d	0.25	0.70	0.98	n.d	1.01	0.20	0.97	1.54
Nd_2O_3	0.06	n.d	1.83	1.44	1.47	1.07	1.59	1.63	1.55	6.02
ThO_2	n.d	n.d	0.16	1.19	2.98	1.67	0.70	0.54	0.29	0.42
TiO_2	55.72	58.16	51.21	48.32	45.52	45.87	43.68	47.50	47.56	40.74
Fe_2O_3	0.98	0.24	1.00	3.04	3.79	3.82	3.85	3.46	3.73	0.58
Nb_2O_5	0.55	0.16	5.37	4.48	5.30	6.26	9.63	4.98	4.91	11.00
Ta_2O_5	n.d	n.d	n.d	0.51	0.80	0.86	n.d	0.68	0.42	1.18
Total	99.26	99.81	98.31	100.20	99.88	98.55	99.38	99.87	100.05	100.21
Structural formulae calculated on the basis of 3 atoms of oxygen										
Ca	0.97	1.00	0.83	0.90	0.90	0.88	0.85	0.89	0.89	0.34
Sr	-	-	-	-	-	-	-	0.01	-	0.01
Na	0.01	-	0.10	0.03	0.04	0.05	0.08	0.04	0.05	0.40
La	0.01	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05
Ce	0.02	-	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.14
Pr	-	-	-	0.01	0.01	-	0.01	-	0.01	0.02
Nd	-	-	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.06
Th	-	-	-	0.01	0.02	0.01	0.01	-	-	-
Ti	0.97	0.99	0.93	0.88	0.85	0.85	0.81	0.87	0.87	0.84
Fe	0.02	-	0.02	0.06	0.07	0.07	0.07	0.06	0.07	0.01
Nb	0.01	-	0.06	0.05	0.06	0.07	0.11	0.05	0.05	0.14
Ta	-	-	-	-	0.01	0.01	-	-	-	0.01
Mol.% end-members										
$CaTiO_3$	98.74	99.61	83.77	81.32	79.84	79.80	73.78	79.87	79.55	41.43
$SrTiO_3$	0.25	0.21	0.13	0.36	-	0.24	0.19	0.48	0.29	1.60
$CaThO_3$	-	-	0.09	-	-	-	-	-	-	0.32
Ca_2FeNbO_6	-	-	-	6.17	7.84	8.03	7.98	6.98	7.50	-
Loparite	1.01	-	11.54	8.71	8.16	6.53	9.30	8.85	9.26	47.20
$NaNbO_3$	-	0.18	4.47	0.14	1.21	2.74	5.24	1.20	1.61	8.89
$Ca_2Nb_2O_7$	-	-	-	3.30	2.95	2.65	3.52	2.62	1.79	-
$Ce_2Ti_2O_7$	-	-	-	-	-	-	-	-	-	0.56

Compositions: 1-3 core, intermediate zone and rim of a zoned perovskite crystal, calcite carbonatite, Sebljavr, 4 unzoned perovskite crystal, calcite carbonatite, Turiy, 5-7 core, intermediate zone and rim of a zoned perovskite crystal, calcite-melilite carbonatite, Turiy, 8 & 9 core and rim of a perovskite crystal, calcite-phlogopite carbonatite, Vuorijarvi, 10 loparite mantle on perovskite, calcite-phlogopite carbonatite, Vuorijarvi. n.d = not detected.

