

## ON THE DEVELOPMENT OF NIOBIUM AND RARE-EARTH MINERALS IN MONTICELLITE – CALCITE CARBONATITE OF THE OKA COMPLEX, QUEBEC

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### ABSTRACT

The niobium minerals in the monticellite – calcite carbonatites of the Oka complex, Quebec, are represented by latrappite and ceriopyrochlore. *LREE*-poor latrappite is a primary concentrator of Nb in the rocks. It is commonly replaced and overgrown by pyrochlore that is remarkably rich in the *LREE* (up to 18.8 wt.%  $Ce_2O_3 + La_2O_3 + Nd_2O_3 + Pr_2O_3$ ). Cериopyrochlore poikilolitically encloses multiple grains of calcite and apatite. The appearance of the niobium mineralization in the monticellite – calcite carbonatites is interpreted to take place at two stages: 1) crystallization of latrappite from a fluorine-deficient carbonate melt, and 2) precipitation of ceriopyrochlore from a *REE*-bearing fluid that interacted with the latrappite-bearing rocks.

**Keywords:** latrappite, pyrochlore, niobium mineralization, carbonatite, Oka, Quebec.

### SOMMAIRE

Les minéraux niobifères de la carbonatite à monticellite + calcite du complexe d'Oka, Québec, sont la latrappite et le cériopyrochlore. La latrappite, à faible teneur en terres rares légères, joue le rôle de concentrateur primaire de Nb dans ces roches. Elle est en général soit remplacée par le pyrochlore ou bien montre une surcroissance de pyrochlore, qui se distingue par un enrichissement remarquable en terres rares légères (jusqu'à 18.8% en poids de  $Ce_2O_3 + La_2O_3 + Nd_2O_3 + Pr_2O_3$ ). Le cériopyrochlore, à texture poecilitique, renferme une multitude de cristaux de calcite et d'apatite. La présence de cet assemblage à niobium dans la carbonatite à monticellite + calcite résulterait de deux stades de concentration: 1) cristallisation de la latrappite à partir d'un magma carbonatitique à faible teneur en fluor, et 2) précipitation du cériopyrochlore à partir d'une phase fluide porteuse de terres rares, suite à une réaction avec les roches contenant la latrappite.

(Traduit par la Rédaction)

**Mots-clés:** latrappite, pyrochlore, minéralisation en Nb, carbonatite, Oka, Québec.

### INTRODUCTION

Perovskite- and pyrochlore-group minerals are compositionally and structurally similar. In both cases, the structural framework is built of  $BO_6$  octahedra usually occupied by Ti, Nb, Ta; the framework accommodates Ca, Na, Sr, and the rare-earth elements (*REE*) in the larger polyhedra, whereas Pb, Th, Fe, Mn, Zr are substituting elements. The similarity predetermines their coexistence in many geological samples, as a rule, related to alkaline igneous or metasomatic rocks. In the literature, perovskite-group minerals are commonly described as being replaced by pyrochlore-group minerals and *vice versa* (Table 1). Unfortunately, most authors have only described such phenomena, and have not provided a genetic interpretation of the replacement reactions. A mode of formation of perovskite – pyrochlore aggregates cannot be modeled directly on the basis of experimental data because of the chemical complexity of natural compounds belonging to these

mineral groups. However, such modeling would undoubtedly shed some light on the petrogenetic problems regarding the origin of niobium and rare-earth mineralization in alkaline rocks.

This study represents an attempt to combine mineralogical observations of a latrappite – pyrochlore relationship in monticellite – calcite carbonatite from the Oka complex, Quebec, with experimental data on the order of crystallization of perovskite- and pyrochlore-type compounds.

The Oka complex has been geologically and petrologically described by Gold (1967) and Gold *et al.* (1986). Data on isotope geochemistry obtained by Powell *et al.* (1966) have established the carbonatitic character of the Oka calcio-carbonate rocks and their comagmatic relationship with the silicate constituents of the complex. The close similarity in texture and phase assemblages between experimentally obtained materials and Oka rocks has allowed Watkinson (1970) to suggest fractional crystallization as a mechanism

