

COMPOSITIONAL VARIATION OF LOPARITE FROM THE LOVOZERO ALKALINE COMPLEX, RUSSIA

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ABSTRACT

Perovskite-group minerals from the Lovozero peralkaline complex, on the Kola Peninsula, Russia, are primarily loparite-rich members of the perovskite – lueshite – loparite-(Ce) solid-solution series. From early-forming poikilitic nepheline syenite to late eudialyte lujavrite, loparite compositions evolve by enrichment in Na, Sr, and Nb, and depletion in Ca, Ti and light rare-earth elements. The evolutionary trend is from calcian niobian loparite-(Ce) in the poikilitic nepheline syenite and rocks of the differentiated complex through niobian calcian loparite-(Ce) in the differentiated complex and eudialyte lujavrite to cerian lueshite in eudialyte lujavrite. This trend coincides with the proposed order of crystallization of the major intrusive series of the massif. Intra- and intergrain compositional variation and diverse patterns of core-to-rim zonation exhibited by loparite grains from the same sample are characteristic of most parageneses and may result from a combination of re-equilibration phenomena and late-stage metasomatic processes.

Keywords: perovskite, loparite, lueshite, nepheline syenite, Lovozero, Russia.

SOMMAIRE

Les minéraux du groupe de la pérovskite du complexe hyperalkalin de Lovozero, péninsule de Kola, en Russie, sont en général proches du pôle loparite dans la solution solide pérovskite – lueshite – loparite-(Ce). La composition de la loparite évolue progressivement, de la syénite néphélinique poéicilitique précoce jusqu'à la lujavrite à eudialyte tardive, comme en témoignent un enrichissement en Na, Sr et Nb, et un appauvrissement en Ca, Ti, et terres rares légères. Ce schéma d'évolution va de loparite-(Ce) calcique et niobienne dans la syénite néphélinique précoce et les roches du complexe différencié, à loparite-(Ce) niobienne calcique dans le complexe différencié et la lujavrite à eudialyte, jusqu'à lueshite cérique dans la lujavrite à eudialyte. Il coïncide avec l'ordre de cristallisation proposé des membres de la série intrusive principale du massif. Les variations en composition à l'intérieur des grains et d'un grain à l'autre, ainsi que la diversité des types de zonation du cœur d'un grain vers la bordure de cristaux de loparite provenant d'un même échantillon, sont caractéristiques de la plupart des associations, et résulteraient à la fois de ré-équilibrage au cours du refroidissement et de métasomatose tardive.

(Traduit par la Rédaction)

Mots-clés: pérovskite, loparite, lueshite, syénite néphélinique, Lovozero, Russie.

INTRODUCTION

The Lovozero peralkaline complex, located in the Kola Peninsula of Russia, is one of a number of large intrusions that collectively comprise the Kola–Karelia Alkaline Province (Kogarko *et al.* 1995). Currently, the two largest intrusions in the province, Khibina (1327 km²) and Lovozero (650 km²), are considered

as a single peralkaline complex because of their proximity and petrological similarities (Arzamastsev 1994). The Lovozero complex is scientifically important because of the unusual composition and diverse mineralogy of the rocks present. In addition, many members of the complex are in places enriched in loparite [(NaREE)Ti₂O₆], and these occurrences are currently exploited as a source of rare-earth elements (REE).

The current study was undertaken primarily to establish the trends of compositional evolution of loparite from the different rock series of the Lovozero

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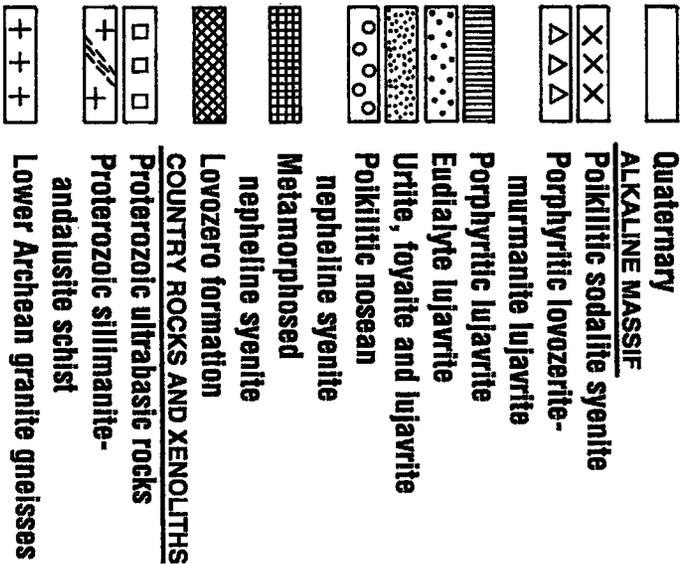
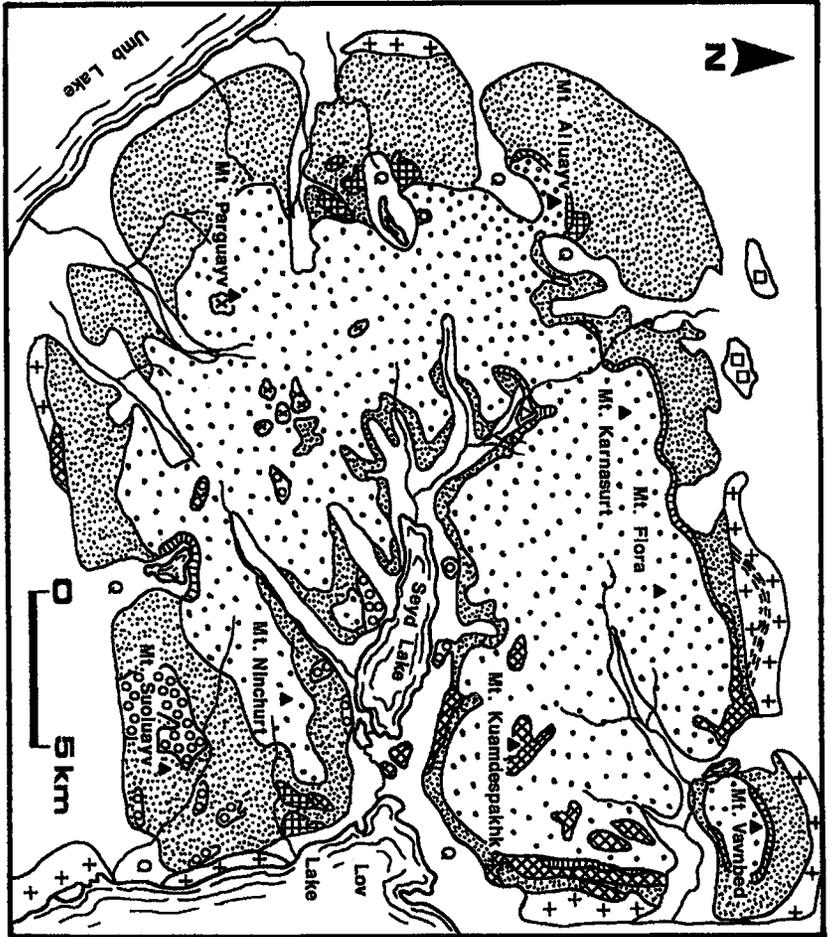


FIG. 1. Schematic geological map of the Lovozero alkaline massif (after Gerasimovsky *et al.*, 1968).

massif (Fig. 1) and to define the evolutionary trend for the pluton as a whole. For this purpose, we selected loparite samples from well-correlated drill cores and outcrops from the main intrusive series occurring in the northwestern part of the massif (Mts. Alluaiv and Karnasurt), from metasomatic and host rocks of the northern part (Mt. Selsurt), and from pegmatites and contact rocks of the differentiated complex at the central and southeastern parts of the massif (Mts. Leppkhe-Nel'm, Ninchurt, Punkaruaiiv).