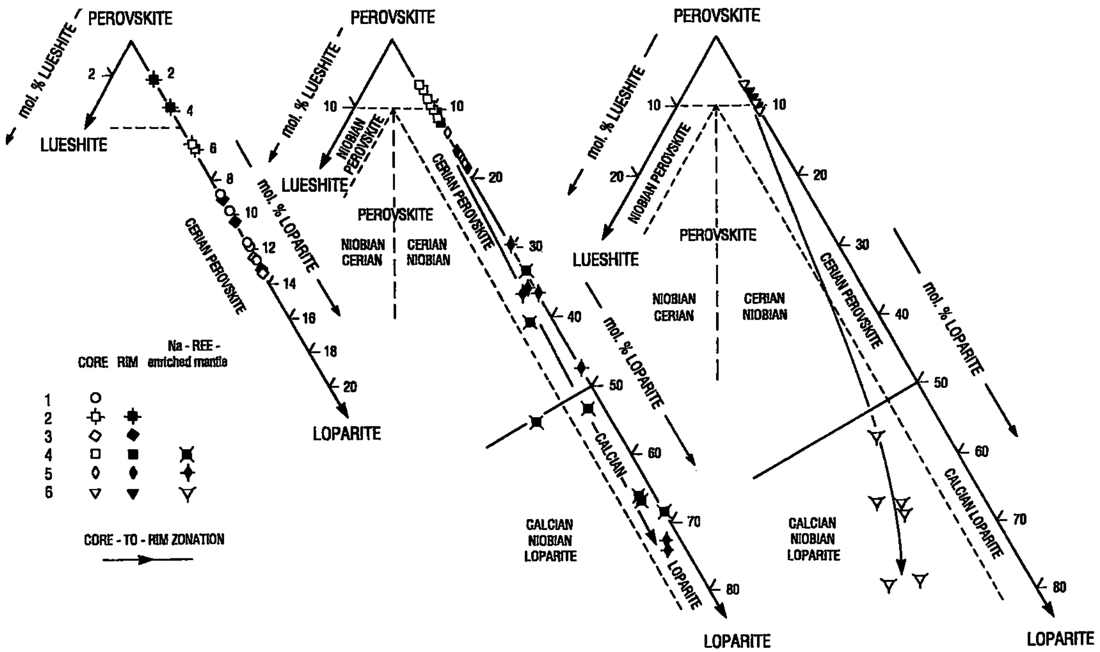

FIG. 4. Composition (mol.%) of perovskite and loparite from calcite carbonatites and kindred rocks: 1 phoscorite, Kovdor, 2 phoscorite, Gardiner, Greenland, 3 phoscorite, Kugda, Siberia, 4 – 5 calcite – amphibole – diopside rock, Afrikanda (hexahedral and cubo-octahedral crystals, respectively), 6 calcite–phlogopite carbonatite, Vuorijarvi.

equations suggested by Megaw (1973), O'Keeffe & Hyde (1977) and Zhao *et al.* (1993). Correspondences between the tilt-angle equations and three space groups suggested for orthorhombic $CaTiO_3$ by different investigators are given in Table 9. In this study, we use the standard space-group setting *Pnma* favored by mineralogists (*e.g.*, Hu *et al.* 1992, Keller & Buseck 1994).

Unit-cell dimensions (*Pnma*, $Z = 4$) for some samples of perovskite examined in this study, and tilt angles and other parameters of the pseudocubic cell a_p ($Pm3m$, $Z = 1$), are given in Table 10. The samples examined are primary perovskite, as sufficient secondary perovskite could not be extracted for X-ray studies. From Table 10 and Figure 8, it is clear that the largest unit-cell dimensions and rotation angles are found in perovskite from the carbonatites. As noted above, these samples are commonly enriched in Na, Nb, Fe and *REE*, compared to perovskite from the comagmatic ultramafic and alkaline rocks. Given the intricate compositional zonation of many perovskite samples, we calculated mean compositions to determine relationships between isomorphic substitution and crystal chemistry. On the basis of these data, we estimated the ionic radii of cations at the *A* and *B* sites ($R_w[A]$ and $R_w[B]$) using ionic radii given by Shannon (1976); Figure 9 illustrates the correspondence between parameters of the pseudocubic cell and estimated ionic radii. Also shown in Figure 9 are trends in which the parameters for the pseudocubic cell increase along the perovskite–loparite (1), perovskite–lueshite (2) and perovskite–latrappite (3) trends. It is also obvious in this figure that the unit-cell parameters of most of the perovskite samples lie between the above trends, corresponding well with the intermediate position of the evolutionary trends in the system perovskite – lueshite – loparite – latrappite (Fig. 7).

DISCUSSION

The evolutionary trends followed by perovskite compositions in the carbonatite complexes may reflect a general tendency of incompatible elements (in particular, *LREE*, Nb and Th) to accumulate in the more evolved fractions of alkaline magmas. The highest concentrations of *LREE*, Sr, Zr, Th and Nb are found mostly in complex oxides and carbonates in these carbonatites (Bell 1989, Heinrich 1966, Kukharenko *et al.* 1965, Tuttle & Gittins 1966). Alternatively, carbonatitic magmas enriched in incompatible elements may have been derived directly from a mantle source. At present, the mineralogical data are insufficient to discriminate between these possibilities.