TABLE 1. RELATIONSHIPS BETWEEN PYROCHLORE- AND PEROVSKITE-GROUP MINERALS IN VARIOUS ROCKS

Massif	Rock type	Initial mineral	Replacement mineral	References
Kovdor Kola, Russia	dolomite carbonatite	luoshite	pyrochlore	Rinskaya-Korsakova <i>et al.</i> (1963)
Saïlamlatvi Kola, Russia	calcite carbonatite	luoshite	pyrochlore	Orlova <i>et al.</i> (1963)
Not specified Siberia, Russia	calcite carbonatite	luoshite	pyrochlore	Bagdasarov <i>et al.</i> (1962)
Oka Quebec	calcite carbonatite	latrappite	pyrochlore	Nickel & McAdam (1963)
Khibina Kola, Russia	aggrims-feldspar veins	loparite	pyrochlore	Kuz'yeva (1991)
Lovozero Kola, Russia	fenite	loparite	pyrochlore	Semenov <i>et al.</i> (1963) Semenov (1972)
Ilmannaq Greenland	fofayite pegmatite	pyrochlore	luoshite	Semenov <i>et al.</i> (1968)
Not specified Siberia, Russia	calcite carbonatite	pyrochlore	luoshite	Bagdasarov <i>et al.</i> (1962)
Not specified East Siberia, Russia	albitized granite	microlite	loparite	Stuin & Leonova (1961)

responsible for the formation of the okaite – carbonatite series. On the basis of field and mineralogical observations, Treiman & Essene (1985) have interpreted the Oka carbonatites to be a possible product of *in situ* silicate – carbonate liquid immiscibility.

As in many other alkaline ultrabasic plutons, perovskite and pyrochlore are major niobium-bearing accessories in the Oka rocks and, in particular, in the carbonatites (although in the latter, niocalite also is found). Experiments on the precipitation of niobates in the system  $\text{CaO} - \text{Nb}_2\text{O}_5 - \text{CO}_2 - \text{H}_2\text{O}$  enabled Watkinson (1970, p. 359) to conclude that “the small but ubiquitous amounts of niobium minerals in the rocks at Oka and other carbonatites may be magmatic and not hydrothermal”. At the same time, the common presence of perovskite and pyrochlore in fenites and late-stage veins (Semenov *et al.* 1963, Es'kova *et al.* 1964, Evdokimov 1982, Mariano 1989, among others) indicates that, in many cases, hydrothermal processes have played a significant role in the development of niobium mineralization in some nepheline syenite and carbonatite complexes.

#### LATRAPPITE AND CERIOPYROCHLORE

The Oka monticellite – calcite carbonatites consist mainly of calcite, monticellite and apatite, with manganese-bearing magnetite, latrappite, pyrochlore, “tetraferriphlogopite” and pyrrhotite as accessory phases.

Latrappite tends to be localized in monticellite-rich carbonatite zones, wherein it is found exclusively as pseudocubic crystals ranging from 0.1 to 2.5 mm along an edge. Such crystals commonly have stepped faces.

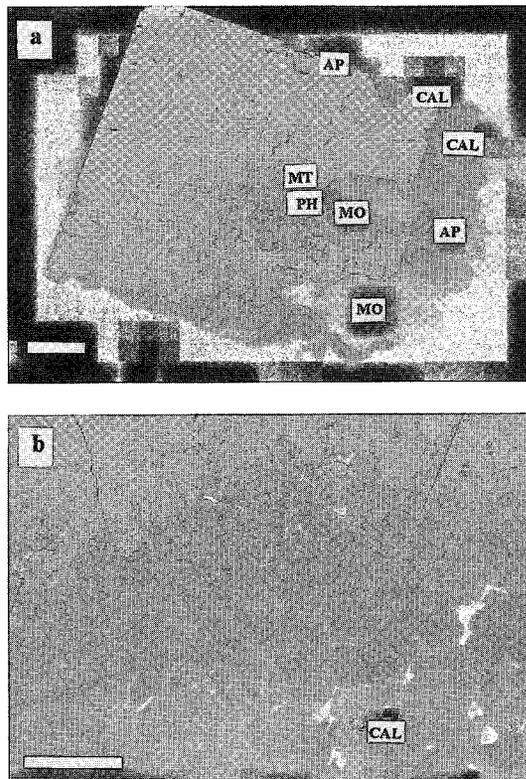


Fig. 1. Back-scattered electron image of latrappite (section parallel to a pseudocube face). (a) General view. Scale bar is 300  $\mu\text{m}$ . (b) Detail showing two latrappite phases. Scale bar is 100  $\mu\text{m}$ . Symbols: AP apatite, CAL calcite, MO monticellite, MT magnetite, PH “tetraferriphlogopite”.

