

## STRONTIUM-APATITE: NEW OCCURRENCES, AND THE EXTENT OF Sr-FOR-Ca SUBSTITUTION IN APATITE-GROUP MINERALS

ANTON R. CHAKHMOURADIAN<sup>§</sup>

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

EKATERINA P. REGUIR and ROGER H. MITCHELL

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

### ABSTRACT

The paragenesis and compositional variation of strontium-apatite from three new localities are characterized. At Lovozero, in the Kola Peninsula, Russia, strontium-apatite forms elongate crystals and thin reaction-induced rims on early strontian fluorapatite in nepheline syenite pegmatites. The apatite-group minerals are enriched in Na and REE, and exhibit the following compositional range:  $(\text{Ca}_{0.34-4.49}\text{Sr}_{0.18-4.54}\text{Na}_{0.05-0.30}\text{REE}_{0.08-0.18}\text{Ba}_{0-0.10})(\text{P}_{2.87-3.03}\text{Si}_{0-0.16})\text{O}_{12}(\text{F},\text{OH})$ . At Murun, in eastern Siberia, Russia, strontium-apatite also occurs in intimate association with strontian fluorapatite in a eudialyte-bearing nepheline syenite pegmatite. The overall compositional variation of these minerals can be expressed as  $(\text{Ca}_{2.26-3.55}\text{Sr}_{1.41-2.74}\text{Na}_{0-0.03}\text{REE}_{0-0.08})(\text{P}_{2.91-3.01}\text{Si}_{0-0.06})\text{O}_{12}(\text{F},\text{OH})$ . At Lac de Gras, Northwest Territories, Canada, strontium-apatite and Sr-rich carbonate-hydroxylapatite compose cores of spherulites confined to vesicles in kimberlite, associated with suolunite and barian phlogopite. In addition to Sr, the apatite is enriched in Ba and V; the proportions of these elements decrease from the center of spherulites outward. The Lac de Gras apatite is inferred to contain carbon substituting for P. The overall compositional variation is  $(\text{Sr}_{0.08-2.58}\text{Ca}_{2.04-4.65}\text{Ba}_{0-0.21}\text{Na}_{0.09-0.28}\text{REE}_{0-0.07}\text{K}_{0-0.03})(\text{P}_{2.20-2.61}\text{C}_{-0.25-0.50}\text{Si}_{0.04-0.26}\text{V}_{0-0.13})\text{O}_{12}(\text{OH},\text{F})$ . Sr-rich apatites (*sensu lato*) from peralkaline rocks and kimberlites differ in concentrations of minor components and evolutionary trends. The available data demonstrate that there is a continuous series of naturally occurring compositions from apatite to strontium-apatite with less than 7 mol.%  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$ . There are implications of these data for the crystal chemistry and nomenclature of apatite-group minerals.

**Keywords:** apatite, strontium-apatite, zoning, peralkaline rocks, kimberlites, Lovozero, Murun, Lac de Gras, Russia, Canada.

### SOMMAIRE

Nous caractérisons la paragenèse et la variation en composition de la strontium-apatite provenant de trois nouveaux indices. A Lovozero, dans la péninsule de Kola, en Russie, la strontium-apatite forme des cristaux allongés et des bordures de réaction sur des cristaux précoces de fluorapatite strontifère dans des pegmatites de composition de syénite néphélinique. Les minéraux du groupe de l'apatite sont enrichis en Na et en terres rares (TR), dans l'intervalle de compositions suivant:  $(\text{Ca}_{0.34-4.49}\text{Sr}_{0.18-4.54}\text{Na}_{0.05-0.30}\text{TR}_{0.08-0.18}\text{Ba}_{0-0.10})(\text{P}_{2.87-3.03}\text{Si}_{0-0.16})\text{O}_{12}(\text{F},\text{OH})$ . A Murun, dans la partie orientale de la Sibérie, en Russie, la strontium-apatite se trouve aussi en association intime avec une fluorapatite strontifère dans une pegmatite de composition de syénite néphélinique à eudialyte. La variation en composition de ces minéraux peut s'exprimer ainsi:  $(\text{Ca}_{2.26-3.55}\text{Sr}_{1.41-2.74}\text{Na}_{0-0.03}\text{TR}_{0-0.08})(\text{P}_{2.91-3.01}\text{Si}_{0-0.06})\text{O}_{12}(\text{F},\text{OH})$ . Au Lac de Gras, dans les Territoires du Nord-Ouest, Canada, la strontium-apatite et une carbonate-hydroxylapatite riche en Sr constituent le noyau de sphérulites qui se présentent dans des cavités d'une kimberlite, en association avec suolunite et phlogopite enrichie en barium. En plus du Sr, l'apatite est enrichie en Ba et V; la proportion de ces éléments diminue du centre des sphérulites vers la bordure. Nous croyons que l'apatite du Lac de Gras contient du carbone en substitution au phosphore. La variation globale en composition serait:  $(\text{Sr}_{0.08-2.58}\text{Ca}_{2.04-4.65}\text{Ba}_{0-0.21}\text{Na}_{0.09-0.28}\text{TR}_{0-0.07}\text{K}_{0-0.03})(\text{P}_{2.20-2.61}\text{C}_{-0.25-0.50}\text{Si}_{0.04-0.26}\text{V}_{0-0.13})\text{O}_{12}(\text{OH},\text{F})$ . Les apatites (*sensu lato*) riches en Sr de roches hyperalkalines et kimberlitiques diffèrent dans leurs concentrations de composants mineurs et dans le tracé de leur évolution. Les données disponibles démontrent qu'il y a une série continue de compositions naturelles à partir de l'apatite jusqu'à la strontium-apatite contenant moins de 7% de  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$  (base molaire). Ces données ont des implications par rapport à la cristallographie et à la nomenclature des minéraux du groupe de l'apatite.

(Traduit par la Rédaction)

**Mots-clés:** apatite, strontium-apatite, zonation, roches hyperalkalines, kimberlites, Lovozero, Murun, Lac de Gras, Russie, Canada.

<sup>§</sup> E-mail address: chakhmou@ms.umanitoba.ca

## INTRODUCTION

Strontium is an important substituent in naturally occurring apatite (*sensu lato*). Sr-rich apatite compositions are particularly common in alkaline igneous and metasomatic rocks of diverse provenance (Table 1). In  $P6_3/m$  apatite, Sr tends to be ordered at the seven-coordinated  $6h$  site denoted as Ca(2) (Hughes *et al.* 1991) or  $A_{II}$  (Khomyakov *et al.* 1997). It is not known whether the degree of order decreases or increases with an increasing proportion of Sr relative to Ca (see discussion in Rakovan & Hughes 2000, p. 840). The Sr-dominant analogues of fluor-, hydroxyl- and chlorapatite all have a  $P6_3/m$ -type structure (Sudarsanan & Young 1972, 1980, Khattech & Jemal 1997). If elements other than Sr substitute for Ca (especially Na and light rare-earth elements, *LREE*), the pattern of order becomes more complex, and may involve up to six crystallographically independent positions (Khomyakov *et al.* 1996). At present, five mineral species are known to have an apatite-like structure and show the predominance of Sr in at least one cation site: strontium-apatite, belovite-(Ce), belovite-(La), deloneite-(Ce) and fluorcaphite. Crystal-

lization of the latter four minerals requires concurrent enrichment of Na, Sr and *LREE*; their occurrence is restricted to well-differentiated peralkaline pegmatites (*e.g.*, Yakovenchuk *et al.* 1999). It is reasonable to propose that strontium-apatite,  $(Sr,Ca)_5(PO_4)_3(OH,F)$ , is significantly more common than the other four minerals, especially in potassic alkaline rocks that are characteristically enriched in Sr relative to *LREE*. However, since its discovery at Inagli in Siberia (Efimov *et al.* 1962), strontium-apatite has been found only at one other locality, the Khibina alkaline complex on the Kola Peninsula (Khomyakov 1995). At both localities, this mineral occurs in differentiated peralkaline pegmatites, in association with Na–Ba titanosilicates (Inagli) or Na carbonates and fluorides (Khibina). Prior to our study, the maximum Sr content (46.4 wt.% SrO or 2.88 atoms per formula unit, *apfu*, Sr) in natural apatite had been observed in the material from Khibina (Khomyakov 1995). The material from both Khibina and Inagli contains relatively low levels of Na, *LREE*, Si and Ba, and thus corresponds essentially to intermediate members of the  $Ca_5(PO_4)_3(OH,F) - Sr_5(PO_4)_3(OH,F)$  series with close to 60 mol.% of the latter end-member. Whether there is