The behavior of the incompatible elements is also controlled by structural factors. In early phoscorites and calcite carbonatites, the *LREE* and Sr have a close

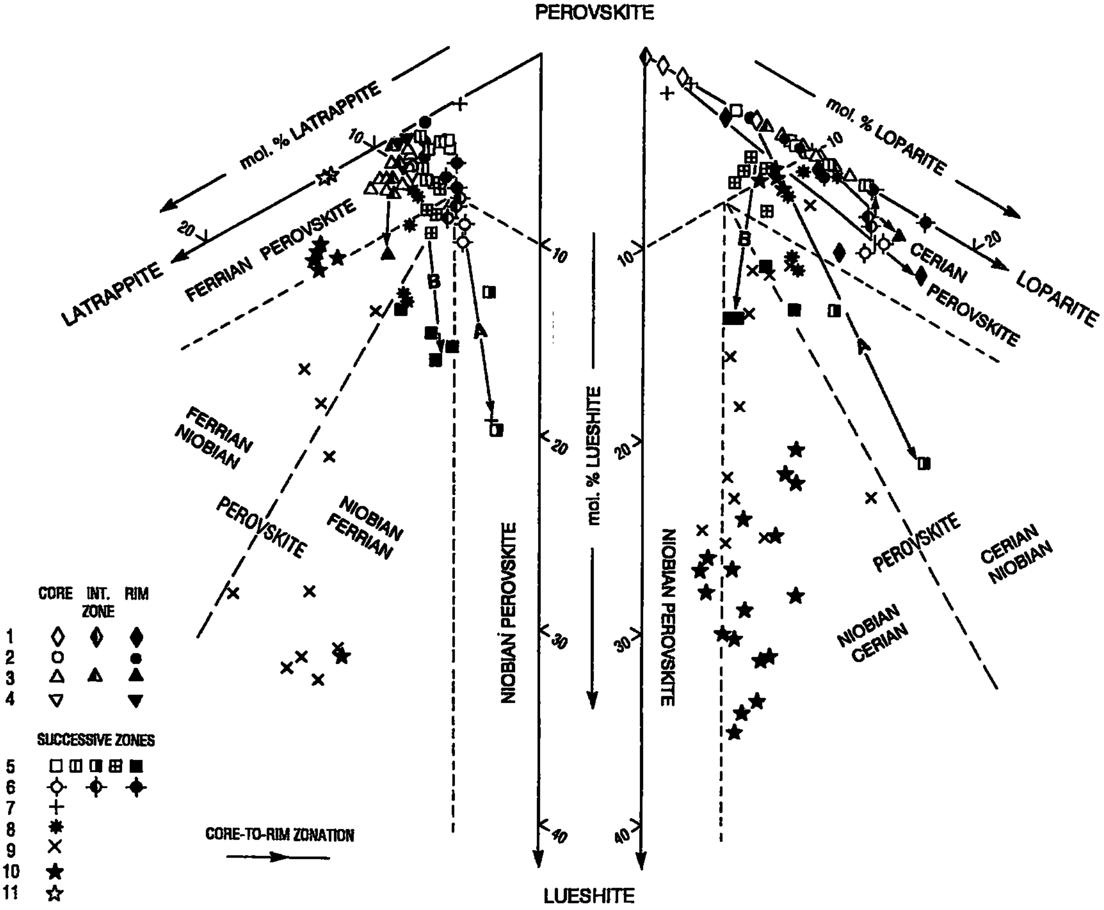

FIG. 5. Composition (mol.%) of perovskite from calcite carbonatites: 1 Sebljavr, 2 & 3 Turiy, 4 Vuorijarvi, 5 Kovdor, 6 Gornoozerskiy, Siberia, 7 Nizhnesayanskiy, Siberia (Chernysheva *et al.* 1991), 8 Guli, Siberia (Williams & Kogarko 1996), 9 Kaiserstuhl, Germany (Hauser 1908, Knop 1877, Meigen & Hugel 1913, Mitchell *et al.* 1998, van Wambeke 1980), 10 Oka, Quebec (Boctor & Yoder 1980, Chakhmouradian 1996, Mitchell *et al.* 1998, Nickel 1964, Treiman & Essene 1985, this study), 11 Magnet Cove, Arkansas (Mitchell *et al.* 1998).