A second objective was to determine if the existing data obtained by older analytical methods obtained on bulk samples of loparite are realistic. For example, Mitchell (1996) has noted that many of the compositions reported by Vlasov *et al.* (1966) give poor structural formulae as a consequence of the inaccurate determination of the amounts of alkali elements, Ti, Ta, and Nb present.

GEOLOGICAL SETTING

The Lovozero complex (Fig. 1) is topographically expressed as the dissected Lujavrut Plateau, which rises to about 800–900 m above the surrounding lowlands. It forms a stratified sheet-like intrusion emplaced in the Archean basement of the central Kola anticlinorium. Emplacement was tectonically controlled by a deep-seated fault zone that may be traced from the Kovdor alkaline ultrabasic complex eastward to the Ivanovka massif (Orlova 1993, Arzamastsev 1994). Contemporaneous extrusive alkaline volcanic rocks and sedimentary lithologies of the Lovozero suite are found in the upper parts of the massif. These, and the occurrence of similar rocks as xenoliths in the syenites, indicate that the currently exposed parts of the pluton crystallized at relatively shallow depths. Age determinations of the pluton range from 396–412 ± 12 Ma (Kononova & Shanin 1971) to 362 ± 17 Ma (Kogarko *et al.* 1983), thus establishing a Middle Paleozoic age.

Most petrologists (Eliseev & Fedorov 1953, Vlasov *et al.* 1966, Gerasimovsky *et al.* 1968) distinguish four intrusive rock series within the pluton (Fig. 1). Each corresponds to a separate stage of magmatic activity. From the base of the massif upward, these are:

(1) Poikilitic nepheline, nosean and sodalite syenites. These rocks are characterized by the presence of large alkali feldspar oikocrysts, which poikilitically enclose the feldspathoids. Although they occur primarily in the lower part of the intrusion, they are also found as inclusions in the later members of the intrusive series (see below).

(2) A differentiated complex, established by drilling to be 2.5 km in thickness, consisting of macro-rhythmically layered alternating urtite – juvite – lujavrite units. Individual modally-graded units in the layered complex are about 15 m in thickness. Lujavrite is a local name for an agpaitic hypersolvus

melanocratic nepheline syenite characterized by a trachytic texture formed by the flow alignment of feldspar prisms.

(3) Eudialyte lujavrite overlies the differentiated series and forms a plate-like body up to 800 m in thickness (Fig. 1). These rocks differ from the lujavrite of the differentiated complex in containing euhedral crystals rather than anhedral grains of eudialyte. Also present in this unit are numerous lenses and irregular minor intrusions of murmanite–lovozerite-bearing lujavrite porphyry. The body of eudialyte lujavrite is typically devoid of layering. It is not considered to be a late differentiate of the layered complex, and formed from a distinct batch of magma (Arzamastsev 1994).

(4) A minor suite of dikes represented mainly by alkali lamprophyres (camptonite, monchiquite), alkali picrites, nephelinites and phonolites.

In addition to the above, Bussen & Sakharov (1972) have described metamorphosed nepheline syenite and alkali syenite porphyries, and assumed that they represent the earliest intrusive stages of the complex. They also subdivided the third series into discrete eudialyte lujavrite and murmanite lujavrite complexes.

The position of the poikilitic sodalite syenite (naujaite) and sodalite foidolite (tawite) relative to the other rock series remains unclear, because of their occurrence both as enclaves in the lujavrites and as the basal unit of the complex. Some petrologists group them with the other types of poikilitic syenite and consider that they represent one of the earliest intrusive stages (Bussen & Sakharov 1972), whereas others interpret them as the latest differentiates or immiscible fractions of evolving agpaitic lujavritic melts (Vlasov *et al.* 1966, Gerasimovsky *et al.* 1968, Kogarko & Ryabchikov 1969).

DISTRIBUTION OF LOPARITE

At Lovozero, loparite occurs mostly as inter-penetration “fluorite-type” twins of cubic and cubo-octahedral habit, ranging in size from a few tenths of a millimeter, in most of the intrusive series, to 4–5 mm in pegmatites. The loparite twins are euhedral in the rocks of the differentiated complex, albitites, microclinites and pegmatites. In contrast, loparite crystals in poikilitic syenites exhibit an irregular habit, owing to their late crystallization relative to the felsic minerals.

Loparite is a common accessory mineral in the poikilitic nepheline syenite, rocks of the differentiated complex and eudialyte lujavrite. Exploration drilling has shown that at a depth of about 1.5 km within the complex, loparite is not common, and the main host minerals of titanium in the nepheline syenite are lorenzenite and ilmenite (Aleksandrov 1973). The dyke rocks of the fourth intrusive phase contain perovskite only as a rare accessory phase (Bussen &

Sakharov 1972) and have not been reported to contain loparite.

The highest concentrations of loparite are found in the rocks of the differentiated complex, particularly in the northwestern part of the pluton. In these, the highest contents of loparite occur in zones adjacent to the boundaries between massive and trachytic-textured rocks. Thus, within one modally graded unit, the lower horizon of urtite and the upper one of lujavrite have the maximum contents of loparite (Vlasov *et al.* 1966, Veselovsky *et al.* 1990). The loparite content of urtite is on the order of 1 vol.%. In melanocratic nepheline syenites ("maliginites") in the upper part of the differentiated complex, loparite may gain the status of a rock-forming mineral and comprise up to 10–12 vol.% of the rock. Despite their small thickness (usually less than 10 cm), loparite-enriched layers in the differentiated complex are continuous along strike, even though the mode of the host rock may change significantly, *e.g.*, from urtite to juvite or from melanocratic nepheline syenite to urtite (Veselovsky *et al.* 1990).

Commonly, albitite, albite aegirinite and microcline veins cutting the loparite-bearing rocks of the differentiated complex also contain loparite. Some of these veins are gradational through albitized rocks, with relict trachytic textures, to unaltered differentiated complex rocks. Loparite crystals in these veins are identical in morphology to those occurring in the host lujavrites. These loparite samples may be regarded as either relict phases that have persisted in an unaltered state during alteration (metasomatism) of the host rocks by deuteric alkaline solutions, or a new generation of loparite produced by reaction of the metasomatizing fluids with pre-existing loparite-bearing rocks. If the latter hypothesis is correct, loparite in the veins should differ in composition from that occurring in the host rocks.

In the eudialyte lujavrite and poikilitic nepheline syenite, loparite is commonly, although not invariably, present as an accessory phase, and does not occur as laterally continuous layers. The poikilitic nosean and sodalite syenites lack loparite, although a pegmatitic facies of this rock commonly contains significant amounts of loparite. In these pegmatites, loparite is found entirely in contact zones composed of microcline, nepheline and early prismatic aegirine, the assemblage having formed during the early, relatively high-temperature stage of pegmatite formation.