TABLE 1. MAXIMUM Sr CONTENTS OBSERVED IN Ca-DOMINANT APATITE-GROUP MINERALS FROM ALKALINE ROCKS AND CARBONATITES

ROCK TYPE	Sr CONTENT		LOCALITY	COMMENTS	REFERENCES
	wt.% SrO	apfu Sr			
Kimberlite	40.2	2.32	Lac de Gras, NWT, Canada	Carbonate-hydroxylapatite, high Si and Ba	This work
Lamproite	5.8	0.29	West Kimberley, Australia	Very high Ba, deficiency of cations in the tetrahedral site; CO <sub>2</sub> not analyzed	Edgar (1989)
Orangeite	21.7	1.18	Besterskraal, South Africa	Moderate <i>REE</i> , Si and Ba	Mitchell (1995)
Lamprophyre <sup>1</sup>	14.0	0.73	Murun, Yakutia, Russia	Fluorapatite; elevated <i>REE</i> and Si	This work
Fergusonite	8.2	0.43	Verkhniy Dunkel' dyk, Pamir Mts., Tajikistan	High deficiency of cations in T-site; CO <sub>2</sub> not analyzed; moderate Si and Ba	Solovova <i>et al.</i> (1993)
Nephelinite	24.6	1.38	Djebel Targou, Morocco	Fluorapatite; high Si and moderate <i>REE</i>	Velde & Rachdi (1988)
Foidolite	12.0	0.63	Lovozero, Russia	Fluorapatite; moderate <i>REE</i>	Bussen & Sakharov (1972)
Phonolite	29.8	1.72	Mt. Karnasurt, Lovozero, Russia	Fluorapatite; high Si and <i>REE</i>	This work
Malignite	8.7	0.44	Gordon Butte, Montana, USA	Fluorapatite	This work
Foyaite	20.2	1.13	Mt. Selsurt, Lovozero, Russia	High Na and <i>REE</i> ; overgrown by belovite-(Ce)	This work
Nepheline-syenitic pegmatites:					
associated with sodic alkaline complexes	37.5	2.33	Mt. Alluav, Lovozero, Russia	Hydroxylapatite; moderate <i>REE</i> and Na	This work
associated with potassic alkaline complexes	39.6	2.49	Murun, Yakutia, Russia	Fluorapatite; negligible Na, Si and <i>REE</i>	This work
Alkali syenite	19.2	1.03	Gordon Butte, Montana, USA	Low Na, <i>REE</i> and Si	This work
Metasomatic rocks:					
fenite	5.6	0.29	Mt. Bisson, BC, Canada	Fluorapatite; moderate <i>REE</i>	Halleran & Russell (1996)
albite-aegirine	26.4	1.63	Mt. Flora, Lovozero, Russia	Fluorcaphite (?); very high Na and <i>REE</i>	This work
charoite	14.2	0.73	Murun, Yakutia, Russia	Hydroxylapatite; significant F; negligible <i>REE</i>	This work
Carbonatites:					
calcite	5.0	0.26	Gatineau, Quebec, Canada	Fluorapatite; moderate Na, <i>REE</i> and Si	Hogarth <i>et al.</i> (1985)
dolomite	13.3	0.70	Lesnaya Varaka, Russia	Fluorapatite; negligible <i>REE</i> and Na	This work
ankerite	8.2	0.41	Chipman Lake, Ontario, Canada		Platt & Woolley (1990)
natrocarbonate (altered)	3.7	0.18	Oldoinyo Lengai, Tanzania	Fluorapatite; high deficiency of cations in T-site; CO <sub>2</sub> not analyzed; moderate Si	Dawson (1993)
barytocalcite (Ba-Sr carbonate)	6.7	0.33	Murun, Yakutia, Russia	Hydroxylapatite; significant F	This work

<sup>1</sup> Up to 20 wt.% SrO was reported in apatite from lamprophyric rocks of the Jharia district (India), but no analyses were given (Rock *et al.* 1992).

a continuous solid-solution between naturally occurring apatite and strontium-apatite has not been yet established.

Our objectives were to determine the extent of Ca  $\leftrightarrow$  Sr substitution in naturally occurring apatite-group minerals and to identify the major evolutionary trends exhibited by these minerals. For this purpose, we examined 62 samples of diverse alkaline, alkali-ultramafic and carbonatitic rocks from 16 localities worldwide, and obtained more than 550 electron-microprobe analyses of apatite (*sensu lato*) from these rocks.

#### ANALYTICAL TECHNIQUES

The compositions of all minerals were determined by energy-dispersion X-ray spectrometry (EDS) using a JEOL JSM-5900LV scanning electron microscope equipped with a LINK ISIS analytical system. Raw EDS spectra were acquired for 130 seconds (live time) with an accelerating voltage of 20 kV and a beam current of 0.54–0.55 nA. The spectra were processed using the LINK ISIS SEMQUANT software package, with full ZAF corrections applied. The following standards and analytical lines were used: CaK $\alpha$ , PK $\alpha$  and FK $\alpha$  (fluorapatite, NHM #1926.665), SrL $\alpha$  (synthetic SrTiO $_3$ ), NaK $\alpha$  (jadeite), LaL $\alpha$ , CeL $\alpha$ , PrL $\alpha$  and NdL $\alpha$  (loparite), BaL $\alpha$  (benitoite), AlK $\alpha$  (corundum), FeK $\alpha$  (ilmenite), KK $\alpha$  (orthoclase), SiK $\alpha$  (wollastonite), ClK $\alpha$  (NaCl) and VK $\alpha$  (metallic V). Although anisotropic diffusion of halogens during the electron-microprobe analysis has been demonstrated to affect X-ray intensities of these elements (Stormer *et al.* 1993), this effect was probably insignificant in our case because we employed low beam-currents, and used a standard whose surface is not perpendicular to the direction of preferential diffusion. The strontian hydroxylapatite from Lac de Gras also was analyzed by wavelength-dispersion spectrometry (WDS) using a CAMECA SX-50 electron microprobe operated at 20 kV and 20 nA. The following standards were employed for the WDS analysis: fluorapatite (Ca, P, F), synthetic SrTiO $_3$  (Sr), albite (Na), REE-doped glasses (La, Ce), barite (Ba), fayalite (Fe), orthoclase (K), diopside (Si), and synthetic VP $_2$ O $_7$  (V). Even though a significantly higher beam-current was employed in this case, the effect of halogen diffusion was again ignored, as the F contents determined by WDS and EDS are in good agreement with each other (see below). False-color back-scattered-electron images (BSE) were obtained using the LINK ISIS AUTO-BEAM and SPEEDMAP applications, and converted to the PCX format using image-capture software.

#### STRONTIUM-APATITE: COMPOSITION AND PARAGENESES

The majority of apatite compositions obtained in this study can be satisfactorily recalculated to the generalized formula  $A_5(TO_4)_3X$ , where  $A = \text{Ca, Sr}$  and other large cations,  $T = \text{P or Si}$ , and  $X$  signifies monovalent

anions (primarily, F and OH). Relatively few samples, mostly from carbonatites and kimberlites, show apparent deviation from the “ideal” stoichiometry, possibly due to the presence of carbon that was not included in the analysis (see below). Table 2, containing sixty-six representative compositions of strontian fluor- and hydroxylapatite (>2.0 wt.% SrO or  $\sim 0.10$  *apfu* Sr) from different localities may be requested from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. During this work, we identified three new occurrences of strontium-apatite, including the Lovozero and Murun alkaline complexes in Russia, and the Lac de Gras kimberlite field in Canada. The parageneses and compositional variation of the strontium-apatite are characterized below. Representative results of analyses of the strontium-apatite and associated Ca-dominant apatite-group phases from these localities are presented in Tables 3–5.

#### *The Lovozero complex, central Kola Peninsula, Russia*

At Lovozero, apatite-group minerals are ubiquitous throughout all major intrusive series, making up to 15 vol.% of some varieties of juvites and ijolites (Bussen & Sakharov 1972). These minerals are systematically enriched in Sr and, commonly, Na and LREE (Table 2). Belovite-(Ce), ideally NaCeSr $_3$ (PO $_4$ ) $_3$ F, is known from several pegmatite bodies in northwestern and southeastern Lovozero (Pekov *et al.* 1995), and compositions intermediate between fluorapatite and belovite occur in aegirine–albite metasomatic rocks and phonolites (Table 2). Veins of nepheline syenite pegmatite containing strontium-apatite crosscut urtites and foyaites of the differentiated series on the northwestern slope of Mt. Alluaiv. A schematic drawing of one of the veins is shown in Figure 1. In some of the bodies, the axial zone contains segregations of ussingite associated with murmanite, steenstrupine-(Ce), mangan-neptunite, and other minerals characteristic of hyperagpaitic parageneses. Elongate euhedral crystals of apatite occur predominantly in the contact zone of pegmatites, in an assemblage with nepheline, perthitic alkali feldspar, magnesio-arfvedsonite, albite, natrolite, aegirine-augite zoned to aegirine, loparite-(Ce), rinkite, eudialyte, lorenzenite and barytolamprophyllite (Appendix 1). The crystals of apatite are complexly zoned, indicating multiple episodes of growth and dissolution (Fig. 2). Most of the crystals correspond to fluorapatite; the observed differences in average atomic number (AZ) result primarily from variations in LREE and Sr contents (Table 3, anal. 1–4). The Si content is generally low; only the LREE-enriched core of some crystals contains 1.7–1.8 wt.% SiO $_2$  (Fig. 2A). The Na content is lowest in the Si-enriched core, and increases to 1.2–1.4 wt.% Na $_2$ O in intermediate high-AZ zones. As the A:T ratio is close to the “ideal” value ( $\sim 1.67$ ) in all of the compo-

sitions obtained, we infer that the primary fluorapatite is stoichiometric. Its compositional variation may be characterized in terms of three major end-members:  $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ,  $\text{Sr}_5(\text{PO}_4)_3\text{X}$  and  $\text{Na}_{2.5}\text{LREE}_{2.5}(\text{PO}_4)_3\text{X}$ , where X represents F or OH. This ternary system has been proven useful for demonstrating the composition of apatite-group minerals from diverse alkaline parageneses (Chakhmouradian & Mitchell 1999, 2002). Depending on whether Ba (as in some lamproites: Edgar 1989) or Si (usually, in carbonatites: Dawson 1993) is present in significant amounts, this system can be augmented with a fourth apex, corresponding to either  $\text{Ba}_5(\text{PO}_4)_3\text{X}$  ("alforsite") or  $\text{LREE}_3\text{Ca}_2(\text{SiO}_4)_3\text{X}$  ("britholite"). In the present work, we use the quaternary diagram incorporating the Ca, Sr, Ba and Na-LREE end-members (Fig. 3). The compositions of primary fluorapatite from the Alluaiv pegmatites plot away from the  $\text{Ca}_5(\text{PO}_4)_3\text{X}$  apex toward  $\text{NaLREESr}_3(\text{PO}_4)_3\text{X}$ , *i.e.*, near the apatite-belovite join. Interestingly, apatite-group minerals in evolved alkaline rocks from other localities (*e.g.*, Bearpaw Mountains and Gordon Butte in Montana) exhibit a similar compositional trend (Fig. 3A and references therein). Notable exceptions are apatite from the Ilímaussaq complex in Greenland (Rønsbo 1989), whose compositions follow the  $\text{Ca}_5(\text{PO}_4)_3\text{X}$  -  $\text{Na}_{2.5}\text{LREE}_{2.5}(\text{PO}_4)_3\text{X}$  join, and Sr-rich fluorapatite from Murun, characterized below. However, it is noteworthy that Rønsbo (1989) did not analyze the Ilímaussaq material for Sr, and further studies are clearly required to establish the compositional variation of apatite-group minerals from that locality.