Clusters of crystals in some cases surround magnetite octahedra. Latrappite poikilically encloses magnetite and euhedral monticellite grains. Only in the peripheral parts are inclusions of apatite present (Fig. 1a). Elongate prisms of apatite commonly lie upon the faces of latrappite crystals, being partially embedded in them. It is therefore likely that apatite formed in the very last stages of crystallization of the latrappite, which pushed apatite prisms and forced them to orient parallel to the surfaces of the pseudocube. Sparse tiny inclusions of calcite are found in both latrappite and magnetite inclusions and are likely to have crystallized from droplets and films of liquid captured by the growing crystals.

Although the latrappite does not show any regular zoning on back-scattered electron images, it consists of two phases. They both have a “latrappitic” composition and are likely to represent products of exsolution. One of them, having a slightly higher average atomic number, constitutes stretched thin (less than 10–15  $\mu\text{m}$ )

TABLE 2. REPRESENTATIVE COMPOSITIONS OF LATRAPPITE FROM OKA

	1	2	3	4	5	6
CaO wt. %	26.4	26.4	24.2	24.3	29.82	26.97
Nb <sub>2</sub> O <sub>5</sub>	4.7	5.9	4.3	4.9	2.33	3.96
La <sub>2</sub> O <sub>3</sub>	0.3	n.d.	1.1	0.3	0.70	0.45
Ce <sub>2</sub> O <sub>3</sub>	1.0	0.6	1.5	0.7	1.66	0.98
Pr <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	0.8	0.5	0.10	0.05
Nd <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	0.4	0.6	0.36	0.26
Sm <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	n.a.	n.a.	0.07	0.01
SrO	0.2	0.4	0.3	0.2	0.19	0.22
ThO <sub>2</sub>	0.4	n.d.	0.1	n.d.	n.d.	0.07
Nb <sub>2</sub> O <sub>5</sub>	48.2	48.5	47.9	49.7	40.53	47.91
TiO <sub>2</sub>	9.2	8.7	9.3	9.7	11.71	8.89
Fe <sub>2</sub> O <sub>3</sub>	7.5	7.5	5.9	5.8	8.92	6.89
Ta <sub>2</sub> O <sub>5</sub>	0.5	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	n.a.	n.a.	2.2	2.1	1.54	1.89
MnO	0.6	0.3	0.5	0.3	0.27	0.34
ZrO <sub>2</sub>	1.0	1.7	0.8	1.0	n.a.	n.a.
Sum	100.0*	100.0*	99.3	100.1	99.19	99.66
Structural formulae based upon 3 atoms of oxygen						
<b>A cations</b>						
Ca <sup>2+</sup>	0.75	0.75	0.70	0.69	0.848	0.766
Na <sup>+</sup>	0.24	0.30	0.23	0.25	0.120	0.204
La <sup>3+</sup>	0.00	0.00	0.01	0.00	0.007	0.004
Ce <sup>3+</sup>	0.01	0.01	0.01	0.01	0.016	0.009
Pr <sup>3+</sup>	n.a.	n.a.	0.01	0.01	0.001	0.000
Nd <sup>3+</sup>	0.00	0.00	0.00	0.01	0.003	0.002
Sm <sup>3+</sup>	n.a.	n.a.	n.a.	n.a.	0.001	0.000
Sr <sup>2+</sup>	0.00	0.01	0.00	0.00	0.003	0.003
Th <sup>4+</sup>	0.00	0.00	0.00	0.00	0.000	0.000
<b>B cations</b>						
Nb <sup>5+</sup>	0.58	0.58	0.58	0.59	0.486	0.574
Ti <sup>4+</sup>	0.18	0.17	0.19	0.19	0.234	0.177
Fe <sup>3+</sup>	0.15	0.15	0.12	0.12	0.198	0.153
Ta <sup>5+</sup>	0.00	0.00	0.00	0.00	0.000	0.000
Mg <sup>2+</sup>	n.a.	n.a.	0.09	0.08	0.061	0.074
Mn <sup>2+</sup>	0.01	0.01	0.01	0.01	0.006	0.008
Zr <sup>4+</sup>	0.01	0.02	0.01	0.01	n.a.	n.a.