affinity to Ca, and are dispersed in calcite and apatite, which are much more abundant than accessory oxides. The large ionic radius of Zr, compared to that of Ti, explains why this element favors structures with seven- or eight-coordinated polyhedra (baddeleyite, calzirtite, zirconolite), and not the perovskite structure. However, Zr is a potential substitute for Ti in perovskite from carbonatites formed under specific P–T conditions, *e.g.*, the Polino diatreme, Italy (Lupini *et al.* 1992). Finally, Nb and Th are distributed mostly between perovskite- (lueshite trend) and pyrochlore-group minerals. According to experimental data (Aleksandrov 1973, Jago & Gittins 1993), the former crystallized under volatile-poor conditions and at higher temperatures than the latter. Evolution of carbonatitic magmas by enrichment in volatile components is commonly reflected in the replacement of early cumulus perovskite-group minerals by relatively late pyrochlore-group phases (Chakhmouradian 1996, Williams & Kogarko 1996).

The low Fe content of primary perovskite from the silicate rocks, and Fe-enrichment in primary perovskite from the calcite carbonatites (latrappite trend), cannot be explained unequivocally. Kimura & Muan (1971a, b) have shown that perovskite forms an extensive solid-solution series with the relatively oxygen-deficient compound $Ca_2Fe^{3+}{}_2O_5$, and does not accommodate substantial Fe^{2+} at the *A* sites. These data are in a good agreement with spectroscopic studies of natural Fe-rich perovskite, which show that Fe enters the structure only as Fe^{3+} substituting for Ti at the *B*

TABLE 7. REPRESENTATIVE COMPOSITIONS OF PEROVSKITE AND LOPARITE FROM CALCITE CARBONATITES

Wt.%	1	2	3	4	5
CaO	35.37	33.87	26.45	35.40	31.46
SrO	0.23	0.26	0.30	0.50	0.32
Na_2O	0.94	1.21	4.33	1.35	2.56
La_2O_3	1.64	1.77	1.64	0.58	0.94
Ce_2O_3	2.97	3.56	5.35	1.88	2.34
Pr_2O_3	0.31	n.d	0.61	n.d	0.56
Nd_2O_3	1.11	0.99	1.68	0.55	0.88
ThO_2	0.27	0.07	2.25	0.48	1.04
TiO_2	49.83	48.40	45.10	48.09	43.20
Fe_2O_3	2.52	3.01	1.14	2.95	2.82
Nb_2O_5	4.31	6.75	11.64	8.49	14.02
Ta_2O_5	0.36	0.27	0.62	0.48	0.94
Total	99.86	100.16	101.11	100.75	101.08
	Structural formulae calculated on the basis of 3 atoms of oxygen				
Ca	0.91	0.87	0.70	0.90	0.81
Sr	-	-	-	0.01	-
Na	0.04	0.06	0.21	0.06	0.12
La	0.01	0.02	0.01	0.01	0.01
Ce	0.03	0.03	0.05	0.02	0.02
Pr	-	-	0.01	-	-
Nd	0.01	0.01	0.01	-	0.01
Th	-	-	0.01	-	0.01
Ti	0.90	0.87	0.84	0.85	0.79
Fe	0.05	0.05	0.02	0.05	0.05
Nb	0.05	0.07	0.13	0.09	0.15
Ta	-	-	-	-	0.01
	Mol.% end-members				
$CaTiO_3$	83.56	79.20	69.06	82.00	72.82
$SrTiO_3$	0.27	0.32	0.43	0.60	0.40
$CaThO_3$	-	-	1.27	-	-
Ca_2FeNbO_6	4.94	6.06	-	5.82	5.77
Loparite	7.84	8.51	16.81	3.64	5.95
$NaNbO_3$	1.64	2.79	12.43	4.96	10.13
$Ca_2Nb_2O_7$	1.75	3.12	-	2.98	4.93

Compositions: 1-5 successive zones (from core to rim), zoned perovskite crystal, calcite carbonatite, Kovdor. n.d = not detected.

sites (Muir *et al.* 1984, Mitchell *et al.* 1998). Thus we suggest that the latrappite evolutionary trend observed in the perovskite-group minerals of carbonatite complexes from the Kola Peninsula, Oka and Kaiserstuhl results from increasing Fe^{3+}/Fe^{2+} values during magmatic differentiation.