The crystals of fluorapatite from the Alluaiv pegmatites commonly exhibit a reaction-induced rim associated with areas of subsolidus alteration in the host rock, *i.e.*, albitization of alkali feldspar and conversion of nepheline to natrolite. In most instances, the rim is discontinuous and appears to consist of individual euhedral overgrowths up to 30  $\mu\text{m}$  in thickness (Figs. 2B, C). The composition of the rim is highly variable, but the proportion of Sr among the large cations commonly exceeds that of Ca. The Sr content ranges from 35.3 to 62.9 wt.% SrO (2.26–4.54 *apfu* Sr). Note that such high Sr contents have not been previously documented in naturally occurring apatite (*sensu lato*). The most Sr-rich compositions obtained in the present work correspond to approximately 90 mol.%  $\text{Sr}_5(\text{PO}_4)_3\text{X}$ . Similar Ca/Sr values are found in minute euhedral crystals of strontium-apatite associated with subsolidus acicular aegirine and albite in the same pegmatite veins (Fig. 2D). The strontium-apatite from Lovozero is poor in Si, and contains elevated levels of Na and LREE (Tables 3, 4). Ba is generally below the detection limit, although a few crystals contain 0.07–0.10 *apfu* Ba (Fig. 3A).

#### *The Murun complex, western Aldan, Siberia, Russia*

Apatite-group minerals are ubiquitous in potassic alkaline rocks of the Murun complex. These minerals are characteristically enriched in Sr ( $\geq 1.4$  wt.% SrO) and poor in Na ( $\leq 0.5$  wt.%) (Table 1). Most of the apatite compositions are also very poor in Si and LREE, with



FIG. 1. Geological setting and zoning of a pegmatite vein at Mt. Alluaiv, Lovozero, Russia. 1 Wallrocks (urtite/foyaite), 2 chilled margins, 3 sodic amphibole, 4 alkali feldspar plus nepheline, 5 eudialyte, 6 aegirine. The vein has a N-S strike and an average thickness of 0.5 m.

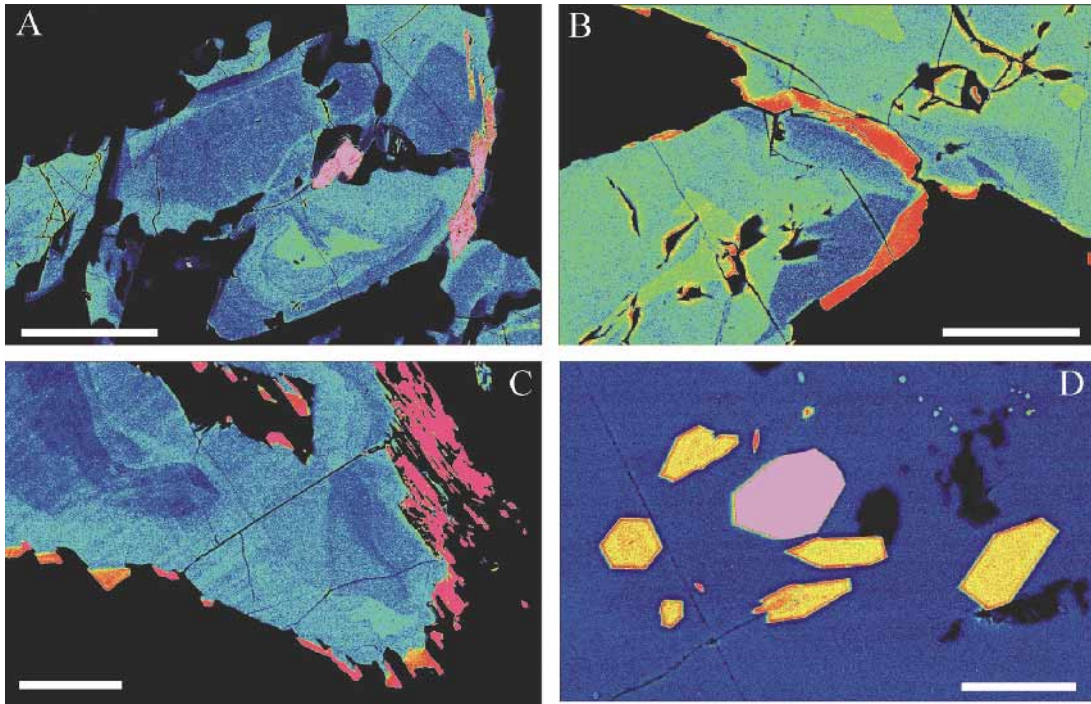


FIG. 2. False-color BSE images of apatite-group minerals from Lovozero. (A) Primary zoning in fluorapatite (green to blue); note the presence of a *LREE*-enriched core (green) and inclusions of rinkite (pink) in the crystals (scale bar 120  $\mu\text{m}$ ). (B) Sr-enriched rim (red) on primary fluorapatite (green-blue); note the euhedral contour of the rim (scale bar 60  $\mu\text{m}$ ). (C) Discontinuous rim of strontium-apatite (purple) deposited on primary fluorapatite (scale bar 10  $\mu\text{m}$ ). (D) Euhedral crystal of strontium-apatite (purple) associated with aegirine (orange), microcline (dark blue) and albite (black) (scale bar 30  $\mu\text{m}$ ).

the exception of some peralkaline syenites and lamprophyres (Table 2). Apatite-group minerals with the highest Sr contents are found in dikes of pegmatitic nepheline syenite containing abundant fibrous aegirine and subordinate amounts of eudialyte. The geological setting and textural characteristics of the pegmatite bodies have been characterized in detail by Vorob'ev *et al.* (1987) and Evdokimov & Chakhmouradian (1994). Strontium-apatite occurs as "patches" (10–20  $\mu\text{m}$  across) along the rim and fractures in anhedral grains of strontian fluorapatite developed along fractures in the K-feldspar. These composite grains are replaced by strontianite at the margin (Fig. 4A). Strontian calcite also occurs in this association, but not in direct contact with the phosphates, which probably reflects the higher mobility of  $\text{Ca}^{2+}$  relative to  $\text{Sr}^{2+}$ . Other minerals found in the pegmatite include lamprophyllite, titanite, manganian pectolite and galena (Appendix 1). The overall variation in Sr content of strontian fluorapatite – strontium-apatite is from 24.7 to 42.6 wt.% SrO (1.41–2.71 *apfu* Sr). As the Na and *LREE* contents in these minerals are negligible (Table 4, *anal.* 5–10), their compositions plot on the  $\text{Ca}_5(\text{PO}_4)_3\text{X} - \text{Sr}_5(\text{PO}_4)_3\text{X}$  join (Fig. 3A).

#### *The Lac de Gras field, Northwest Territories, Canada*

Archetypal kimberlites typically contain accessory apatite that occurs as slender prismatic, spindle-shaped or hopper crystals, and radiating clusters. In most cases, this apatite is hydroxylapatite with low to moderate levels of Si, *LREE* and F, and characteristically low Sr contents (<1.0 wt.% SrO). The Lac de Gras kimberlites are unusual inasmuch as hydroxylapatite from these rocks is commonly enriched in Sr (Table 5, *anal.* 1–2). One of the samples examined contains, in addition to prismatic crystals, spherulites of apatite <70  $\mu\text{m}$  in diameter. This sample corresponds to hypabyssal kimberlite with abundant phenocrysts of monticellite and sieve-textured groundmass plates of tetra-ferriphlogopite. Opaque minerals are represented by complexly zoned crystals of spinel, *LREE*–Th–Nb–Fe-enriched perovskite, and heazlewoodite. The spherulites of apatite occur in a cavernous groundmass in intimate association with calcite, acicular suolunite and rosettes of phlogopite. In contrast to the groundmass plates, this phlogopite is poor in Si (2.52–2.91 *apfu*), enriched in Ba (up to 0.11 *apfu*), and displays a zoning pattern with a decrease in Ba, and an increase in K, Mg and Si con-

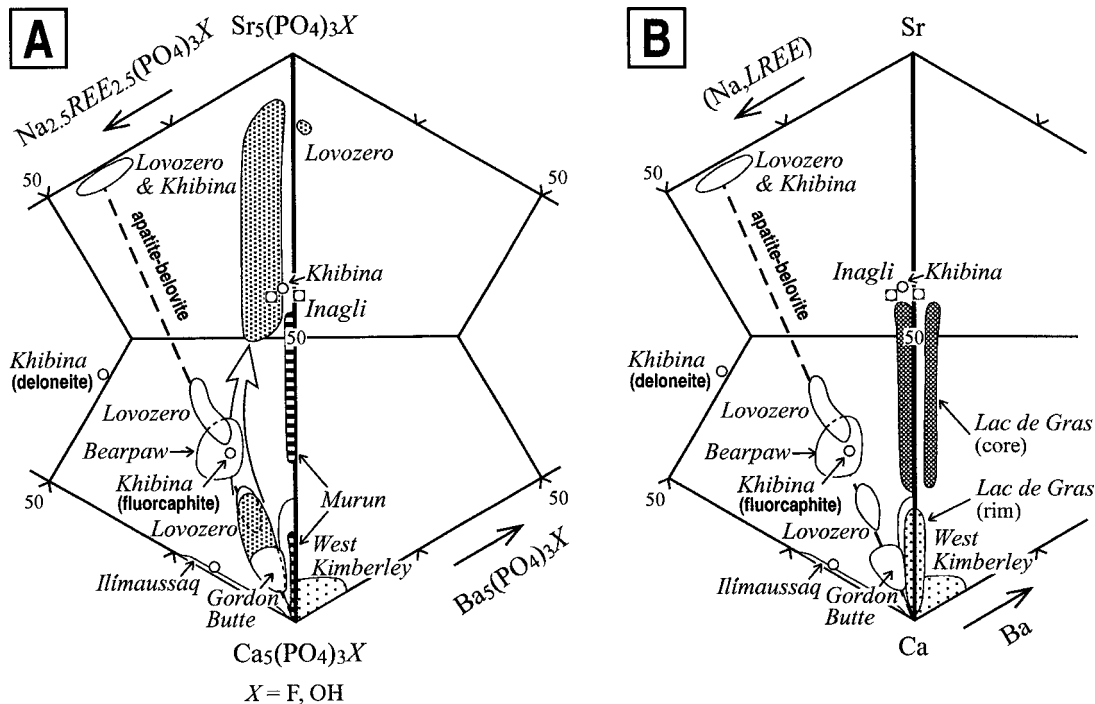


FIG. 3. Compositional variation of apatite-group minerals from alkaline rocks. (A) Peralkaline pegmatites of Lovozero (heavily dotted) and Murun (hatched); (B) Lac de Gras kimberlite. Also shown are compositional data for apatite-group minerals from diverse alkaline rocks of the Lovozero, Khibina, Inagli, Ilmaussaq, Bearpaw Mountains, and Gordon Butte (Rønso 1989, Pekov *et al.* 1995, Khomyakov 1995, Khomyakov *et al.* 1996, 1997, Chakhmouradian & Mitchell 1999, 2002), and from lamproites of the West Kimberley area, Australia (Edgar 1989).

tents toward a rim. Representative compositions of these minerals are given in Appendix 2.