ANALYTICAL TECHNIQUES

All mineral compositions were determined by X-ray energy-dispersion spectrometry (EDS) using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm MnK) at Lakehead University. EDS spectra of loparite crystals

were acquired for 300 seconds, those of lueshite for 100 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–SEMQANT software package. Full ZAF corrections were applied to the raw X-ray data. The following well-characterized standards were employed for the determination of loparite compositions: Khibina loparite (Na, La, Ce, Pr, Nd, Nb, Ti), Magnet Cove perovskite (Ca, Fe), synthetic SrTiO₃ (Sr), BaSiO₃ (Ba), and 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 LOPARITE FROM POIKILITIC NEPHELINE SYENITE AND JUVITE FROM THE DIFFERENTIATED COMPLEX, LOVOZERO

Wt.%	1	2	3	4	5	6
Nb ₂ O ₅	6.60	5.96	5.91	5.94	5.71	6.22
Ta ₂ O ₅	0.37	0.40	0.93	0.83	0.80	0.82
TiO ₂	40.97	41.05	41.15	41.33	39.66	41.12
FeO	0.54	0.48	0.70	0.57	0.50	0.58
ThO ₂	0.41	0.78	0.43	0.46	0.34	0.34
La ₂ O ₃	9.95	9.78	11.90	11.62	11.29	12.02
Ce ₂ O ₃	19.90	19.73	20.58	19.75	19.50	20.35
Pr ₂ O ₃	2.15	2.68	1.23	1.08	3.79	1.14
Nd ₂ O ₃	5.85	6.01	4.08	4.08	4.26	4.18
CaO	4.34	5.17	4.77	5.38	4.94	4.83
SrO	0.85	1.12	1.10	1.20	0.96	1.18
Na ₂ O	7.33	7.17	7.14	7.61	7.33	7.56
Total	99.23	100.33	100.11	99.78	98.99	100.40
Structural formulae based on 3 atoms of oxygen						
Nb	0.087	0.078	0.078	0.078	0.076	0.081
Ta	0.003	0.003	0.007	0.006	0.006	0.006
Ti	0.898	0.894	0.898	0.897	0.882	0.893
Fe	0.013	0.012	0.017	0.014	0.012	0.014
Th	0.003	0.005	0.003	0.003	0.002	0.002
La	0.107	0.105	0.127	0.124	0.123	0.128
Ce	0.212	0.209	0.219	0.209	0.211	0.215
Pr	0.023	0.028	0.013	0.011	0.041	0.012
Nd	0.061	0.062	0.042	0.042	0.045	0.043
Ca	0.135	0.160	0.148	0.163	0.157	0.149
Sr	0.014	0.019	0.019	0.020	0.017	0.020
Na	0.414	0.403	0.402	0.426	0.420	0.423
Mol.% End-members						
CaThO ₃	0.37	0.67	0.38	0.39	0.29	0.29
SrTiO ₃	1.94	2.46	2.48	2.60	2.10	2.59
NaNbO ₃	6.07	5.31	5.67	5.45	5.29	5.74
Ce ₂ Ti ₂ O ₇	7.97	8.11	8.47	4.27	7.91	6.15
CaTiO ₃	17.94	20.33	19.45	20.78	19.71	19.28
Loparite	65.71	63.11	63.55	66.50	64.69	65.95

Compositions 1, 2: core and rim of loparite, poikilitic syenite, Mt. Aluiv; 3, 4: core and rim of loparite from endocontact juvite, Little Punkaruiv Mt.; 5, 6: core and rim of loparite, pegmatite vein in endocontact juvite (nos. 3 & 4), Little Punkaruiv Mt. All data obtained in this investigation. Total Fe expressed as FeO.

With few exceptions, in which the composition varies dramatically within the same grain, back-scattered electron imagery of the samples studied, at the low beam currents used for the analyses, did not reveal any heterogeneity in the distribution of the major elements. However, several analyses were undertaken at different points within each apparently homogeneous grain of loparite grain to ensure that any zoning that results in a similar average atomic number was recognized.

Mitchell (1996) has demonstrated that the compositions of most naturally occurring perovskite-group minerals can be expressed in terms of relatively few end-member compositions, namely: CaTiO_3 (perovskite), $\text{Na}(\text{REE})\text{Ti}_2\text{O}_6$ (loparite), NaNbO_3

(lueshite), SrTiO_3 (tausonite), PbTiO_3 (macedonite), $\text{Ca}_2\text{Fe}^{3+}\text{NbO}_6$ (lattrappite), $\text{Ca}_2\text{Nb}_2\text{O}_7$, $\text{REE}_2\text{Ti}_2\text{O}_7$, CaThO_3 , CaZrO_3 , KNbO_3 and BaTiO_3 . Compositional data were recalculated into these perovskite-group end members using an APL program for PC following methods suggested by Mitchell (1996).

The majority of the loparite and lueshite grains examined in this study were found to be essentially members of the $\text{CaTiO}_3 - \text{Na}(\text{REE})\text{Ti}_2\text{O}_6 - \text{NaNbO}_3$ system. They contain low levels of the SrTiO_3 (tausonite), CaThO_3 , $(\text{REE})\text{Ti}_2\text{O}_7$ and other perovskite-type end members. Accordingly, the ternary system (mol.%) perovskite - loparite - lueshite is used to illustrate the compositional variation of the minerals analyzed (Figs. 2-7).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM ROCKS OF THE DIFFERENTIATED COMPLEX, LOVOZERO

Wt.%	1	2	3	4	5	6	7	8	9	10
Nb_2O_5	7.24	7.95	7.60	7.60	9.88	9.61	11.49	9.73	10.91	11.14
Ta_2O_5	1.09	0.96	0.88	1.15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TiO_2	40.68	39.07	39.80	40.31	39.31	40.01	38.98	39.45	38.33	35.14
FeO	0.22	0.33	0.39	0.34	0.32	0.19	0.16	0.25	0.08	0.22
ThO_2	0.40	0.40	0.46	0.48	0.72	0.99	0.58	1.05	0.87	1.18
La_2O_3	11.53	11.23	11.28	10.65	8.86	9.21	8.57	9.20	8.20	8.67
Ce_2O_3	19.55	19.45	19.58	19.01	17.78	17.34	17.51	18.35	17.08	17.14
Pr_2O_3	2.13	2.78	2.54	2.15	2.70	1.68	2.14	2.00	2.60	2.03
Nd_2O_3	4.23	4.37	3.94	4.19	4.05	3.61	4.37	3.99	4.95	3.79
CaO	4.45	4.14	4.11	4.56	4.42	4.52	4.77	4.46	3.21	1.88
SrO	2.06	2.09	2.05	2.30	3.31	3.35	3.52	2.94	4.38	3.08
Na_2O	7.32	7.82	7.40	7.88	8.03	7.89	8.04	7.84	7.76	9.70
Total	100.82	100.59	100.04	100.62	99.36	98.40	100.14	99.27	98.37	98.82
Structural formulae based on 3 atoms of oxygen										
Nb	0.094	0.105	0.100	0.099	0.129	0.126	0.149	0.128	0.145	0.156
Ta	0.009	0.008	0.007	0.009	-	-	-	-	-	-
Ti	0.883	0.857	0.873	0.874	0.856	0.872	0.839	0.860	0.848	0.820
Fe	0.005	0.008	0.010	0.008	0.008	0.005	0.004	0.006	0.002	0.006
Th	0.003	0.003	0.003	0.003	0.005	0.007	0.004	0.007	0.006	0.008
La	0.123	0.121	0.121	0.113	0.095	0.098	0.091	0.098	0.089	0.099
Ce	0.207	0.208	0.209	0.201	0.188	0.184	0.184	0.195	0.184	0.195
Pr	0.022	0.030	0.027	0.023	0.029	0.018	0.022	0.021	0.028	0.023
Nd	0.044	0.046	0.041	0.043	0.042	0.038	0.045	0.041	0.052	0.042
Ca	0.138	0.129	0.129	0.141	0.137	0.140	0.146	0.139	0.101	0.096
Sr	0.035	0.035	0.035	0.038	0.056	0.056	0.058	0.049	0.075	0.055
Na	0.404	0.442	0.419	0.440	0.451	0.443	0.446	0.441	0.443	0.583
Mol.% End-members										
CaThO_3	0.35	0.34	0.41	0.41	0.62	0.87	0.50	0.92	0.79	0.84
SrTiO_3	4.62	4.59	4.63	5.01	7.28	7.50	7.71	6.56	10.15	5.59
NaNbO_3	6.91	7.29	7.16	7.04	8.47	8.39	9.81	8.47	9.86	15.75
$\text{Ce}_2\text{Ti}_2\text{O}_7$	9.48	7.17	8.73	4.61	3.14	2.00	4.30	4.22	5.63	-
CaTiO_3	18.10	16.44	16.74	17.95	17.34	17.82	18.80	17.47	12.95	5.46
Loparite	60.54	64.17	62.34	64.98	63.15	63.42	58.88	62.36	60.62	72.36