Total Fe as Fe<sub>2</sub>O<sub>3</sub>. Compositions 1 and 3: "gray" latrappite; 2 and 4: "white" latrappite (this work); 5 and 6: core and rim of zoned euhedral crystal (Mitchell 1996). n.a.: not analyzed; n.d.: not detected. \* normalized compositions. Analyses 1 and 2 carried out at the MECHANOB-ANALIT Research Center with a CamScan 4 electron microscope, LINK-400 analytical system, 20 kV, 2 nA, focused beam, CORREX correction procedure applied to raw results; standards: albite (Na), celestite (Sr), wollastonite (Ca), LREE molybdates, synthetic ThO<sub>2</sub>, metallic Ti, Nb, Ta, Fe, Mn, Zr. Analyses 3 and 4 carried out at Lakehead University with a Hitachi 570 SEM, LINK ISIS analytical system, 20 kV, 0.86 nA, focused beam, ZAF correction procedure applied to raw results; standards: perovskite (Ca, Fe), loparite (Na, La, Ce, Pr, Nd, Nb, Ti), periclase (Mg), Mn-rich fayalite (Mn), synthetic SrTiO<sub>3</sub> (Sr), metallic Th, Ta, Zr.

zones within the other (Fig. 1b). Further in the text and in Table 2, they are referred to as "white" and "gray" latrappite. Compositions of both phases were determined by energy-dispersion X-ray spectrometric method using a CamScan 4 electron microprobe equipped with a LINK-400 analytical system at the MECHANOB-ANALIT Research Center, St. Petersburg. Measurements were repeated at Lakehead University, using a Hitachi 570 SEM equipped with a LINK ISIS analytical system. Operating conditions, standards selected for the analyses and results obtained in both cases are given in Table 2. The "white"

latrappite is enriched in Nb and depleted in the light rare-earth elements (LREE) relative to the "gray" variety; contents of other major and trace elements are similar in the two coexisting phases (Table 2) and close to those for the type latrappite sample (Nickel & McAdam 1963). Both "white" and "gray" latrappites contain considerably lower levels of the REE than most of the previously described perovskite-group minerals from the Oka complex (Eby 1975, Boctor & Yoder 1980, Treiman & Essene 1985) and are similar in LREE<sub>2</sub>O<sub>3</sub> content (Ce<sub>2</sub>O<sub>3</sub> + La<sub>2</sub>O<sub>3</sub> + Nd<sub>2</sub>O<sub>3</sub> + Pr<sub>2</sub>O<sub>3</sub>) to the zoned latrappite from Oka studied by Mitchell (1996, Table 2, anal. 5, 6).

Unit-cell parameters of the latrappite examined were calculated on the basis of its X-ray diffraction (XRD) pattern measured on a DRON-2.0 diffractometer with an internal standard of metallic Ge. Because of the compositional heterogeneity of this material, the values obtained represent mean unit-cell dimensions. The *a* and *b* unit-cell dimensions of the "classic" latrappite described by Nickel & McAdam (1963) and re-investigated by Mitchell are greater, whereas *c* is much shorter [*a* 0.54479, *b* 0.55259, *c* 0.71575 nm (Mitchell 1996)] than the values obtained here [*a* 0.5399(2), *b* 0.5501(1), *c* 0.7724(1) nm (cubic subcell parameter *a*<sub>0</sub> is approximately 0.386 nm)].

The latrappite grains commonly are overgrown and partly replaced by pyrochlore (Fig. 2). The latter occurs as octahedral crystals reaching 2.5–3 mm across. The mineral is strikingly poikilitic and contains numerous randomly oriented inclusions of apatite and calcite

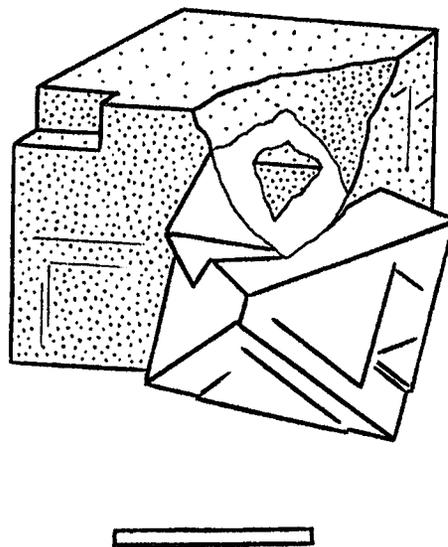


FIG. 2. Latrappite crystal (dotted) overgrown and partially replaced by ceriopyrochlore. Scale bar is 1 mm.