BSE imaging reveals a complex internal structure of the apatite spherulites, with gradual and step-like changes in AZ from a core outward (Figs. 4B–D). Note that individual crystals in a spherulite show a longitudinal pattern of zoning rather than a more common core-to-rim pattern. “Roots” of the crystals are enriched in Sr, Ba and V relative to their terminations, whereas the Si, Na, LREE and K contents do not exhibit a regular variation across the spherulite (Fig. 5). The cores of some spherulites have  $Sr > Ca$  (*apfu*), and thus are strontium-apatite (Table 5, anals. 3–4; Fig. 3B). Secondary-electron imaging reveals that the outermost shell of spherulites consists of closely spaced prismatic crystals arranged into a honeycomb-like pattern. Compositionally, the terminations of crystals forming the spherulites are indistinguishable from discrete crystals of relatively Sr-poor hydroxylapatite found elsewhere in the ground-mass (Table 5, anals. 18–19). Comparatively smaller spherulites (<40  $\mu\text{m}$  across) are devoid of a high-AZ core. Many spherulites are incomplete, indicating that they grew attached to the surface of vesicles (Fig. 4B).

Neither the compositions of strontium-apatite nor Ca-dominant compositions can be satisfactorily recalculated to formulae on the basis of a total of 8 cations because the A:T cation ratio is invariably higher than 1.67. Elements other than P, Si and V capable of substituting in the tetrahedral site (*i.e.*, S, As, Se and Al) were sought, but not detected on the EDS spectra. Analyses were repeated several times using alternative standards for Ca, Sr and P and slightly different conditions of spectrum acquisition. A series of reference samples of strontian apatite with  $A:T \approx 1.67$  were analyzed alternately with the Lac de Gras specimen to ensure that the abnormal ratio of cations was not an artifact. In all these experiments, the A:T ratio in the spherulitic apatite was consistently higher than the “ideal” value. Finally, WDS analysis was employed to confirm the range of elements present in this apatite, as well as its deviation from stoichiometry. Taking into account the dramatic compositional variation across the spherulites, the results obtained by WDS are in reasonable agreement with the EDS data (*cf.* Table 5, anals. 8–11). Therefore, we suggest that both strontium-apatite and strontian apatite from Lac de Gras contain C substituting for P in the T

TABLE 3. REPRESENTATIVE COMPOSITIONS OF APATITE-GROUP MINERALS FROM LOVOZERO

Wt.%	1	2	3	4	5	6	7	8	9	10
Na <sub>2</sub> O	0.59	0.39	0.66	1.36	1.30	1.00	1.10	0.56	0.56	0.74
CaO	44.09	46.23	44.61	38.27	37.82	36.55	35.44	21.52	17.71	16.65
FeO	n.d.	0.68	0.47	n.d.	n.d.	n.d.	n.d.	0.74	0.79	0.51
SrO	3.40	4.74	5.53	9.58	11.60	14.54	15.64	36.53	40.90	41.68
La <sub>2</sub> O <sub>3</sub>	1.52	0.71	0.97	1.98	1.54	1.13	1.52	0.43	0.53	0.46
Ce <sub>2</sub> O <sub>3</sub>	3.86	1.80	1.91	4.08	3.16	2.21	2.89	1.58	1.85	2.03
Pr <sub>2</sub> O <sub>3</sub>	0.60	0.39	0.10	0.33	0.19	0.20	0.42	0.19	0.14	0.31
Nd <sub>2</sub> O <sub>3</sub>	1.57	0.69	0.69	1.64	1.26	1.36	1.27	0.61	0.66	0.58
SiO <sub>2</sub>	1.66	n.d.	n.d.	0.46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P <sub>2</sub> O <sub>5</sub>	36.23	39.35	38.53	36.57	36.99	36.52	36.36	33.04	32.29	31.97
F	2.09	1.75	1.07	2.20	2.49	2.13	2.17	0.93	0.89	1.02
-O=F <sub>2</sub>	0.88	0.74	0.45	0.93	1.05	0.90	0.91	0.39	0.38	0.43
Total	94.73	95.99	93.09	95.54	95.30	94.74	95.90	95.74	96.06	95.52

Structural formulae calculated on the basis of 8 cations:

Na	0.107	0.069	0.118	0.252	0.242	0.189	0.208	0.116	0.119	0.159
Ca	4.424	4.490	4.414	3.926	3.889	3.809	3.695	2.462	2.082	1.978
Fe	-	0.052	0.036	-	-	-	-	0.066	0.072	0.047
Sr	0.185	0.249	0.296	0.532	0.646	0.820	0.883	2.261	2.601	2.679
Ba	-	-	-	-	-	-	-	-	-	-
La	0.052	0.024	0.033	0.070	0.055	0.041	0.055	0.017	0.021	0.019
Ce	0.132	0.060	0.065	0.143	0.111	0.079	0.103	0.062	0.074	0.082
Pr	0.020	0.013	0.003	0.012	0.007	0.007	0.015	0.007	0.006	0.013
Nd	0.053	0.022	0.023	0.056	0.043	0.047	0.044	0.023	0.026	0.023
Si	0.155	-	-	0.044	-	-	-	-	-	-
P	2.872	3.021	3.012	2.965	3.007	3.008	2.997	2.986	2.999	3.000
Σ	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
F	0.619	0.502	0.312	0.666	0.756	0.655	0.668	0.314	0.347	0.358

n.d = not detected.

TABLE 4. REPRESENTATIVE COMPOSITIONS OF APATITE-GROUP MINERALS FROM LOVOZERO AND MURUN

Wt.%	1	2	3	4	5	6	7	8	9	10
Na <sub>2</sub> O	0.83	0.91	0.73	0.21	0.07	0.11	0.06	n.d.	n.d.	0.16
CaO	11.27	4.24	4.34	2.59	32.56	31.95	28.54	24.97	21.18	19.17
FeO	0.88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SrO	48.40	53.75	56.54	62.86	25.70	26.76	31.09	34.95	39.73	42.56
BaO	n.d.	1.89	1.67	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
La <sub>2</sub> O <sub>3</sub>	0.84	1.46	1.13	0.74	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ce <sub>2</sub> O <sub>3</sub>	3.05	2.86	2.02	0.71	n.d.	0.11	n.d.	n.d.	n.d.	n.d.
Pr <sub>2</sub> O <sub>3</sub>	0.53	0.43	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nd <sub>2</sub> O <sub>3</sub>	0.34	0.81	0.29	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SiO <sub>2</sub>	0.03	0.32	0.10	0.39	0.21	0.24	n.d.	n.d.	0.45	0.39
P <sub>2</sub> O <sub>5</sub>	31.17	28.04	28.54	27.86	35.29	35.20	34.56	33.50	32.12	31.78
F	0.74	1.26	1.70	2.42	1.90	2.05	1.75	2.35	2.13	1.69
-O=F <sub>2</sub>	0.31	0.53	0.72	1.02	0.80	0.86	0.74	0.99	0.90	0.71
Total	97.77	95.44	96.47	96.99	94.93	95.56	95.26	94.78	94.71	95.04

Structural formulae calculated on the basis of 8 cations:

Na	0.182	0.219	0.174	0.051	0.014	0.021	0.006	-	-	0.034
Ca	1.368	0.565	0.572	0.346	3.488	3.421	3.139	2.839	2.474	2.256
Fe	0.083	-	-	-	-	-	-	-	-	-
Sr	3.178	3.878	4.030	4.540	1.490	1.551	1.851	2.151	2.512	2.711
Ba	-	0.092	0.080	-	-	-	-	-	-	-
La	0.035	0.067	0.051	0.034	-	-	-	-	-	-
Ce	0.126	0.130	0.091	0.032	-	0.004	-	-	-	-
Pr	0.022	0.019	0.006	-	-	-	-	-	-	-
Nd	0.014	0.036	0.013	0.010	-	-	-	-	-	-
Si	0.003	0.040	0.013	0.049	0.021	0.024	-	-	0.049	0.043
P	2.989	2.954	2.970	2.938	2.987	2.979	3.004	3.010	2.965	2.956
Σ	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
F	0.265	0.496	0.661	0.953	0.601	0.648	0.568	0.789	0.734	0.587

n.d = not detected. 1-4 Lovozero; 5-10 Murun.

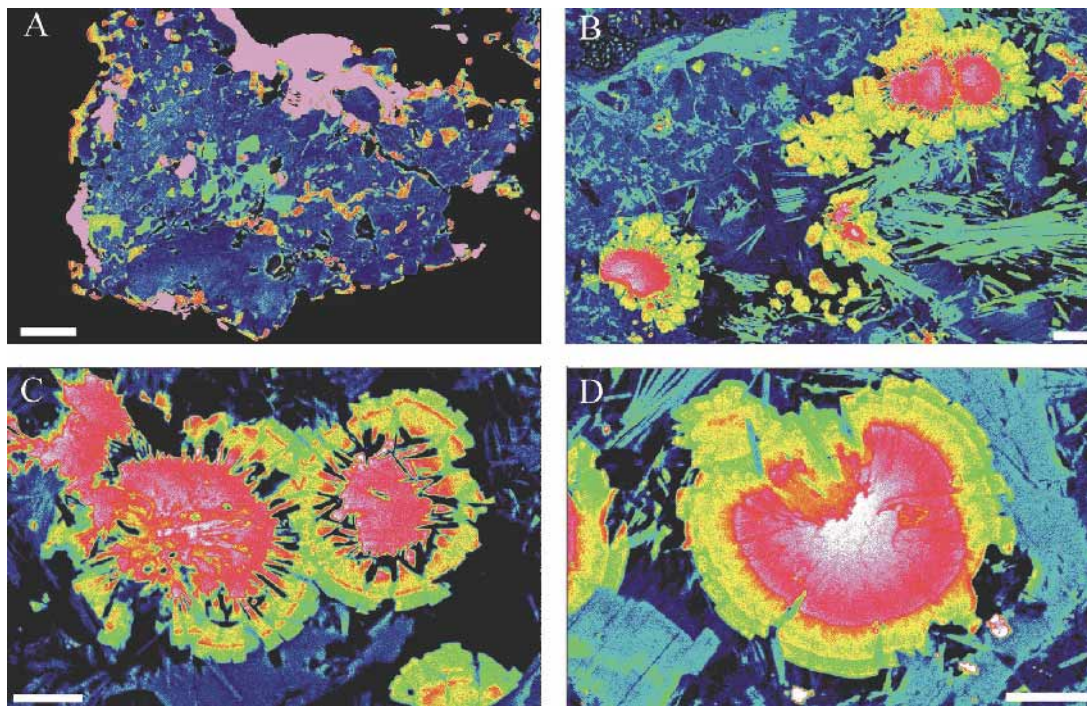


FIG. 4. False-color BSE images of apatite-group minerals from Murun (A) and Lac de Gras (B–D). (A) Anhedronal strontian fluorapatite (green-blue) and strontium-apatite (orange) rimmed by strontianite (mauve). (B) Spherulites and discrete crystals of apatite-group minerals (purple to yellow) associated with acicular suolunite (green). (C) Spherulites zoned from strontium-apatite (purple) to strontian carbonate-hydroxylapatite (yellowish green). (D) Zoned spherulite of strontian carbonate-hydroxylapatite associated with barian phlogopite (greenish blue). Scale bar 20  $\mu\text{m}$  for all images.