The late-stage enrichment of Na and *LREE* perovskite (loparite trend) undoubtedly resulted from two different processes. One of them involved interaction of primary perovskite with a *LREE*-rich fluid probably derived from the carbonatite source. Wendlandt & Harrison (1979) have demonstrated that the *LREE* tend to fractionate from carbonatitic melt into CO_2-rich fluid. A similar model was suggested by Platt (1994) for *LREE*-enrichment in the assemblage perovskite–loparite in melnoite of the Schryburt Lake complex. The other process does not necessarily require reaction with *LREE*-enriched magmatic fluid, but with a secondary fluid containing Na and *LREE* leached from primary perovskite.

$$\underset{\text{perovskite}}{(Ca_{1-x}Na_{0.5x}Ce_{0.5x})TiO_3} + (SiO_2)_{aq} \rightarrow \underset{\text{titanite}}{(1-x)\,CaTiSiO_5}$$

$$+ \underset{\text{loparite}}{0.5x\ NaCeTi_2O_6}$$

This process was probably more important in the ultramafic rocks, where secondary perovskite and loparite occur in intimate association with titanite.

The enrichment of primary perovskite in the components $NaNbO_3$ and Ca_2FeNbO_6 leads to an increase in unit-cell dimensions and rotation angle Φ of the $(Ti,Fe,Nb)O_6$ octahedra. The latter effect reflects increasing deviation of the structure from cubic symmetry: in $NaNbO_3$ $\Phi = 12.4°$ (Sakowski-Cowley *et al.* 1969), in latrappite, $\Phi = 11.7°$ (Mitchell *et al.* 1998), and in $CaTiO_3$, $\Phi = 10.1°$. Relatively high Na and Nb contents in some perovskite samples from carbonatites may indicate that the tilting of the octahedra in the structure is complicated by displacement of Na and Nb from the center of the polyhedra, analogous to the cation offset in synthetic $NaNbO_3$ at room temperature (Sakowski-Cowley *et al.* 1969). Structural effects of the *REE* on the perovskite structure are not certain, and further X-ray-diffraction studies of the series $CaTiO_3$ – Na*REE*Ti_2O_6 are required.

TABLE 8. REPRESENTATIVE COMPOSITIONS OF LUESHITE FROM DOLOMITE CARBONATITE

Wt.%	1	2	3	4	5
CaO	0.95	1.18	1.93	2.21	2.35
SrO	0.31	0.19	0.19	0.28	0.19
Na_2O	14.29	15.88	15.69	15.89	15.19
La_2O_3	1.81	1.28	0.88	1.05	1.09
Ce_2O_3	3.13	2.13	1.58	1.48	1.71
Pr_2O_3	0.57	n.d	n.d	n.d	n.d
Nd_2O_3	0.78	0.35	0.22	0.24	0.51
ThO_2	1.29	1.51	2.43	0.50	0.37
TiO_2	3.46	4.08	5.29	4.43	5.00
Fe_2O_3	n.d	n.d	n.d	0.13	0.24
Nb_2O_5	74.28	73.16	73.24	74.70	72.79
Total	100.87	99.76	101.45	100.91	99.44
	Structural formulae calculated on the basis of 3 atoms of oxygen				
Ca	0.03	0.03	0.06	0.06	0.07
Sr	0.01	-	-	-	-
Na	0.77	0.85	0.82	0.83	0.81
La	0.02	0.01	0.01	0.01	0.01
Ce	0.03	0.02	0.02	0.01	0.02
Pr	0.01	-	-	-	-
Nd	0.01	-	-	-	-
Th	0.01	0.01	0.02	-	-
Ti	0.07	0.08	0.11	0.09	0.10
Fe	-	-	-	-	-
Nb	0.93	0.92	0.90	0.91	0.90
	Mol.% end-members				
$CaTiO_3$	2.32	2.74	4.51	6.56	7.31
$SrTiO_3$	0.58	0.33	0.33	0.47	0.33
$CaThO_3$	0.94	1.02	1.65	0.33	0.25
Loparite	14.74	8.21	5.85	5.91	7.27
$NaNbO_3$	81.42	87.70	87.66	86.73	84.84

Compositions: 1-3 core, intermediate zone and rim of a zoned crystal, dolomite carbonatite, Lesnaya Varaka, 4 & 5 core and rim of an unzoned crystal, dolomite carbonatite, Kovdor. Total Fe expressed as Fe_2O_3; n.d = not detected; Ta was sought, but not found.