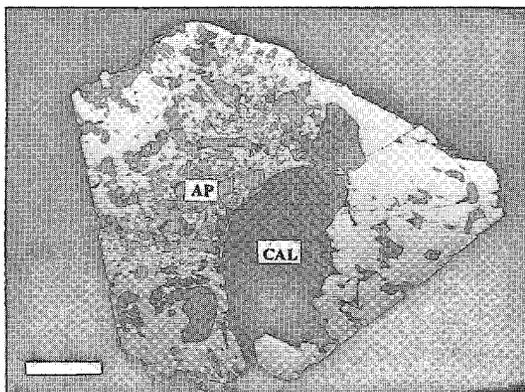


FIG. 3. Back-scattered electron image of ceriopyrochlore. Section parallel to (111). Symbols: AP apatite, CAL calcite. Scale bar is 300  $\mu\text{m}$ .

(Fig. 3). Latrappite relics are also found in some crystals of pyrochlore. The relationships between pyrochlore and the associated phases point to its appearance after the formation of the apatite – carbonate matrix as a result of postmagmatic processes.

TABLE 3. REPRESENTATIVE COMPOSITIONS OF CERIOPYROCHLORE FROM OKA

	1	2	3	4	1*	2*	3*	
CaO wt%	19.8	17.5	17.6	9.80	Ca <sup>2+</sup>	1.37	1.22	1.24
Na <sub>2</sub> O	1.3	0.8	0.9	n.a.	Na <sup>+</sup>	0.16	0.10	0.11
La <sub>2</sub> O <sub>3</sub>	2.4	2.1	2.4	2.22	La <sup>3+</sup>	0.06	0.05	0.06
Ce <sub>2</sub> O <sub>3</sub>	11.2	13.7	14.2	18.9	Ce <sup>3+</sup>	0.26	0.32	0.34
Pr <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	0.8	n.a.	Pr <sup>3+</sup>	n.a.	0.04	0.02
Nd <sub>2</sub> O <sub>3</sub>	1.2	1.6	1.6	n.a.	Nd <sup>3+</sup>	0.03	0.04	0.04
Gd <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	n.a.	1.62				
SrO	n.d.	0.2	0.1	n.a.	Sr <sup>2+</sup>	0.00	0.01	0.00
MnO	0.3	0.2	0.2	1.56	Mn <sup>2+</sup>	0.02	0.02	0.01
U <sub>3</sub> O <sub>8</sub>	n.a.	n.a.	n.a.	1.43				
Nb <sub>2</sub> O <sub>5</sub>	52.6	51.8	50.5	47.20	Nb <sup>5+</sup>	1.53	1.53	1.50
TiO <sub>2</sub>	4.2	2.9	3.5	6.69	Ti <sup>4+</sup>	0.20	0.14	0.17
Fe <sub>2</sub> O <sub>3</sub>	2.7	3.1	2.9	3.01	Fe <sup>3+</sup>	0.13	0.15	0.14
Ta <sub>2</sub> O <sub>5</sub>	n.d.	0.3	0.3	2.46	Ta <sup>5+</sup>	0.00	0.00	0.00
ZrO <sub>2</sub>	1.3	2.6	2.9	0.66	Zr <sup>4+</sup>	0.04	0.08	0.10
SiO <sub>2</sub>	n.a.	n.a.	n.a.	3.84				
H <sub>2</sub> O <sub>2</sub>	n.a.	n.a.	n.a.	2.21				
F	n.a.	n.a.	n.a.	0.85				
Sum	97.0	98.2	97.9	102.31				

\* Structural formulae based upon 6.5 atoms of oxygen; A cations are Ca, Na, La, Ce, Pr, Nd, Sr and Mn; B cations are Nb, Ti, Fe<sup>3+</sup>, Ta and Zr. Total Fe as Fe<sub>2</sub>O<sub>3</sub>, total U as U<sub>3</sub>O<sub>8</sub>. Compositions 1 and 2: cores of crystals from monticellite–calcite carbonatites; 3: rim of a crystal from monticellite–calcite carbonatite (this work); 4: ceriopyrochlore from a niobium orebody at Oka (Kalogeropoulos 1977). Composition 1 determined at the MECHANOBRAANALIT, compositions 2 and 3 determined at Lakhhead University. For operating conditions and standards used, see Table 2.