site. Although the incorporation of C may also generate vacancies in the A sites (see below), we calculated all formulae to a total of five Ca-site cations for lack of a better approach. The structural environment of C in apatite (*sensu lato*) is poorly understood. The major mechanism by which C may be incorporated into the structure involves substitution of  $(\text{CO}_3)^{2-}$  for  $(\text{PO}_4)^{3-}$ , accompanied by the replacement of one of the apical oxygen atoms in the tetrahedra by either  $\text{F}^{1-}$  or  $(\text{OH})^{1-}$  (e.g., McClellan & Van Kauwenbergh 1990, Sommerauer & Katz-Lehnert 1985, respectively). At present, the latter substitution is favored (especially, for low-temperature apatites), albeit it is not completely understood in terms of charge-balance mechanisms. In some studies (e.g., Regnier *et al.* 1994, Kol'tsov *et al.* 2000), it was suggested that charge compensation may also occur *via* the  $\text{Ca}^{2+} \leftrightarrow \text{Na}^{1+}$  substitution or the appearance of vacancies in the A positions simultaneously with the replacement of  $(\text{PO}_4)^{3-}$  by  $(\text{CO}_3)^{2-}$ . Neither alkalis nor F show any correlation with the proportion of C in strontian carbonate-hydroxylapatite studied in this work, assuming that this proportion corresponds to the apparent deficit of cations in the T site. In many cases, compositions with a similar number of cations differ

significantly in their F and Na + K contents (*cf.* Table 5, anals. 5 and 7, and 8 and 10, respectively).

## DISCUSSION AND CONCLUSIONS

### Crystal chemistry

Strontium is ubiquitous in apatite-group minerals from peralkaline, carbonatitic and alkali-ultramafic rocks. In most cases, this element is incorporated into the apatite structure *via* one of the following substitutions (Pushcharovskii *et al.* 1987, Rakovan & Hughes 2000, Fig. 3): 1)  $^{71}\text{Ca}^{2+} \leftrightarrow ^{71}\text{Sr}^{2+}$  (solid solution toward strontium-apatite), or 2)  $3^{71}\text{Ca}^{2+} + 2^{91}\text{Ca}^{2+} \leftrightarrow 3^{71}\text{Sr}^{2+} + ^{91}\text{Na}^{1+} + ^{91}\text{LREE}^{3+}$  (solid solution toward belovite).

Note that these schemes are simplified and only reflect the tendency of individual elements to partition into a specific site, but they do not account for cation disorder observed in the actual minerals. The rare mineral deloneite-(Ce) exemplifies an alternative mechanism of substitution involving six different large-cation sites; the overall distribution of cations in this structure is poorly ordered (Khomyakov *et al.* 1996).



TABLE 5. REPRESENTATIVE COMPOSITIONS OF APATITE-GROUP MINERALS FROM LAC DE GRAS

Wt.%	1	2	3	4	5	6	7	8‡	9	10‡
Na <sub>2</sub> O	0.12	0.15	0.61	0.52	0.66	0.68	0.84	0.54	1.00	0.70
K <sub>2</sub> O	n.d.	n.d.	0.11	0.12	0.19	0.05	0.22	0.10	0.21	0.11
CaO	53.28	53.88	18.88	18.65	23.05	23.31	27.58	27.44	29.00	29.58
FeO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.13	n.a.	0.13
SrO	2.71	2.86	43.11	42.55	39.15	36.80	31.40	30.52	30.64	27.41
BaO	0.35	n.d.	4.70	5.18	3.52	3.45	3.85	3.98	3.77	4.08
La <sub>2</sub> O <sub>3</sub>	0.06	0.25	0.18	0.53	0.50	0.40	0.35	0.23	n.d.	0.26
Ce <sub>2</sub> O <sub>3</sub>	0.02	0.30	0.16	0.46	0.53	0.45	0.19	0.09	0.22	0.18
Nd <sub>2</sub> O <sub>3</sub>	n.d.	0.02	n.d.	n.d.	0.21	0.14	0.03	n.d.	n.d.	n.d.
SiO <sub>2</sub>	1.02	0.88	1.67	1.50	2.55	2.55	2.33	1.97	2.16	1.65
P <sub>2</sub> O <sub>5</sub>	40.57	41.29	25.82	25.62	27.10	26.36	28.07	28.99	29.54	30.18
V <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	1.58	1.41	1.42	1.50	1.05	1.23	1.08	1.05
F	1.52	1.52	1.49	1.75	1.03	1.12	1.56	1.46	1.16	1.36
-O=F <sub>2</sub>	0.64	0.64	0.63	0.74	0.43	0.47	0.66	0.61	0.49	0.57
Total	98.01	100.51	97.68	97.55	99.48	96.34	96.81	96.07	98.29	96.12
Structural formulae calculated on the basis of:										
	8 cations:					5 A-cations:				
Na	0.020	0.024	0.122	0.105	0.126	0.133	0.158	0.105	0.184	0.133
K	-	-	0.014	0.016	0.024	0.006	0.027	0.013	0.025	0.014
Ca	4.836	4.824	2.085	2.072	2.433	2.528	2.875	2.937	2.954	3.110
Fe	-	-	-	-	-	-	-	0.011	-	0.011
Sr	0.133	0.139	2.576	2.559	2.236	2.159	1.772	1.768	1.689	1.560
Ba	0.012	-	0.190	0.211	0.136	0.137	0.147	0.156	0.140	0.157
La	0.002	0.008	0.007	0.020	0.018	0.015	0.013	0.008	-	0.009
Ce	0.001	0.009	0.006	0.017	0.019	0.017	0.007	0.003	0.008	0.006
Nd	-	0.001	-	-	0.007	0.005	0.001	-	-	-
Si	0.086	0.074	0.172	0.156	0.251	0.258	0.227	0.197	0.205	0.162
P	2.910	2.921	2.253	2.250	2.260	2.258	2.312	2.452	2.377	2.507
V	-	-	0.108	0.097	0.092	0.100	0.068	0.081	0.068	0.068
Σ	8.000	8.000	7.533	7.503	7.602	7.616	7.607	7.731	7.650	7.737
F	0.407	0.402	0.486	0.574	0.321	0.358	0.480	0.461	0.349	0.422

‡ Analyses obtained by WDS. n.d = not detected; n.a = not analyzed.

Our data demonstrate conclusively that the solid solution between naturally occurring apatite and strontium-apatite is continuous, and miscibility in that series is not affected by the presence of a minor proportion of the belovite component (Fig. 3). In the most Sr-rich compositions observed in this study (Table 4, anal. 4), *all* large cation sites must be occupied predominantly by Sr. Because of the very small size of the crystals, neither X-ray diffraction nor infrared spectroscopic study of this strontium-apatite was possible. From previous studies (Sudarsanan & Young 1972, Noetzold & Wulff 1998), we infer that compositions approaching Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH) are isostructural with fluorapatite, whereas intermediate members with higher Ca contents *may* have the P<sub>6</sub><sub>3</sub> symmetry proposed for the strontium-apatite from Inagli and Khibina (Klevtsova 1964, Pushcharovskii *et al.* 1987). The poor refinement statistics in both latter studies, as well as the fact that Pushcharovskii *et al.* (1987) did not test other possible structural models in their work, necessitate further structural studies.

According to Klevtsova (1964), the P<sub>6</sub><sub>3</sub>/m ⇒ P<sub>6</sub><sub>3</sub> reduction in symmetry results from splitting of the nine-fold-coordinated A<sub>I</sub> site into two symmetrically non-

equivalent sites. If this were the case, further increase in Ca content must lead to another phase transition, as apatite with minor to moderate contents of Sr does not depart from the P<sub>6</sub><sub>3</sub>/m symmetry (Hughes *et al.* 1991, Rakovan & Hughes 2000). Unfortunately, the compositions at which the P<sub>6</sub><sub>3</sub>/m ⇒ P<sub>6</sub><sub>3</sub> and P<sub>6</sub><sub>3</sub> ⇒ P<sub>6</sub><sub>3</sub>/m phase transitions occur have not been constrained. Preferential partitioning of Sr into the seven-coordinated A<sub>II</sub> site suggests that Ca *versus* Sr ordering at the A<sub>I</sub> site occurs where the A<sub>II</sub> site has been completely filled with Sr, *i.e.*, above 60 mol.% Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH). The compositions of strontium-apatite from both Inagli and Khibina plot near this composition (Fig. 2). It is noteworthy that Khattech & Jemal (1997) recorded an increase in the standard enthalpy of mixing near Sr<sub>3</sub>Ca<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>F in synthetic systems, which they interpreted as an indication of cation order. The transition back to the P<sub>6</sub><sub>3</sub>/m structure should occur at a point where all A sites are occupied predominantly by Sr, *i.e.*, at 90 mol.% Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH), or at somewhat lower Sr contents if Ca is partly disordered over two or three different sites.