Compositions 1, 2 and 3, 4: cores and rims of loparites from successive lujavrite and urtite layers, respectively, Great Punkaruiv Mt.; 5-6; 7-8; 9-10: cores and rims of loparites from successive foyaitite, melanopheline syenite and urtite layers, respectively, Mt. Alluaiv. All data obtained in this investigation. Total Fe expressed as FeO; n.a. = not analyzed.

COMPOSITIONAL VARIATION

Only a few chemical compositions of loparite from Lovozero have been previously published. These data were obtained primarily by wet-chemical bulk analyses of loparite from the differentiated complex and pegmatites. The compositions of loparite from samples of poikilitic nepheline syenite, eudialyte lujavrite and metasomatic rocks have previously only been cursorily investigated. Vlasov *et al.* (1966), Semenov (1972), and Ifantopulo & Osokin (1979) have indicated that from the bottom units of the differentiated complex upward, loparite compositions evolve by becoming enriched in Sr, Th, Nb, and Ta, with concomitant depletion in the rare-earth elements and Ti.

Representative compositions of loparite obtained in this work are given in Tables 1–5. Although our data are in general agreement with the bulk compositional data obtained in earlier studies, they differ in that we did not find any significant Si or Al contents in any of the loparite examined. We attribute previous reports of the presence of these elements to the occurrence of micro-inclusions of silicates (nepheline, aegirine, *etc.*) in the material used for bulk analysis. Data obtained in the present work thus are considered to be more accurate than those presented in earlier studies, in that structural formulae are satisfactory, and assignment of cations to end-member components typically results in less than 1 or 5% departure from the ideal occupancy of the perovskite *A* and *B* site,

TABLE 3. REPRESENTATIVE COMPOSITIONS OF LOPARITE AND LUESHITE FROM ROCKS OF THE DIFFERENTIATED COMPLEX, LOVOZERO

Wt. %	1	2	3	4	5	6	7	8	9	10
Nb ₂ O ₅	9.46	11.33	7.77	22.88	27.48	10.81	74.70	9.77	8.76	9.30
Ta ₂ O ₅	0.63	0.64	0.62	n.a.	n.a.	n.a.	n.d.	n.a.	0.57	n.a.
TiO ₂	39.47	38.05	40.88	31.81	29.73	39.81	2.48	40.30	41.14	41.00
FeO	0.18	0.08	0.22	n.d.	0.12	0.18	0.18	0.11	0.36	0.28
ThO ₂	0.81	1.24	0.82	1.06	0.93	1.13	0.09	0.56	0.54	1.20
La ₂ O ₃	8.78	9.06	9.34	9.91	9.52	8.80	n.d.	9.60	9.83	9.23
Ce ₂ O ₃	17.61	17.90	17.95	16.82	15.20	17.25	0.25	19.03	19.46	18.04
Pr ₂ O ₃	1.63	2.39	1.74	0.75	1.18	1.89	0.17	2.42	2.11	1.48
Nd ₂ O ₃	5.05	5.75	6.30	2.07	1.91	4.05	n.d.	3.67	4.15	4.36
CaO	4.47	2.23	3.99	1.57	1.41	3.89	0.05	4.24	3.91	4.34
SrO	3.40	3.55	3.50	1.69	1.86	3.64	0.38	3.13	2.31	3.23
Na ₂ O	7.45	8.26	7.63	10.41	10.58	8.27	17.15	8.03	7.96	7.80
Total	98.95	100.48	100.74	98.84	99.92	99.16	98.98	100.85	101.11	100.24
Structural formulae based on 3 atoms of oxygen										
Nb	0.124	0.149	0.101	0.301	0.357	0.141	0.961	0.126	0.113	0.119
Ta	0.005	0.005	0.005	-	-	-	-	-	0.004	-
Ti	0.864	0.835	0.884	0.696	0.642	0.853	0.053	0.864	0.880	0.879
Fe	0.004	0.002	0.005	-	0.003	0.004	0.004	0.003	0.009	0.008
Th	0.005	0.008	0.005	0.007	0.006	0.007	0.006	0.004	0.004	0.008
La	0.094	0.098	0.099	0.106	0.101	0.094	-	0.101	0.103	0.097
Ce	0.188	0.191	0.189	0.179	0.160	0.183	0.003	0.199	0.203	0.188
Pr	0.017	0.025	0.018	0.008	0.012	0.020	0.002	0.025	0.022	0.015
Nd	0.053	0.060	0.065	0.022	0.019	0.042	-	0.037	0.042	0.044
Ca	0.139	0.070	0.123	0.049	0.043	0.120	0.002	0.129	0.119	0.133
Sr	0.057	0.060	0.058	0.029	0.031	0.061	0.006	0.052	0.038	0.053
Na	0.420	0.468	0.426	0.586	0.589	0.484	0.946	0.444	0.439	0.431
Mol. % End-members										
CaThO ₃	0.72	1.14	0.71	1.03	0.94	0.99	0.21	0.48	0.48	1.05
SrTiO ₃	7.72	8.32	7.76	4.20	4.79	8.16	0.63	6.86	5.19	7.23
NaNbO ₃	8.71	10.70	7.04	22.17	27.60	9.45	98.12	8.35	7.97	8.12
Ce ₂ Ti ₂ O ₇	6.12	6.36	5.12	3.17	6.99	1.59	-	4.39	4.88	3.43
CaTiO ₃	18.03	8.51	15.63	6.18	5.77	15.13	-	16.69	15.75	16.90
Loparite	58.70	64.97	63.73	63.26	53.91	64.68	1.04	63.23	65.74	63.25

Compositions 1: core; 2-3: rim of loparite, foyaite, Mt. Karnasurt; 4-6: core, intermediate zone and rim of loparite from trachytoidal foyaite, Mt. Selsurt; 7: lueshite from natrolitized foyaite, Mt. Selsurt; 8-10: loparite from lujavrite, lujavrite-hosted albitite and microclinite, respectively, Mt. Selsurt. All data obtained in this investigation. Total Fe expressed as FeO; n.a. = not analyzed; n.d. = not detected.