The composition of the pyrochlore was determined using the same equipment and techniques as those applied for the investigation of the above-described latrappite. The pyrochlore examined is relatively close in composition to the “ordinary” pyrochlore at Oka (Hogarth 1961, Perrault 1968, variety 2; Petruk & Owens 1975, variety D), except for the lower Na, Sr, Nb and the higher LREE contents in our samples. The rim of the pyrochlore crystals is enriched in LREE and Ti, whereas it is depleted in Nb relative to the core. The sum of Ce<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> in these samples of pyrochlore reaches 18.8 wt.% (Table 3). Similar LREE-high pyrochlore (Ce<sub>2</sub>O<sub>3</sub> + La<sub>2</sub>O<sub>3</sub> + Gd<sub>2</sub>O<sub>3</sub> = 22.7 wt.%) has been described from a niobium orebody at Oka by Kalogeropoulos (1977, Table 3, anal. 4). Since the light rare-earth elements, dominated by Ce, constitute more than 20% of the total A atoms (where the Pr<sub>2</sub>O<sub>3</sub> content is known), the pyrochlore described here also should be regarded as ceriopyrochlore according to the classification scheme proposed by Hogarth (1989).

The sample of ceriopyrochlore described here is not metamict and produces an appropriate X-ray-diffraction pattern without heating. The unit-cell parameter measured from this pattern is 1.03884(5) nm.

## DISCUSSION

According to the available experimental data, pyrochlore-type niobates precipitate in Nb-bearing carbonate systems at lower temperatures than perovskite-type niobates (Aleksandrov *et al.* 1969, Aleksandrov 1973); the crystallization of pyrochlore also is promoted by the presence in a mineral-forming system of elements that may more easily be adopted by pyrochlore rather than by perovskite (*e.g.*, fluorine: Jago & Gittins 1993; uranium: Aleksandrov 1973). Also, material scientists describe the transformation of anion-deficient pyrochlore ceramics into those having the perovskite structure owing to an increase in pressure or temperature (Venetsev *et al.* 1970). Although the unit-cell parameters of the above-described Oka minerals satisfy the ratio necessary for such a transition [ $a_0$  of perovskite divided by  $a$  of pyrochlore < 0.40: Venetsev *et al.* (1970)], the relationship between latrappite and pyrochlore as well as the great difference in their compositions suggest that the formation of ceriopyrochlore in the Oka monticellite – calcite carbonatites was a result of more complex phenomena. However, such transitions can be expected to take place in some “extreme” geological environments, *e.g.*, in carbonatites undergoing high-grade metamorphism.

Our ion-selective determinations show that the whole-rock fluorine content ranges between 0.07 and 0.12 wt.%, *i.e.* significantly lower than 1 wt.% necessary for crystallization of pyrochlore (Jago & Gittins 1993). This fact may be an explanation why

latrappite is the primary concentrator of Nb in the monticellite – calcite carbonatites. According to Jago & Gittins (1993), subsequent increase of fluorine content during evolution of the carbonate melt may cause partial replacement of a perovskite phase by pyrochlore. It is well established that in nature (e.g., Vlasov *et al.* 1966, Kukhareno *et al.* 1965) and in experiments (Nagasawa *et al.* 1980), perovskite-type compounds selectively adsorb the *LREE* from a parent liquid and are major concentrators of these elements in the resultant rocks. One would therefore expect *cerian perovskite*, *loparite* or *cerian lueshite* to form as a result of crystallization of the carbonatite at Oka. However, the latrappite from the Oka monticellite – calcite carbonatite is very low in the *LREE*, compared with the associated pyrochlore phase. If it is assumed that the parent carbonatitic melt or an immiscible silicate – carbonate pair at Oka coexisted with a CO<sub>2</sub>-rich fluid, the partition coefficients of the *LREE* would be in favor of the latter, as documented by Wendlandt & Harrison (1979) in experimental systems. Interaction between such a relatively fluorine-enriched fluid (Jago & Gittins 1993) and the monticellite – calcite carbonatite with decreasing temperature might explain the appearance of ceriopyrochlore in the carbonatite. In this process, the latrappite played a role of nuclei for the crystallization of ceriopyrochlore. It is noteworthy that similar relationships were observed for the pair niobian perovskite – cerian pyrochlore from the Bond Zone, Oka (Mitchell & Chakmouradian, unpubl. data).