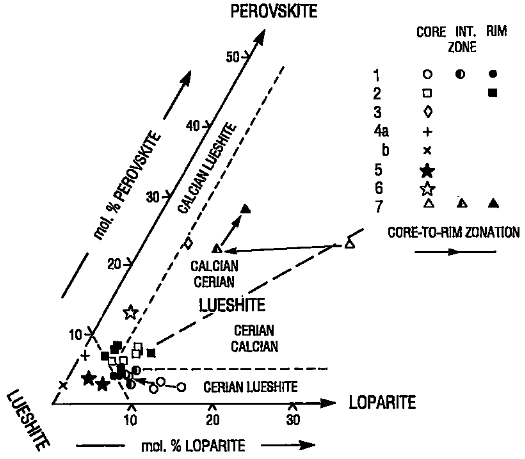

FIG. 6. Composition (mol.%) of lueshite from carbonatites and aegirine–zeolite rock: 1 dolomite carbonatite, Lesnaya Varaka, 2 dolomite carbonatite, Kovdor, 3 calcite carbonatite, Sebljavr (Subbotin & Men'shikov 1987), 4a and 4b calcite and dolomite carbonatites, respectively, Sallanlatvi (Subbotina & Subbotin 1990), 5 calcite carbonatite, Lueshe, Democratic Republic of Congo, 6 calcite carbonatite, unspecified locality, Siberia (Bagdasarov *et al.* 1962). 7 aegirine–zeolite rock. Kovdor

CONCLUSIONS

(1) The carbonatite complexes of the Kola Alkaline Province contain perovskite *sensu stricto*. Perovskite enriched in lueshite and latrappite occurs only in calcite carbonatites. Members of the perovskite – loparite solid-solution series are found as a thin secondary mantle on primary perovskite from some varieties of ultramafic rocks, foidolites and carbonatites.

(2) The composition of perovskite from the carbonatite complexes evolves along three distinct trends, *i.e.*, toward lueshite, latrappite or loparite. The lueshite and latrappite contents are lowest in primary perovskite from ultramafic rocks and highest in primary perovskite from carbonatite. The lueshite trend culminates in the appearance of lueshite in late dolomite carbonatite. The loparite trend results from interaction of the primary perovskite with late-stage fluids derived from alkaline and carbonatitic melts.

(3) Increasing enrichment of lueshite and latrappite in perovskite components produces larger unit-cell parameters and a larger tilt (rotation) angle of the $(Ti,Fe,Nb)O_6$ octahedra.