It is not clear why an ordered P<sub>6</sub><sub>3</sub>-type phase has not been documented in synthetic systems (Sudarsanan & Young 1980, Noetzold & Wulff 1998). Although it is

TABLE 5 (Continued)

Wt.%	11	12	13	14	15	16	17	18	19
Na <sub>2</sub> O	0.79	1.03	1.41	1.16	1.30	1.72	1.46	1.23	1.60
K <sub>2</sub> O	0.17	0.16	0.23	0.04	0.07	0.18	0.08	0.06	0.04
CaO	31.49	32.92	34.64	46.45	50.37	50.62	52.09	53.23	54.17
SrO	28.08	25.72	22.71	10.64	7.23	6.44	5.02	3.08	1.95
BaO	3.92	3.73	3.59	0.04	n.d	0.15	0.02	0.12	n.d
La <sub>2</sub> O <sub>3</sub>	n.d	n.d	0.54	0.19	0.17	0.07	n.d	0.12	0.17
Ce <sub>2</sub> O <sub>3</sub>	0.21	n.d	0.47	0.33	0.17	0.08	n.d	n.d	0.26
SiO <sub>2</sub>	1.72	1.98	2.20	2.97	2.94	2.40	2.64	2.71	0.52
P <sub>2</sub> O <sub>5</sub>	29.85	29.70	29.51	32.64	34.44	33.78	34.35	35.11	38.39
V <sub>2</sub> O <sub>5</sub>	1.22	0.92	0.83	0.59	0.08	0.19	0.27	0.30	n.d
F	1.36	1.45	1.51	2.14	1.85	2.09	1.66	1.88	1.82
-O=F <sub>2</sub>	0.57	0.61	0.64	0.90	0.78	0.88	0.70	0.79	0.77
Total	98.24	97.00	97.00	96.29	97.84	96.84	96.89	97.05	98.15

Structural formulae calculated on the basis of 5 A-cations:

Na	0.143	0.185	0.248	0.192	0.207	0.270	0.230	0.194	0.248
K	0.020	0.019	0.027	0.004	0.007	0.019	0.008	0.006	0.004
Ca	3.160	3.275	3.369	4.259	4.431	4.399	4.526	4.646	4.645
Sr	1.525	1.385	1.195	0.528	0.344	0.303	0.236	0.146	0.090
Ba	0.144	0.136	0.128	0.001	-	0.005	0.001	0.004	-
La	-	-	0.018	0.006	0.005	0.002	-	0.004	0.005
Ce	0.007	-	0.016	0.010	0.005	0.002	-	-	0.008
Si	0.161	0.184	0.200	0.254	0.241	0.195	0.214	0.221	0.042
P	2.367	2.335	2.268	2.364	2.394	2.320	2.358	2.422	2.601
V	0.075	0.056	0.050	0.033	0.004	0.010	0.014	0.016	-
Σ	7.602	7.575	7.519	7.651	7.638	7.525	7.587	7.659	7.643
F	0.403	0.426	0.433	0.579	0.480	0.536	0.426	0.484	0.461

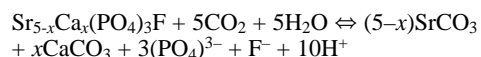
n.d = not detected.

possible that such a phase is stable only in a narrow compositional range or does not crystallize in these systems, the calorimetric measurements of Khattech & Jemal (1997) suggest otherwise. The lack of such data may result from the failure to recognize cation order in synthetic apatite-type compounds on the basis of their X-ray-diffraction patterns. Indeed, the *P6<sub>3</sub>/m* and *P6<sub>3</sub>* space groups have identical reflection-limiting conditions, and the two corresponding structures differ only in the intensity of some minor diffraction lines (Fig. 6). Alternatively, the degree of order may strongly depend on crystallization temperature and thermal history of the sample; neither of these parameters has been explored in relation to structural variations in Sr-bearing apatites.

#### Conditions of formation

Strontium-apatite from Lovozero and Murun is a late-stage mineral formed by reaction of the primary fluorapatite with deuterium fluids probably consanguineous with the pegmatites. In both cases, the apatite-group minerals evolved by becoming progressively enriched in Sr at essentially constant levels of Na, *LREE* and Si. At Murun, this evolutionary trend culminated at approximately 54 mol.% Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,OH). Further interaction between the fluid and apatite produced Sr-Ca

carbonates, which reflects decreasing  $\alpha(\text{PO}_4^{3-})$  and increasing alkalinity in the system, according to the reaction:



The potassic alkaline rocks of Murun (the pegmatites, especially) are significantly enriched in Sr relative to their sodic counterparts at Lovozero and other intracratonic complexes (Konev *et al.* 1996, Chakhmouradian & Mitchell 2002), and new occurrences of strontium-apatite at Murun are to be expected.

In the Lac de Gras kimberlite, the Sr-rich apatite (*sensu lato*) is an early groundmass mineral. Its mode of occurrence and unusual chemical composition indicate rapid crystallization following degassing of a kimberlitic magma. The apatite incorporated a significant amount of CO<sub>2</sub>, and also served as an effective sink for the "incompatible" elements accumulated in the fluid (Sr, Ba, *LREE* and V). Note that the phlogopite found in this environment is enriched in Ba (0.7–3.7 wt.% BaO), and the amount of Ba decreases toward the rim of the phlogopite crystals, mimicking the behavior of Ba in the apatite. The noticeable change in apatite morphology from the uniform spherical core to the outer

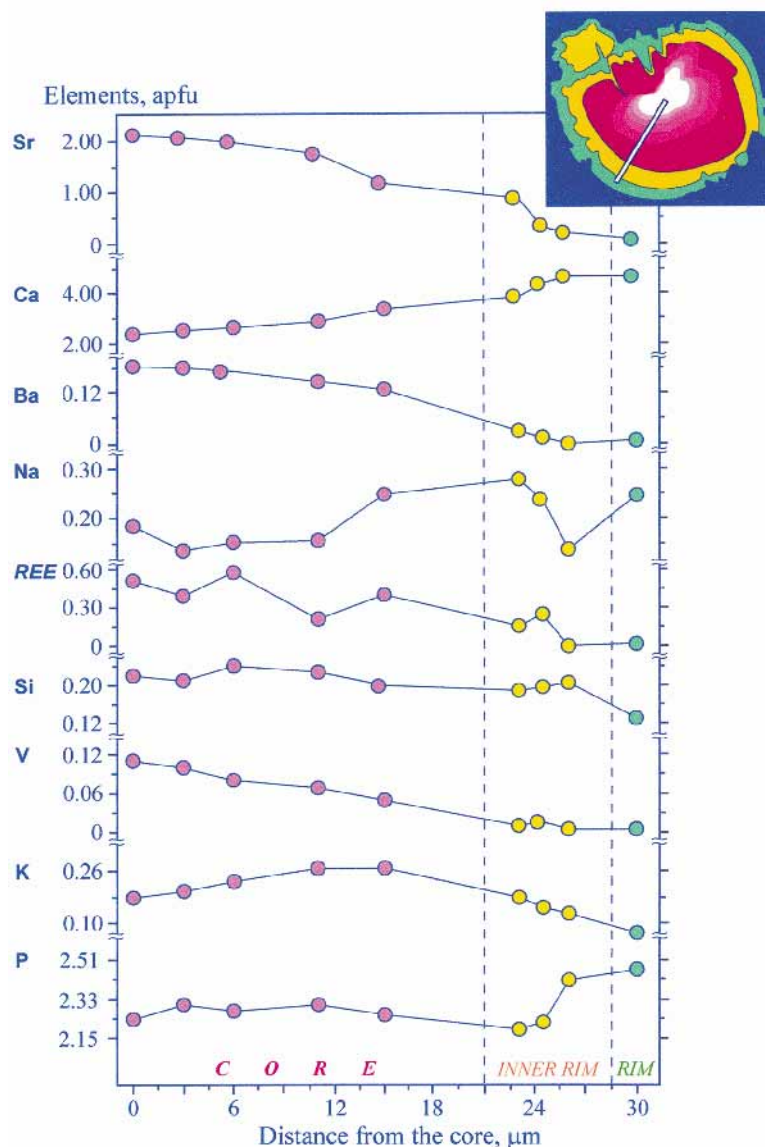


FIG. 5. Compositional variation of strontian hydroxylapatite along the contoured line shown in the inset (cf. Fig. 4D).

zone of the spherulites may be explained by an abrupt decrease in supersaturation of the fluid (Kozlova & Orlova 1985).

#### Nomenclature

The formula of strontium-apatite is given in Mandarino (1999) as  $(\text{Sr},\text{Ca})_5(\text{PO}_4)_3(\text{OH},\text{F})$ . However, the material studied by Efimov *et al.* (1962) and

Khomyakov (1995) is F-dominant (0.58 and 0.69 apfu F, respectively). Recently, Pekov *et al.* (1995) re-analyzed the type material from Inagli, and found it to contain 0.42 apfu F, and to lack detectable Mg, Fe and Al, unlike what was reported originally (Efimov *et al.* 1962). Note that samples from both Khibina and Inagli have been characterized structurally (Inorganic Crystal Structure Database Nos. 62899 and 20705, respectively), and their physical properties reported in much

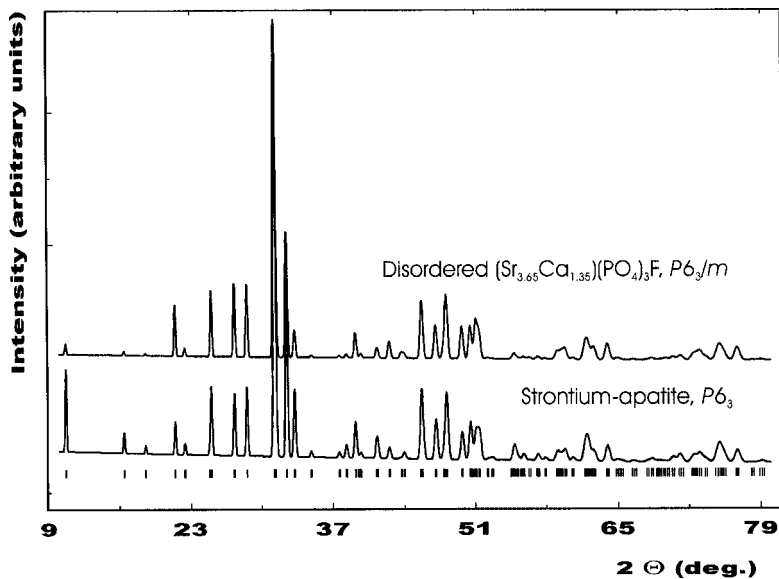


FIG. 6. X-ray diffraction patterns of partly disordered strontium-apatite from Khibina, and a hypothetical fully disordered compound of the same composition. The patterns were calculated using the FULLPROF full-profile refinement program for a wavelength of 1.5406 Å. The structural models used for calculations were based on the data of Pushcharovskii *et al.* (1987), and Rakovan & Hughes (2000).

detail. Hence, following the classification principles applied to the Ca-dominant members of the apatite group, the existence of two distinct mineral species should be recognized, namely “strontium-fluorapatite” and “strontium-hydroxylapatite”. Our analytical data (Tables 3–5) provide further evidence in support of such distinction. The relevant proposal for the Commission on New Minerals and Mineral Names of the IMA is being presently prepared by Chakhmouradian, Pekov and Khomyakov.