TABLE 4. REPRESENTATIVE COMPOSITIONS OF LOPARITE AND LUESHITE FROM EUDIALYTE LUJAVRITE

Wt.%	1	2	3	4	5	6	7
Nb ₂ O ₅	12.97	14.55	11.83	11.62	45.29	16.03	12.08
Ta ₂ O ₅	n.a.	n.a.	n.a.	n.a.	n.a.	0.74	0.82
TiO ₂	37.39	36.67	39.01	39.16	19.35	36.35	38.78
FeO	0.19	0.03	n.d.	0.25	n.d.	0.04	n.d.
ThO ₂	1.46	0.92	1.30	1.02	0.42	0.59	0.88
La ₂ O ₃	7.70	7.84	8.67	8.11	6.57	8.39	8.92
Ce ₂ O ₃	15.25	15.76	16.39	16.63	8.62	15.44	17.11
Pr ₂ O ₃	1.66	2.34	1.06	1.49	0.69	1.32	1.51
Nd ₂ O ₃	4.20	4.48	3.94	3.69	1.29	3.58	3.87
CaO	2.85	3.07	3.09	2.81	0.67	3.12	2.79
SrO	6.82	7.05	6.15	6.36	2.16	5.05	4.52
Na ₂ O	8.47	7.80	7.80	8.02	13.68	8.56	8.51
Total	98.96	100.51	99.24	99.15	98.76	99.23	99.77
Structural formulae based on 3 atoms of oxygen							
Nb	0.171	0.190	0.155	0.152	0.584	0.209	0.157
Ta	-	-	-	-	-	0.008	0.006
Ti	0.821	0.798	0.850	0.853	0.415	0.789	0.841
Fe	0.005	0.004	-	0.006	-	0.001	-
Th	0.010	0.006	0.009	0.007	0.003	0.004	0.008
La	0.083	0.084	0.093	0.087	0.069	0.089	0.095
Ce	0.163	0.167	0.174	0.176	0.090	0.163	0.181
Pr	0.018	0.025	0.011	0.016	0.007	0.014	0.016
Nd	0.044	0.043	0.041	0.038	0.013	0.037	0.040
Ca	0.099	0.095	0.096	0.087	0.021	0.096	0.086
Sr	0.116	0.118	0.103	0.107	0.036	0.085	0.076
Na	0.479	0.438	0.438	0.450	0.757	0.479	0.476
Mol.% End-members							
CaThO ₃	0.98	0.82	1.18	0.92	0.45	0.54	0.80
SrTiO ₃	11.66	16.09	14.19	14.60	5.84	11.84	10.63
NaNbO ₃	17.28	12.94	10.64	10.40	47.70	15.06	11.27
Ce ₂ Ti ₂ O ₇	-	7.58	3.63	1.91	0.85	4.12	1.97
CaTiO ₃	8.02	12.12	12.00	11.00	2.90	12.97	11.08
Loparite	62.06	50.44	58.36	61.16	42.27	55.48	64.48

Compositions: 1 core, 2 - 3 rim of irregularly zoned crystal, Mt. Kamasurt; 4 loparite rimmed by 5, lueshite, Mt. Kamasurt; 6, 7: core and rim of loparite from the uppermost horizons of the eudialyte lujavrite suite, Mt. Alluav. All data were obtained in this investigation. Total Fe expressed as FeO; n.a. = Not analyzed; n.d. = not detected.

respectively.

Stage 1: poikilitic nepheline syenites

Anhedral grains of loparite from poikilitic nosean- and sodalite-bearing nepheline syenites are relatively uniform in composition and do not show any core-to-rim zonation. They are calcian niobian loparite-(Ce) with Ca and Nb contents in the ranges 4.3–5.2 wt.% CaO and 6.0–7.0 wt.% Nb₂O₅, respectively (Table 1, Fig. 2). In these rocks, the loparite is poor in Sr (0.8 – 1.2 wt.% SrO), Th (0.4 – 0.8 wt.% ThO₂) and Ta (0.4 – 0.6 wt.% Ta₂O₅).

Pegmatite veins genetically related to the nosean- and sodalite-bearing nepheline syenites contain primarily calcian niobian loparite-(Ce). Many loparite grains are compositionally homogeneous (Table 5, anal. 8–10, Fig. 3). However, some exhibit core-to-rim enrichment in Na and Nb, coupled with depletion in REE, Ca, and Ti (Table 5, anal. 1–5, Fig. 3), whereas

others display the opposite compositional trend (Table 5, anal. 6, 7). Variations in Sr, Th and Ta contents do not correlate with changes in major-element contents and may differ in the sense of enrichment or depletion in loparite, which exhibits generally similar trends of zonation in Na and Nb enrichment (*cf.* compositions 1 and 3–5 in Table 5).

Stage 2: rocks of the differentiated complex

Loparite from juvite occurring near the contact of the complex with the country rocks (endocontact juvite) do not show any pronounced core-to-rim zonation. They are calcian niobian loparite-(Ce), with Ca and Nb contents in the ranges 4.8 – 5.4 wt.% CaO and 5.7 – 6.2 wt.% Nb₂O₅, respectively (Table 1, Figs. 2, 4). The composition overlaps that of loparite from the poikilitic nepheline syenite. Minor-element contents (1.0 – 1.2 wt.% SrO, 0.1 – 0.5 wt.% ThO₂, 0.8 – 1.2 wt.% Ta₂O₅) also are similar, with Ta contents being slightly higher in the samples from the endocontact juvites. In a “comb-structured” pegmatite vein developed in juvite at Little Punkaruav Mtn., loparite is compositionally very similar to calcian niobian loparite from the host rock (Table 1, *cf.* anal. 3 and 4, 5 and 6). Typically, the rim of these loparite grains is enriched in REE and Ti, and depleted in Ca, compared to the core, whereas Sr and Nb contents remain constant (Fig. 4).

Loparite grains in a given urtite stratum and even in the same hand-specimen may or may not be zoned. Individual zoned grains exhibit distinct core-to-rim zonation patterns (Fig. 5). Most of these loparite grains are calcian niobian loparite-(Ce), with Ca and Nb contents in the ranges 3.7 – 4.9 wt.% CaO and 8.9 – 10.1 wt.% Nb₂O₅, respectively (Fig. 5). Sr, Th and Fe contents vary insignificantly within the ranges of 3.1 – 3.8% SrO, 0.6 – 1.2% ThO₂ and 0 – 0.4% FeO, respectively. One of the grains examined shows a strong compositional variation from calcian niobian loparite toward niobian calcian loparite, with Sr contents increasing to about 4.5 wt.% SrO in the rim (Table 2, Fig. 5).