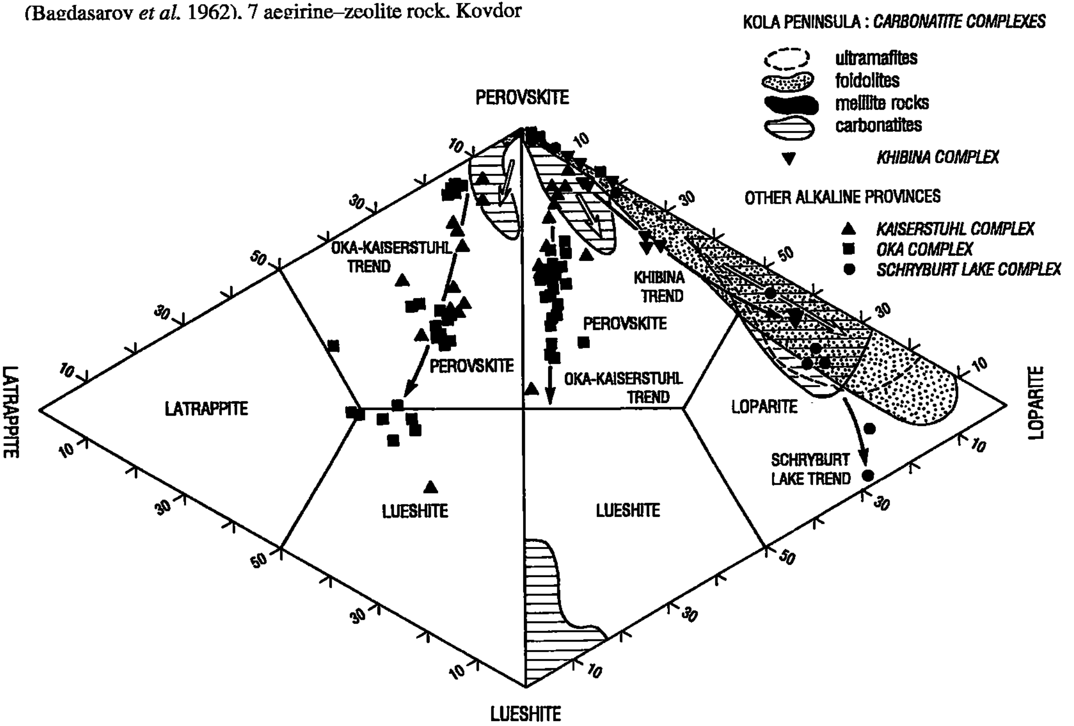

FIG. 7. Composition (mol.%) of perovskite-group minerals from the carbonatite complexes of the Kola Alkaline Province (this study) compared to that of perovskite and loparite from the Khibina complex (Chakhmouradian & Mitchell 1998) and Schryburt Lake complex (Platt 1994), of perovskite from the Kaiserstuhl complex (Hauser 1908, Knop 1877, Meigen & Hugel 1913, Mitchell *et al.* 1998, van Wambeke 1980), and of perovskite and latrappite from the Oka complex (Boctor & Yoder 1980, Chakhmouradian 1996, Mitchell *et al.* 1998, Nickel 1964, Treiman & Essene 1985, this study).

TABLE 9. CORRESPONDENCE BETWEEN SPACE GROUP, UNIT-CELL PARAMETERS AND TILT ANGLES FOR $CaTiO_3$

SPACE GROUP	Pcmm	Pbnm	Pnma
a, Å	5.3670(1)	5.3796(1)	5.4405
b, Å	7.6438(1)	5.4423(3)	7.6436
c, Å	5.4439(1)	7.6401(5)	5.3812
REFERENCE	Kay & Bailey (1957)	Sasaki *et al.* (1987)	ASTM 22-153
TILT ANGLES			
Tetrad axis	$\cos\phi = (\sqrt{2}a)/b$	$\cos\phi = (\sqrt{2}a)/c$	$\cos\phi = (\sqrt{2}c)/b$
Diad axis	$\cos\theta = a/c$	$\cos\theta = a/b$	$\cos\theta = c/a$
Triad axis	$\cos\Phi = (\sqrt{2}a^2)/bc$	$\cos\Phi = (\sqrt{2}a^2)/bc$	$\cos\Phi = (\sqrt{2}c^2)/ab$

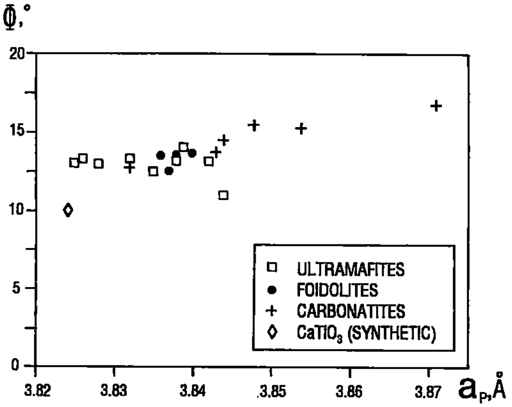

FIG. 8. Unit-cell parameter a_p, calculated on the basis of a pseudocubic cell, *versus* rotation angle Φ in perovskite from the carbonatite complexes.