Both strontium-apatite (which is taken to be hydroxyl-dominant) and strontian hydroxylapatite appear to have significant capacity for the replacement of phosphate groups by  $(\text{CO}_3)^{2-}$ ; according to our data, as much as one sixth of the tetrahedral positions may be occupied by C (~3.6–4.4 wt.%  $\text{CO}_2$ ). McClellan & Van Kauwenbergh (1990) estimated the maximum possible C content in sedimentary apatite as 25% of the tetrahedral site (6–7 wt.%  $\text{CO}_2$ ). In the literature, compositions with the C content ranging from 0.03 to 0.62 *apfu* have been described as carbonate-apatites (*e.g.*, Chang *et al.* 1996, p. 310–313). Because the practice of naming  $(\text{CO}_3)^{2-}$ -bearing apatite clearly does not follow the “50% rule” (Nickel & Grice 1998), the Sr-dominant phosphate from the Lac de Gras kimberlites could be termed “strontium-carbonate-hydroxylapatite”. Unfortunately, the available data are insufficient for approval of the Lac de Gras material as a new mineral species,

and further studies of this unusual mineral are currently under way.

#### ACKNOWLEDGEMENTS

This study is supported by the Natural Sciences and Engineering Research Council of Canada, University of Manitoba (ARC), Lakehead University (EPR, RHM), and Ontario Ministry of Training (EPR). We gratefully acknowledge the help of Allan MacKenzie and Ron Chapman with analytical work. The insightful and constructive comments of John M. Hughes, Robert F. Martin and an anonymous reviewer helped to improve the manuscript. Igor Pekov is thanked for his comments on the nomenclature of apatite-group minerals, and Anne Hammond for sample preparation.

#### REFERENCES

- BUSSEN, I.V. & SAKHAROV, A.S. (1972): *Petrology of the Lovozero Alkaline Massif*. Nauka Press, Moscow, Russia (in Russ.).
- CHAKHMOURADIAN, A.R. & MITCHELL, R.H. (1999): Primary, apatitic and deuteric stages in the evolution of accessory Sr, REE, Ba and Nb-mineralization in nepheline-syenite pegmatites at Pegmatite Peak, Bearpaw Mts, Montana. *Mineral. Petrol.* **67**, 85–110.

- \_\_\_\_\_ & \_\_\_\_\_ (2002): The mineralogy of Ba- and Zr-rich alkaline pegmatites from Gordon Butte, Crazy Mountains (Montana, USA): Comparisons between potassic and sodic apatitic pegmatites. *Contrib. Mineral. Petrol.* (in press).
- CHANG, L.L.Y., HOWIE, R.A. & ZUSSMAN, J. (1996): *Rock-Forming Minerals. 5B. Non-Silicates: Sulphates, Carbonates, Phosphates, Halides.* Longman Group Ltd., Burnt Mill, U.K.
- DAWSON, J.B. (1993): A supposed sövite from Oldoinyo Lengai, Tanzania: result of extreme alteration of alkali carbonatite lava. *Mineral. Mag.* **57**, 93-101.
- EDGAR, A.D. (1989): Barium- and strontium-enriched apatites in lamproites from West Kimberley, Western Australia. *Am. Mineral.* **74**, 889-895.
- EFIMOV, A.F., KRAVCHENKO, S.M. & VASIL'eva, Z.V. (1962): Strontiapatite – a new mineral. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **142**, 113-116.
- EVDOKIMOV, M.D. & CHAKHMOURADIAN, A.R. (1994): Pegmatites of the Little Murun massif of ultrapotassic alkaline rocks. *Mineral. Zh.* **16**(3-4), 8-21.
- HALLERAN, A.D. & RUSSELL, J.K. (1996): REE-bearing alkaline pegmatites and associated light REE-enriched fenites at Mount Bisson, British Columbia. *Econ. Geol.* **91**, 451-459.
- HOGARTH, D.D., HARTREE, R., LOOP, J. & SOLBERG, T.N. (1985): Rare-earth element minerals in four carbonatites near Gatineau, Quebec. *Am. Mineral.* **70**, 1135-1142.
- HUGHES, J.M., CAMERON, M. & CROWLEY, K.D. (1991): Ordering of divalent cations in the apatite structure: crystal structure refinements of natural Mn- and Sr-bearing apatite. *Am. Mineral.* **76**, 1857-1862.
- KHATTECH, I. & JEMAL, M. (1997): Thermochemistry of phosphate products. II. Standard enthalpies of formation and mixing of calcium and strontium fluorapatites. *Thermochim. Acta* **298**, 23-30.
- KHOMYAKOV, A.P. (1995): *Mineralogy of Hyperapaitic Alkaline Rocks.* Clarendon Press, Oxford, U.K.
- \_\_\_\_\_, KULIKOVA, I.M. & RASTSVETAeva, R.K. (1997): Fluorcapthite  $\text{Ca}(\text{Sr}, \text{Na}, \text{Ca})(\text{Ca}, \text{Sr}, \text{Ce})_3(\text{PO}_4)_3\text{F}$  – a new mineral with an apatite-like structural motif. *Zap. Vser. Mineral. Obshchest.* **126**(3), 87-97 (in Russ.).
- \_\_\_\_\_, LISITSYN, D.V., KULIKOVA, I.M. & RASTSVETAeva, R.K. (1996): Deloneite-(Ce)  $\text{NaCa}_2\text{SrCe}(\text{PO}_4)_3\text{F}$  – a new mineral with a belovite-like structure. *Zap. Vser. Mineral. Obshchest.* **125**(5), 83-94 (in Russ.).
- KLEVTsoVA, R.F. (1964): On the crystal structure of strontium-apatite. *J. Struct. Chem.* **5**, 292-294.
- KOL'TSOV, A.B., FRANK-KAMENETSKAYA, O.V., ZORINA, M.L., KAMINSKAYA, T.N. & VERNIGORA, N.YU. (2000): Complex isomorphism in synthetic carbonate-apatites. *Zap. Vser. Mineral. Obshchest.* **129**(2), 109-117 (in Russ.).
- KONEV, A.A., VOROBEV, E.I. & LAZEBNIK, K.A. (1996): *Mineralogy of the Murun Alkaline Massif.* Siberian Branch, Russian Acad. Sci., Novosibirsk, Russia (in Russ.).
- KOZLOVA, O.G. & ORLOVA, A.O. (1985): Formation of spherulites. *Sov. Phys. Dokl.* **30**, 11-12.
- MANDARINO, J.A. (1999): *Fleischer's Glossary of Mineral Species.* The Mineralogical Record Inc., Tucson, Arizona.
- MCCLELLAN, G.H. & VAN KAUWENBERGH, S.J. (1990): Mineralogy of sedimentary apatites. In *Phosphorite Research and Development* (A.J.G. Notholt & I. Jarvis, eds.). *Geol. Soc., Spec. Publ.* **52**, 23-31.
- MITCHELL, R.H. (1995): *Kimberlites, Orangeites, and Related Rocks.* Plenum Press, New York.
- NICKEL, E.H. & GRICE, J.D. (1998): The IMA Commission on New Minerals and Mineral Names: procedures and guidelines on mineral nomenclature, 1998. *Can. Mineral.* **36**, 913-926.
- NOETZOLD, D. & WULFF, H. (1998): Structural and optical properties of the system  $(\text{Sr}, \text{Eu})_5(\text{PO}_4)_3(\text{Cl}, \text{F})$ . *Phys. Stat. Sol., Sect. B* **207**, 271-282.
- PEKOV, I.V., CHUKANOV, N.V., ELETskAYA, O.V., KHOMYAKOV, A.P. & MEN'SHIKOV, YU.P. (1995): Belovite-(Ce): new data, refined formula and relationships with other minerals of apatite group. *Zap. Vser. Mineral. Obshchest.* **124**(2), 98-110 (in Russ.).
- PLATT, R.G. & WOOLLEY, A.R. (1990): The carbonatites and fenites of Chipman Lake, Ontario. *Can. Mineral.* **28**, 241-250.
- PUSHCHAROVskII, D.YU., NADEZHINA, T.N. & KHOMYAKOV, A.P. (1987): Crystal structure of strontium-apatite from Khibiny. *Sov. Phys. Crystallogr.* **32**, 524-526.
- RAKOVAN, J.F. & HUGHES, J.M. (2000): Strontium in the apatite structure: strontian fluorapatite and belovite-(Ce). *Can. Mineral.* **38**, 839-845.
- REGNIER, P., LASAGA, A.C., BERNER, R.A., HAN, O.H. & ZILM, K.W. (1994): Mechanism of  $\text{CO}_3^{2-}$  substitution in carbonate-fluorapatite: evidence from FTIR spectroscopy,  $^{13}\text{C}$  NMR, and quantum mechanical calculations. *Am. Mineral.* **79**, 809-818.
- ROCK, N.M.S., GRIFFIN, B.J., EDGAR, A.D., PAUL, D.K. & HERGT, J.M. (1992): A spectrum of potentially diamondiferous lamproites and minettes from the Jharia coalfield, eastern India. *J. Volcan. Geotherm. Res.* **50**, 55-83.
- RÖNSBO, J.G. (1989): Coupled substitutions involving REEs and Na and Si in apatites in alkaline rocks from Ilímaussaq intrusion, South Greenland, and the petrological implications. *Am. Mineral.* **74**, 896-901.