In foyaitite, loparite exhibits the same compositional features as found in loparite from urtite, namely various degrees of compositional variation and distinct patterns of core-to-rim zonation in loparite grains from the same samples. Most of these loparite grains contain 3.4 – 5.6% CaO, 7.2 – 10.4% Nb₂O₅, 3.0 – 3.6% SrO and 0.6 – 2.3% ThO₂ (Fig. 2, Table 2).

In the most evolved foyaites, *i.e.*, trachytoidal types containing significant amounts of murmanite, lamprophyllite, nenadkevichite and other minerals indicative of hyperagpaitic conditions of formation (Khomyakov 1995), the loparite grains are strongly zoned (Table 3, anal. 1–6, Fig. 2). In one of the foyaitite samples studied, lueshite is found as a late-stage phase occurring between microcline and natrolitized

TABLE 5. REPRESENTATIVE COMPOSITIONS OF LOPARITE FROM PEGMATITES OF THE POIKILITIC NOSEAN AND SODALITE SYENITES

Wt.%	1	2	3	4	5	6	7	8	9	10
Nb ₂ O ₅	7.56	17.58	7.53	8.26	12.96	15.27	10.89	6.67	6.87	6.83
Ta ₂ O ₅	0.82	1.05	0.75	0.75	0.55	0.34	0.80	0.64	0.53	0.16
TiO ₂	41.76	36.03	42.12	41.21	38.92	37.68	39.77	42.23	42.05	42.28
FeO	0.30	n.d.	0.22	0.12	n.d.	0.10	0.10	0.30	0.14	0.31
ThO ₂	0.58	1.05	0.70	0.92	0.98	0.88	1.10	0.60	0.55	0.50
La ₂ O ₃	9.47	8.07	8.92	8.86	7.50	7.39	8.16	9.48	9.80	9.33
Ce ₂ O ₃	19.76	15.98	18.23	18.40	17.36	16.67	17.76	19.09	19.72	19.11
Pr ₂ O ₃	1.65	1.46	1.65	1.62	1.58	1.47	1.51	1.63	1.77	1.78
Nd ₂ O ₃	4.80	3.80	4.64	4.58	4.20	3.95	4.36	4.38	4.42	4.51
CaO	4.98	3.30	5.14	4.47	4.90	4.95	4.60	5.18	4.56	5.51
SrO	0.94	2.75	3.10	2.83	2.72	2.97	2.72	2.17	1.45	2.14
Na ₂ O	7.77	9.22	7.56	7.89	8.14	8.27	7.94	7.38	7.74	7.31
Total	100.34	100.30	100.90	99.81	99.89	99.91	98.71	99.75	99.60	99.77
Structural formulae based on 3 atoms of oxygen										
Nb	0.097	0.226	0.097	0.107	0.166	0.196	0.141	0.086	0.089	0.088
Ta	0.006	0.008	0.006	0.006	0.004	0.003	0.006	0.005	0.004	0.001
Ti	0.894	0.771	0.898	0.887	0.832	0.803	0.856	0.908	0.907	0.909
Fe	0.007	-	0.005	0.003	0.002	0.002	0.002	0.007	0.003	0.007
Th	0.004	0.007	0.005	0.006	0.006	0.006	0.007	0.004	0.004	0.003
La	0.099	0.085	0.093	0.094	0.079	0.077	0.086	0.100	0.104	0.098
Ce	0.206	0.167	0.189	0.193	0.181	0.173	0.186	0.200	0.207	0.199
Pr	0.017	0.015	0.017	0.017	0.016	0.015	0.016	0.017	0.019	0.018
Nd	0.049	0.039	0.047	0.047	0.043	0.040	0.045	0.045	0.045	0.046
Ca	0.152	0.101	0.156	0.137	0.149	0.150	0.141	0.159	0.140	0.168
Sr	0.016	0.045	0.051	0.047	0.045	0.049	0.045	0.036	0.024	0.035
Na	0.429	0.509	0.416	0.438	0.448	0.455	0.440	0.409	0.431	0.403
Mol. % End-members										
CaThO ₃	0.51	0.97	0.60	0.80	0.87	0.79	0.98	0.52	0.48	0.43
SrTiO ₃	2.09	6.50	6.77	6.29	6.17	6.79	6.19	4.80	3.24	4.68
NaNbO ₃	6.94	16.79	6.79	7.55	11.75	13.78	10.09	6.08	6.26	5.91
Ce ₂ Ti ₂ O ₇	4.59	3.28	2.31	2.50	4.17	5.10	4.02	4.36	3.75	4.68
CaTiO ₃	19.97	13.45	20.13	17.55	19.67	20.11	18.36	20.64	18.34	21.84
Loparite	65.90	59.00	62.40	65.31	57.36	53.43	60.36	63.60	67.93	62.47

Compositions: 1, 2: core and rim of a zoned crystal, Little Punkaruiv Mt.; 3, 4, 5: core, intermediate zone and rim of a zoned crystal, Mt. Leppke-Nel'm; 6, 7: core and rim of a zoned crystal, Mt. Leppke-Nel'm; 8, 9, 10: "intermediate" zones and margin of a zonation-free crystal, Great Punkaruiv Mt. All data were obtained in this investigation. Total Fe expressed as FeO; n.d. = not determined.

nepheline (Table 3, anal. 7). Our observations support a previous report of the occurrence of niobian loparite in natrolitized urtite from Mt. Leppkhe-Nel'm (Semenov 1972).

There is a continuous layer of melanocratic nepheline syenite ("malignite") occurring between foyaitite (juvite) and urtite that can be traced laterally practically through the whole massif; it is used as a correlation horizon within the differentiated complex. In this rock, loparite contents locally reach 10–12 vol.%. In terms of composition, the loparite from this melanocratic nepheline syenite unit does not differ significantly from that of loparite occurring in the underlying foyaitite or the overlying urtite (Table 2).

Its composition corresponds to the calcian niobian loparite-(Ce) which, where zoned, shows diverse patterns of core-to-rim zonation from one grain to the next (Fig. 2). Ca and Nb contents vary in the range 3.5 – 4.9 wt.% CaO and 7.7 – 11.5 wt.% Nb₂O₅, respectively.

The loparite in the lujavrite is calcian niobian loparite-(Ce) that rarely shows any zonation (Fig. 5, Table 2). It contains 3.3 – 5.8% CaO, 7.3 – 12.5% Nb₂O₅, 2.5 – 4.3% SrO and 0.5 – 1.2% ThO₂. Its composition at the top of a macrorhythmic unit in lujavrite is similar to that occurring in the overlying urtite of the next unit (Table 2, anal. 1–4).