TABLE 10. UNIT-CELL PARAMETERS AND TILT ANGLES OF PEROVSKITE

ROCK	a, Å	b, Å	c, Å	a_p, Å	φ, °	θ, °	Φ, °
Olivinite *Lesnaya Varaka*	5.451(3)	7.656(4)	5.362(7)	3.825	7.8	10.4	13.0
Olivinite *Afrikanda*	5.453(2)	7.661(2)	5.362(5)	3.826	8.2	10.5	13.3
Phlogopitized olivinite *Kovdor*	5.475(2)	7.681(6)	5.404(4)	3.844	5.8	9.2	10.9
Clinopyroxenite *Afrikanda*	5.454(3)	7.667(3)	3.368(7)	3.828	8.0	10.2	12.9
Ore schlieren *Afrikanda*	5.473(2)	7.682(2)	5.380(4)	3.838	7.9	10.6	13.2
Ore schlieren *Sebljavr*	5.464(2)	7.672(2)	5.381(5)	3.835	7.3	10.0	12.4
Pegmatoid clinopyroxenite *Afrikanda*	5.481(2)	7.687(2)	5.385(5)	3.842	7.8	10.7	13.1
Pegmatoid clinopyroxenite *Sebljavr*	5.463(2)	7.674(2)	5.371(5)	3.832	8.2	10.5	13.3
Phlogopite rock *Kovdor*	5.476(1)	7.691(2)	5.374(4)	3.839	8.8	11.1	14.1
"Hybrid" pegmatite *Afrikanda*	5.471(2)	7.677(2)	5.374(5)	3.836	8.1	10.8	13.5
Ijolite pegmatite *Afrikanda*	5.473(2)	7.684(2)	5.378(5)	3.838	8.2	10.7	13.4
Urtite *Afrikanda*	5.465(2)	7.681(3)	5.384(6)	3.837	7.6	9.9	12.4
Ijolite *Kovdor*	5.473(3)	7.694(4)	5.379(9)	3.840	8.6	10.6	13.6
Carbonatite *Sebljavr*	5.459(2)	7.670(2)	5.375(4)	3.832	7.7	10.1	12.7
Carbonatite *Kovdor*	5.486(2)	7.701(3)	5.377(7)	3.844	9.1	11.4	14.5
Carbonatite *Turiy*	5.545(2)	7.755(2)	5.396(4)	3.871	10.3	13.3	16.7
Carbonatite *Vuorijarvi*	5.508(2)	7.721(3)	5.386(7)	3.854	9.4	12.1	15.3
Cal-Am-Di rock (hexahedral) *Afrikanda*	5.481(1)	7.694(2)	5.382(6)	3.843	8.4	10.9	13.7
Cal-Am-Di rock (cubo-octahedral) *Afrikanda*	5.490(3)	7.722(4)	5.376(9)	3.848	10.1	11.7	15.4

Cal-Am-Di = calcite-amphibole-diopside. Unit-cell parameters calculated assuming the space group Pnma. For composition of the listed perovskite samples see Tables 1-3, 5-7.

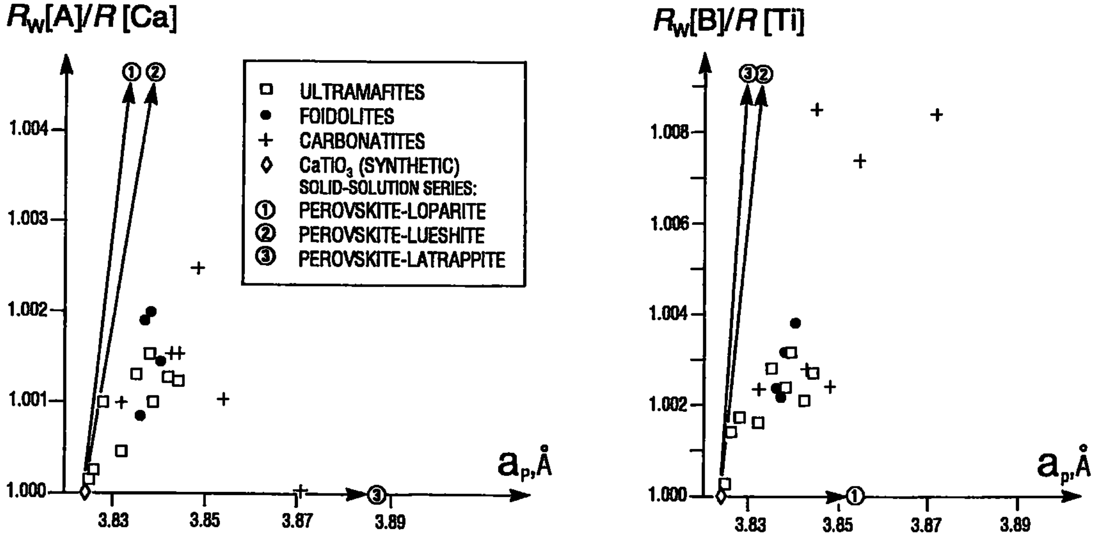

FIG. 9. Correspondence between unit-cell parameters a_p of perovskite, calculated on the basis of a pseudocubic cell, and weighted ionic radii of cations at the *A* and *B* sites *versus* ionic radii of Ca ($R_w[A]/R[Ca]$) and Ti ($R_w[B]/R[Ti]$).

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