The “opposite” order of crystallization, *i.e.*, overgrowth and replacement of the pyrochlore-group minerals by perovskite-group phases (Table 1: Bagdasarov *et al.* 1962, Sitnin & Leonova 1961, Semenov *et al.* 1968), presumably is a result of partial dissolution of the pyrochlore material and subsequent precipitation of the perovskite-type compounds in a “dry” and fluorine-deficient environment.

#### CONCLUSIONS

The niobium enrichment in the Oka monticellite – calcite carbonatites was formed in two stages: 1) crystallization of carbonate melt, and 2) precipitation from a *REE*-Nb-bearing fluid. The former process caused latrappite, a major Nb-concentrator, to appear. The subsequent interaction of the carbonatites with the fluid led to the crystallization of the poikilitic crystals of ceriopyrochlore that in some cases replace the early-formed grains of latrappite.

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#### REFERENCES

- ALEKSANDROV, I.V. (1973): *Models of Endogenic Tantalum–Niobium Mineralization*. Nauka Press, Moscow, Russia (in Russ.).
- \_\_\_\_\_, TRUSIKOVA, T.A. & TUPITSIN, B.P. (1969): Niobium and tantalum in carbon dioxide solutions. *Geochem. Int.* 6(3), 558-566.
- BAGDASAROV, YU.A., GAYDUKOVA, V.S., KUZNETSOVA, N.N. & SIDORENKO, G.A. (1962): Lueshite from the carbonatites of Siberia. *Dokl. Acad. Sci. USSR, Earth-Sci. Sect.* 147, 157-159.
- BOCTOR, N.Z. & YODER, H.S., JR. (1980): Distribution of rare earth elements in perovskite from Oka carbonatite, Quebec. *Carnegie Inst. Wash., Year Book* 79, 304-307.
- EBY, G.N. (1975): Abundance and distribution of the rare-earth elements and yttrium in the rocks and minerals of the Oka carbonatite complex, Quebec. *Geochim. Cosmochim. Acta* 39, 597-620.
- ES'KOVA, E.M., ZHABIN, A.G. & MUKHITDINOV, G.N. (1964): *The Mineralogy and Geochemistry of the Rare-Earth Elements in the Vishnevye Mts.* Nauka Press, Moscow, Russia (in Russ.).
- EVDOKIMOV, M.D. (1982): *Fenites of the Turii Peninsula*. Leningrad Univ. Press, Leningrad, Russia (in Russ.).
- GOLD, D.P. (1967): Alkaline ultrabasic rocks in the Montreal area, Quebec. In *Ultramafic and Related Rocks* (P.J. Wyllie, ed.). John Wiley & Sons, New York, N.Y. (288-302).
- \_\_\_\_\_, EBY, G.N., BELL, K. & VALLÉE, M. (1986): Carbonatites, diatremes, and ultra-alkaline rocks in the Oka area, Quebec. *Geol. Assoc. Can. – Mineral. Assoc. Can. – Can. Geophys. Union, Field Trip Guidebook* 21.
- HOGARTH, D.D. (1961): A study of pyrochlore and betafite. *Can. Mineral.* 6, 610-633.
- \_\_\_\_\_ (1989): Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite. In *Carbonatites: Genesis and Evolution* (K. Bell, ed.). Unwin Hyman Ltd., London, U.K. (105-148).