In microcline, aegirinite, albitite and modally

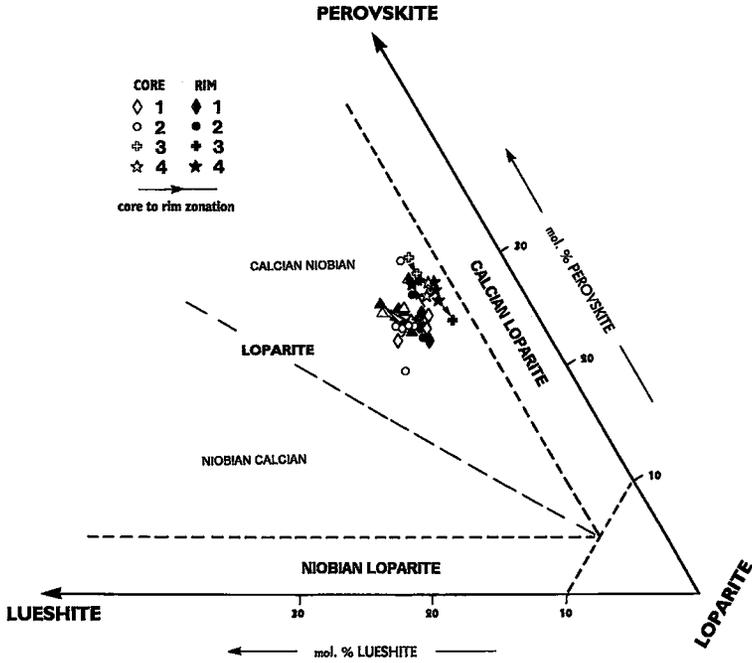


FIG. 4. Compositions (mol.%) of loparite from metasomatic rocks and pegmatite vein in juvite: 1, 2 and 3: albitite, microclinite and host lujavrite, respectively, Mt. Selsurt, 4 and 5: pegmatite vein and host juvite, Little Punkaruaiiv Mtn.

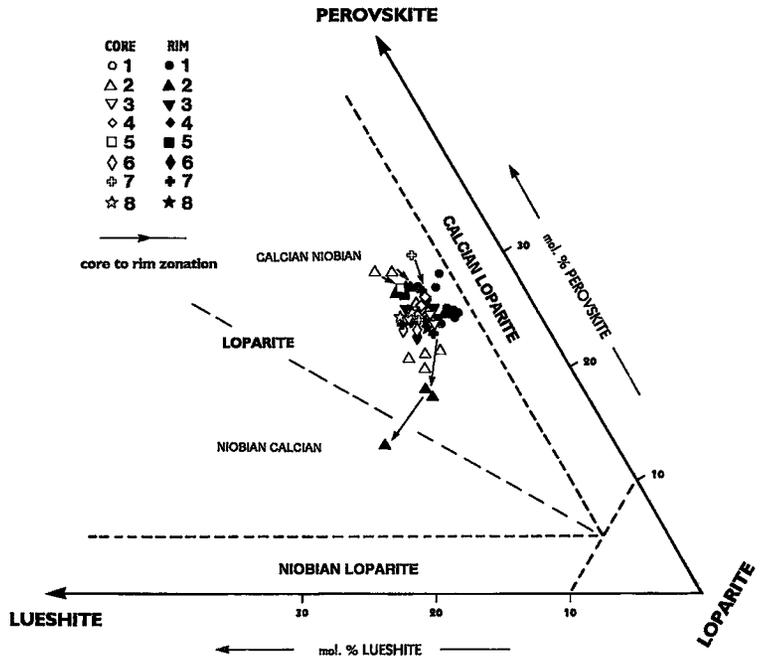


FIG. 5. Compositions (mol.%) of loparite from poikilitic nepheline syenites and rocks of the differentiated complex: 1 poikilitic nepheline syenite, Mt. Alluaiv, 2 urtite, Mt. Alluaiv, 3 urtite, Great Punkaruaiiv Mtn., 4 lujavrite, Great Punkaruaiiv Mtn., 5 lujavrite, Mt. Karnasurt, 6 lujavrite, Mt. Karnasurt, 7 lujavrite, Mt. Selsurt, 8 lujavrite, Mt. Kuetnyuchorr.

transitional vein-rocks (*e.g.*, microcline albitite or aegirine albitite), accessory loparite has a composition similar to that of loparite from the rocks of the differentiated complex (Table 3). Trends of core-to-rim zonation differ from one grain to another within the same sample (Fig. 4).

Stage 3: eudialyte lujavrite

In the eudialyte lujavrite, the loparite is strongly zoned. Two principal types of core-to-rim zonation are found:

(1) In the uppermost eudialyte lujavrite facies at Mt. Alluaiv, loparite compositions evolved by enrichment in REE and Ti, and depletion in Nb and Sr (Fig. 6, Table 4). This trend of zonation is similar to that observed in niobian loparite from pegmatite veins in the melteigite – urtite – rischorrite series of the Khibina massif (Mitchell *et al.* 1996).

(2) In the bottom facies of eudialyte lujavrite at Mt. Karnasurt, some loparite grains have a rim enriched in the lueshite end-member and contain up to 13.7 wt.% Na₂O and 45.4 wt.% Nb₂O₅. Thus, these minerals evolved from calcian niobian or niobian calcian loparite toward cerian lueshite during the course of crystallization (Fig. 6). Such loparite grains coexist with irregularly zoned loparite of less variable composition (Table 4). In general, loparite from eudialyte lujavrite contains more Nb (10.9 – 45.4 wt.% Nb₂O₅) and Sr (up to 7.3 wt.% SrO) and less Ca (0.3 – 3.1 wt.%

CaO) and LREE (17.2 – 31.4 wt% total [REE]₂O₃), than loparite from the poikilitic nepheline syenites and rocks of the differentiated complex.

DISCUSSION

In the ternary system perovskite – lueshite – loparite, the majority of the compositions of perovskite-group minerals from the intrusive, metasomatic rocks and pegmatites of the Lovozero complex correspond to calcian niobian loparite-(Ce), with some compositions being niobian calcian loparite-(Ce). Lueshite is found as a late-stage mineral in natrolitized foyaite at Mt. Alluaiv, and as a mantle on loparite in eudialyte lujavrite at Mt. Karnasurt.

The general trend of compositional evolution is essentially from calcian niobian loparite (poikilitic nepheline syenites and differentiated complex) through niobian calcian loparite (differentiated complex and eudialyte lujavrite) to cerian lueshite (eudialyte lujavrite) (Fig. 7). The Sr content of loparite also increases according to this sequence of intrusion, with loparite from eudialyte lujavrites having the highest Sr content (up to 16 mol.% SrTiO₃).

The similarity in composition of loparite within and between successive macrorhythmically layered units of the differentiated complex (foyaite or lujavrite and urtite) suggests that each unit was produced from compositionally similar batches of magma. The absence of strong cryptic compositional variation and

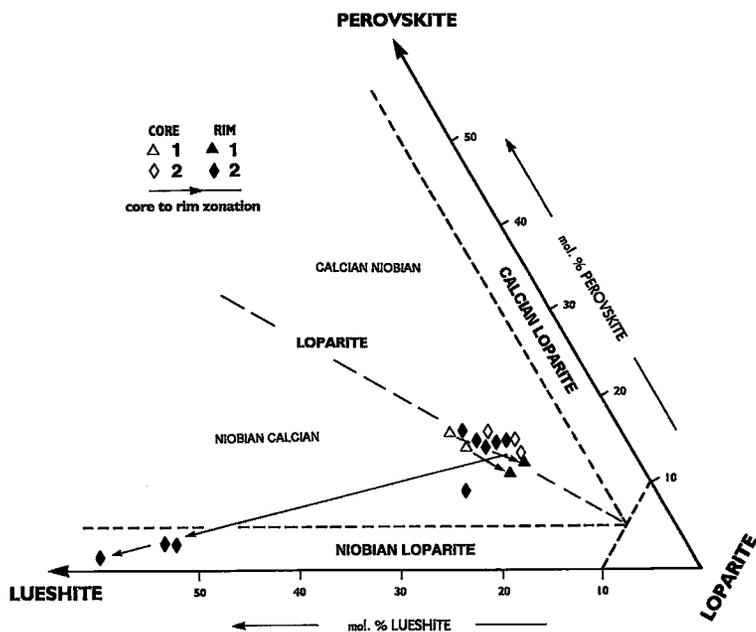


FIG. 6. Compositions (mol.%) of loparite and lueshite from eudialyte lujavrites: 1 Mt. Alluaiv, 2 Mt. Karnasurt.

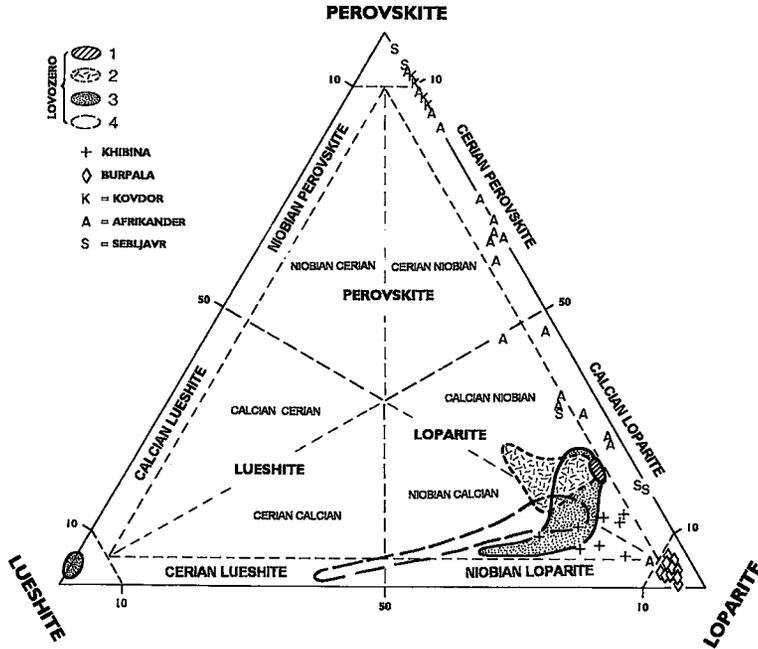


FIG. 7. Composition (mol.%) of loparite and lueshite from the Lovozero complex compared with that of loparite from the Khibina and Burpala alkaline complexes, and cerian perovskite from the Kovdor, Afrikander and Sebljavr alkaline ultrabasic complexes (all data obtained in this study): 1-4 Lovozero; 1 poikilitic nepheline syenites, 2 pegmatites of the poikilitic sodalite and nosean syenites, 3 differentiated complex, 4 eudialyte lujavrites.

lueshite-rich members of the lueshite-lopaprite solid-solution series is particularly notable. These data might indicate that the formation of *in situ* modal layering was not accompanied by strong chemical differentiation and that the parental magma was strongly enriched in REE at the time of emplacement. Alternatively, the diverse intergrain compositions and various patterns of core-to-rim zonation exhibited by individual crystals from the same sample might result from a combination of magmatic re-equilibration and metasomatic-hydrothermal processes. The fluids responsible for the latter might be derived from the magma and thus be essentially deuteric in origin. Further discussion of these problems is beyond the scope of this paper, as detailed modern mineralogical investigations of the macrorhythmic layered units are required.

The observation that loparite in albitite, microcline and other vein-like rocks is similar in crystal morphology and composition to that occurring in the host rocks of the differentiated complex suggests that loparite in the former was "inherited" from precursor rocks that have undergone metasomatic alteration. If

this hypothesis is correct, it may be concluded that loparite is stable under conditions of alkaline metasomatism.

The weak compositional trends found among loparite samples in the Lovozero suite coincides with the order of crystallization of the intrusive series as proposed by most petrologists (Eliseev & Fedorov 1953, Bussen & Sakharov 1972, Borutsky 1988). This general trend is in agreement with experimental data on the crystallization of loparite in the loparite-nepheline and lujavrite-lopaprite pseudobinary systems (Veksler *et al.* 1985, Veksler & Tepteleev 1990), which indicate that, with decreasing temperature, loparite become depleted in REE and enriched in Sr and Nb. Thus, our data are in accord with the magmatic origin of the loparite mineralization in the Lovozero intrusive series, as proposed by Kogarko *et al.* (1984) and Veksler *et al.* (1985).

It is significant that a wide range of perovskite-group minerals was not encountered in this very large layered intrusion. Lueshite is found in the eudialyte lujavrite, suggesting that Na and Nb were concentrated in the most evolved batches of magma. However, even

in these rocks, lueshite is not abundant and appears to be formed by reaction of earlier-formed loparite with residual fluids. Less evolved, Ca-rich, REE-poor members of the perovskite–loparite solid-solution series are notably absent from all of the rocks examined. This observation suggests that either all of the rocks currently exposed at Lovozero are relatively evolved members of the complex or perovskite-group minerals are not sensitive indicators of the differentiation processes. This latter hypothesis is not tenable given that perovskite-group minerals in other alkaline complexes exhibit wide ranges in composition (Mitchell 1996), and that the compositional trends observed in loparite in this work, although limited, are real and correspond with the postulated stages of evolution of the parental magma. It is significant that the loparite-bearing rocks at Lovozero are hyperagpaitic syenites (Khomyakov 1995), in which the associated minerals have near-end-member compositions and are apparently highly evolved (Arzamastsev 1994). Consequently, it is suggested that the loparite compositions found lie close to, or at, the termination of the evolutionary trend of primary magmatic perovskite-group minerals. Further, it is postulated that less-evolved perovskite-group minerals may be expected to occur in the plutonic rocks that must comprise the inaccessible infrastructure of the complex.

Loparite from Lovozero is generally richer in Nb and poor in Ca than that from the Khibina pluton (Fig. 7). The unusual Th-rich compositions reported for Khibina loparite (Borodin & Kazakova 1954) are not found at Lovozero. Loparite from carbonatite-bearing ultramafic complexes of the Kola Peninsula and the Burpala alkaline massif (northern Transbaikalia) are generally poorer in Nb than those from Lovozero. The samples of loparite from the Kovdor, Afrikander and Sebljavr ultramafic complexes are essentially members of the perovskite–loparite solid-solution series, whereas at Burpala, the loparite is Ca-, Sr-, and Nb-poor, and approaches the ideal end-member composition (Fig. 7).

CONCLUSIONS

(1) The majority of the loparite in the Lovozero complex is calcian niobian loparite-(Ce), with relatively low levels of Sr and Th, and negligible Ta contents. Niobian calcian loparite-(Ce) also is present but is less common. Lueshite was observed as a rim surrounding a core of loparite in the eudialyte lujavrite and as a late-stage phase in natrolitized foyaite of the differentiated complex.

(2) The general trend of compositional evolution of loparite from the major intrusive series of the complex is from calcian niobian loparite-(Ce) through niobian calcian loparite-(Ce) to cerian lueshite. This corresponds with the proposed order of formation of

the Lovozero intrusive series and with experimental studies of loparite crystallization in the system nepheline–loparite.

(3) Loparite in albitite, microcline, aegirinite and modally transitional rocks, which occur as veins cutting rocks of the differentiated complex, is not a product of metasomatism, but a relict mineral that was stable under conditions of alkaline metasomatism.

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