- JAGO, B.C. & GITTINS, J. (1993): Pyrochlore crystallization in carbonatites: the role of fluorine. *S. Afr. J. Geol.* **96**, 149-159.
- KALOGEROPOULOS, P. (1977): *Geochemistry and Mineralogy of the St. Lawrence Pyrochlore Deposit, Oka, P.Q.* M.Sc. thesis, Queen's Univ., Kingston, Ontario.
- KOZYREVA, L.V. (1991): Aegirine-feldspar veins of the north-eastern part of the Khibiny massif. In *Shchelochnoi Magmatizm Severo-Vostochnoi Chasti Baltiyskogo Shchita*. Geol. Inst. Press, Apatity, Russia (42-56; in Russ.).
- KUKHARENKO, A.A., ORLOVA, M.P., BULAKH, A.G., BAGDASAROV, E.A., RIMSKAYA-KORSAKOVA, O.M., NEFEDOV, E.I., ILINSKIY, G.A., SERGEEV, A.S. & ABAKUMOVA, N.B. (1965): *The Caledonian Complex of Ultrabasic, Alkaline Rocks and Carbonatites of the Kola Peninsula and North Karelia*. Nedra Press, Moscow, Russia (in Russ.).
- MARIANO, A.N. (1989): Nature of economic mineralization in carbonatites and related rocks. In *Carbonatites. Genesis and Evolution* (K. Bell, ed.). Unwin Hyman Ltd., London, U.K. (149-176).
- MITCHELL, R.H. (1996): Perovskites: a revised classification scheme for an important rare earth element host in alkaline rocks. In *Rare Earth Minerals: Chemistry, Origin and Ore Deposits. Mineral. Soc. Ser., Vol. 5* (in press).
- NAGASAWA, H., SCHREIBER, H.D. & MORRIS, R.V. (1980): Experimental mineral/liquid partition coefficients of the rare earth elements (REE), Sc and Sr for perovskite, spinel and melilite. *Earth Planet. Sci. Lett.* **46**, 431-437.
- NICKEL, E.H. & MCADAM, R.C. (1963): Niobian perovskite from Oka, Quebec; a new classification for minerals of the perovskite group. *Can. Mineral.* **7**, 683-697.
- ORLOVA, M.P., ROZHDESTVENSKIY, YU.P. & BARANOVA, E.N. (1963): On the mineralogy of rare-metal carbonatites of the Sallanlatvi massif. *Trudy VSEGEI, Nov. Ser.* **96**, 3-20 (in Russ.).
- PERRAULT, G. (1968): La composition chimique et la structure cristalline du pyrochlore d'Oka, P.Q. *Can. Mineral.* **9**, 383-402.
- PETRUK, W. & OWENS, D.R. (1975): Electron microprobe analyses for pyrochlores from Oka, Quebec. *Can. Mineral.* **13**, 282-285.
- POWELL, J.L., HURLEY, P.M. & FAIRBAIRN, N.W. (1966): The strontium isotopic composition and origin of carbonatites. In *Carbonatites* (O.F. Tuttle & J. Gittins, eds.). John Wiley & Sons, New York (365-378).
- RIMSKAYA-KORSAKOVA, O.M., BUROVA, T.A. & FRANK-KAMENETSKIY, V.A. (1963): Lueshite from carbonatites of the Kovdor massif. *Zap. Vses. Mineral. Obshchest.* **92**, 173-183 (in Russ.).
- SEMENOV, E.I. (1972): *Mineralogy of the Lovozero Alkaline Massif*. Nauka Press, Moscow, Russia (in Russ.).
- , SØRENSEN, H. & KATAJEVA, Z.T. (1968): On the mineralogy of pyrochlore from the Ilfmaussaq alkaline intrusion, South Greenland. *Medd. Grønland* **181**, 9-24.
- , SPITSYN, A.N. & BUROVA, Z.N. (1963): Hydrous pyrochlore from the Lovozero alkaline massif. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **150**, 127-131.
- SITNIN, A.A. & LEONOVA, T.N. (1961): Loparite – a new accessory mineral of albitized and greisenized granites. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **140**, 1090-1093.
- TREIMAN, A.H. & ESSENE, E.J. (1985): The Oka carbonatite complex, Quebec: geology and evidence for silicate – carbonate liquid immiscibility. *Am. Mineral.* **70**, 1101-1113.
- VENEVTSEV, YU.N., KAPYSHEV, A.G., SHVORNEVA, L.I., TOMASHPOL'SKIY, YU.YA., VISKOV, A.S., ZUBOVA, YE.V., IVANOVA, V.V., DEMUROV, D.G., DZHMURAKHADZE, D.F., SAL'NIKOV, V.D. & ZHDANOV, G.S. (1970): New ferro-electrics and seignettomagnets of the perovskite and pyrochlore type: synthesis and study of the crystal structure and properties. *J. Phys. Soc. Japan* **28**, Suppl., 139-144.
- VLASOV, K.A., KUZ'MENKO, M.V. & ES'KOVA, E.M. (1966): *The Lovozero Alkali Massif*. Oliver and Boyd Ltd., Edinburgh, U.K.
- WATKINSON, D.H. (1970): Experimental studies bearing on the origin of the alkalic rock – carbonatite complex and niobium mineralization at Oka, Quebec. *Can. Mineral.* **10**, 350-361.
- WENDLANDT, R.F. & HARRISON, W.J. (1979): Rare earth partitioning between immiscible carbonate and silicate liquids and CO<sub>2</sub> vapor: results and implications for the formation of light rare earth-enriched rocks. *Contrib. Mineral. Petrol.* **69**, 409-419.

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