- SOLOVOVA, I.P., GIRNIS, A.V. & GUZHOVA, A.V. (1993): Carbonatite melts in East Pamir alkali basalts. *Geochem. Int.* **30**(10), 74-85.
- SOMMERAUER, J. & KATZ-LEHNERT, K. (1985): A new partial substitution mechanism of  $\text{CO}_3^{2-}/\text{CO}_3\text{OH}^{3-}$  and  $\text{SiO}_4^{4-}$  for the  $\text{PO}_4^{3-}$  group in hydroxylapatite from the Kaiserstuhl alkaline complex (SW-Germany). *Contrib. Mineral. Petrol.* **91**, 360-368.
- STORMER, J.C., JR., PIERSON, M.L. & TACKER, R.C. (1993): Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. *Am. Mineral.* **78**, 641-648.
- SUDARSANAN, K. & YOUNG, R.A. (1972): Structure of strontium hydroxide phosphate,  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ . *Acta Crystallogr.* **B28**, 3668-3670.
- \_\_\_\_\_ & \_\_\_\_\_ (1980): Structure of partially substituted chlorapatite  $(\text{Ca,Sr})_5(\text{PO}_4)_3\text{Cl}$ . *Acta Crystallogr.* **B36**, 1525-1530.
- VELDE, D. & RACHDI, H.E.-N. (1988): Influence of Sr on an established petrological incompatibility: the association melilite + K-feldspar in a nepheline from Djebel Targou, central Morocco. *J. Petrol.* **29**, 585-597.
- VOROB'EV, E.I., KONEV, A.A., MALYSHONOK, YU.V., AFONINA, G.G. & PARADINA, L.F. (1987): *Tausonite: Geological Conditions of Formation and Mineral Parageneses*. Nauka Press, Novosibirsk, Russia. (in Russ.).
- YAKOVENCHUK, V.N., IVANYUK, G.YU., PAKHOMOVSKIY, YA.A. & MEN'SHIKOV, YU.P. (1999): *Minerals of the Khibina Massif*. Zemlya Press, Moscow, Russia.

Received July 23, 2001, revised manuscript accepted February 10, 2002.

APPENDIX 1. REPRESENTATIVE COMPOSITIONS OF MINERALS ASSOCIATED WITH STRONTIUM-APATITE FROM LOVOZERO AND MURUN

Wt.%	1*	2*	3	4	5	6	7	8	9	10
Nb <sub>2</sub> O <sub>5</sub>	n.a	n.a	n.a	2.13	n.d	n.a	1.69	n.d	n.a	n.a
SiO <sub>2</sub>	51.98	51.46	49.60	29.56	30.83	51.24	47.56	49.99	54.03	n.a
TiO <sub>2</sub>	1.44	1.37	1.17	26.97	28.36	0.73	0.57	1.15	n.a	n.a
ZrO <sub>2</sub>	1.05	0.66	n.d	0.16	0.74	n.d	11.95	11.25	n.a	n.a
Al <sub>2</sub> O <sub>3</sub>	0.83	0.72	1.13	0.29	n.d	0.28	n.d	n.d	0.09	n.a
Fe <sub>2</sub> O <sub>3</sub>	19.75	23.59	7.77	0.45‡	3.04‡	29.43	-	-	-	n.a
FeO	3.71	1.84	12.65	-	-	2.94	4.12	5.49	0.35	n.a
MnO	0.70	0.35	1.45	1.63	2.21	1.31	2.87	1.75	2.26	n.a
MgO	4.27	3.39	7.76	0.25	0.31	0.52	n.d	n.d	0.26	n.a
CaO	9.41	7.03	1.36	0.26	1.25	3.53	10.39	10.89	31.49	2.86
SrO	n.a	n.a	n.a	7.67	19.88	n.a	5.33	4.17	n.d	64.62
BaO	n.a	n.a	n.a	17.95	1.13	n.a	n.d	n.d	n.d	1.31
K <sub>2</sub> O	n.d	n.d	1.47	0.76	1.12	n.d	1.37	1.63	0.07	n.a
Na <sub>2</sub> O	8.62	9.90	8.87	11.26	10.39	11.26	9.88	9.58	9.17	n.a
Cl	n.a	n.a	n.a	n.a	n.a	n.a	0.36	0.57	n.a	n.a
CO <sub>2</sub>	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	30.07 <sup>§</sup>
-O=Cl <sub>2</sub>	-	-	-	-	-	-	0.08	0.13	-	-
Total	101.76	100.31	93.23	99.34	99.26	101.24	96.01	96.34	97.72	98.86
Structural formulae calculated on the basis of:										
	O = 6	O = 23	12 cations		O = 6	O = 29	O = 8.5	O = 3		
Nb	-	-	-	0.132	-	-	0.406	-	-	-
Si	1.956	1.960	7.813	4.035	4.020	1.966	25.270	25.731	2.992	-
Ti	0.041	0.039	0.139	2.770	2.782	0.021	0.228	0.445	-	-
Zr	0.019	0.012	-	0.011	0.047	-	3.096	2.824	-	-
Al	0.037	0.032	0.210	0.047	-	0.013	-	-	0.006	-
Fe <sup>3+</sup>	0.559	0.676	0.891	0.046	0.298	0.850	-	-	-	-
Fe <sup>2+</sup>	0.117	-	1.697	-	-	0.094	1.831	2.363	0.016	-
Mn	0.022	0.011	0.193	0.189	0.244	0.043	1.292	0.763	0.106	-
Mg	0.240	0.193	1.823	0.051	0.060	0.030	-	-	0.021	-
Ca	0.380	0.287	0.230	0.038	0.175	0.145	5.915	6.006	1.869	0.075
Sr	-	-	-	0.607	1.503	-	1.642	1.245	-	0.912
Ba	-	-	-	0.961	0.058	-	-	-	-	0.013
K	-	-	0.295	0.132	0.186	-	0.929	1.070	0.005	-
Na	0.629	0.730	2.709	2.981	2.627	0.838	10.179	9.561	0.985	-
Cl	-	-	-	-	-	-	0.324	0.497	-	-
CO <sub>3</sub>	-	-	-	-	-	-	-	-	-	1.000

n.a = not analyzed; n.d = not detected; \* Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio calculated from stoichiometry; ‡ total Fe given as Fe<sub>2</sub>O<sub>3</sub>; § calculated from stoichiometry. 1-4: Lovozero: 1-2 aegirine-augite, 3 magnesio-arfvedsonite, 4 barytolamprophyllite; 5-11 Murun: 5 lamprophyllite, 6 aegirine, 7-8 eudialyte, 9 pectolite, 10 strontianite.

APPENDIX 2. REPRESENTATIVE COMPOSITIONS OF MINERALS ASSOCIATED WITH STRONTIUM-APATITE FROM LAC DE GRAS

Wt.%	1	2*	3*	4*	5*	6	7	8*	9*	10	11
Nb <sub>2</sub> O <sub>5</sub>	n.a	n.a	n.a	n.a	n.a	2.32	3.45	n.a	n.a	n.a	n.a
SiO <sub>2</sub>	37.17	n.a	n.a	n.a	n.a	0.65	0.36	32.98	37.82	44.22	46.13
TiO <sub>2</sub>	n.d	1.42	1.64	8.58	7.26	44.98	44.15	0.09	0.26	n.d	n.d
ThO <sub>2</sub>	n.a	n.a	n.a	n.a	n.a	1.30	0.35	n.a	n.a	n.a	n.a
Al <sub>2</sub> O <sub>3</sub>	n.d	5.59	48.30	14.23	0.07	1.24	0.77	10.74	11.93	3.94	4.03
Fe <sub>2</sub> O <sub>3</sub>	-	7.81	20.04	42.42	56.92	4.60	5.36	14.58	7.15	-	-
Cr <sub>2</sub> O <sub>3</sub>	n.d	58.09	0.01	0.11	0.05	n.d	n.d	n.d	n.d	n.a	n.a
La <sub>2</sub> O <sub>3</sub>	n.a	n.a	n.a	n.a	n.a	1.90	3.01	n.a	n.a	n.a	n.a
Ce <sub>2</sub> O <sub>3</sub>	n.a	n.a	n.a	n.a	n.a	4.86	7.18	n.a	n.a	n.a	n.a
Nd <sub>2</sub> O <sub>3</sub>	n.a	n.a	n.a	n.a	n.a	2.11	1.89	n.a	n.a	n.a	n.a
FeO	8.32	13.45	11.12	22.08	29.23	-	-	3.81	5.92	0.10	0.24
MnO	0.34	0.26	0.24	0.46	1.54	n.d	n.d	0.24	0.40	0.07	n.d
MgO	22.40	13.32	19.43	12.37	4.46	n.d	n.d	21.17	22.37	0.07	0.37
CaO	33.44	n.a	n.a	n.a	n.a	33.59	31.32	n.d	n.d	36.22	36.17
SrO	n.a	n.a	n.a	n.a	n.a	0.35	0.44	n.d	n.d	n.d	n.d
BaO	n.a	n.a	n.a	n.a	n.a	n.d	n.d	3.72	0.68	n.d	n.d
K <sub>2</sub> O	n.d	n.a	n.a	n.a	n.a	n.d	n.d	9.03	10.59	0.87	1.17
Na <sub>2</sub> O	n.d	n.a	n.a	n.a	n.a	0.27	0.57	0.02	0.03	0.16	n.d
Total	101.67	99.94	100.78	100.25	99.53	98.38‡	99.59 <sup>#</sup>	96.38	97.15	85.65	88.11
Structural formulae calculated on the basis of:											
	O = 4	O = 4			O = 3		O = 11		4 cations		
Nb	-	-	-	-	-	0.026	0.039	-	-	-	-
Si	0.986	-	-	-	-	0.016	0.009	2.520	2.754	1.979	2.008
Ti	-	0.035	0.033	0.299	0.203	0.839	0.830	0.005	0.014	-	-
Th	-	-	-	-	-	0.007	0.002	-	-	-	-
Al	-	0.218	1.529	0.544	0.003	0.036	0.023	0.967	1.024	0.208	0.207
Fe <sup>3+</sup>	-	0.194	0.405	1.035	1.590	0.086	0.101	0.838	0.392	-	-
Cr	-	1.518	-	0.003	0.001	-	-	-	-	-	-
La	-	-	-	-	-	0.017	0.028	-	-	-	-
Ce	-	-	-	-	-	0.044	0.066	-	-	-	-
Nd	-	-	-	-	-	0.019	0.017	-	-	-	-
Fe <sup>2+</sup>	0.185	0.372	0.250	0.599	0.907	-	-	0.243	0.361	0.004	0.009
Mn	0.008	0.007	0.005	0.013	0.048	-	-	0.016	0.025	0.003	-
Mg	0.886	0.656	0.778	0.598	0.247	-	-	2.411	2.430	0.005	0.024
Ca	0.950	-	-	-	-	0.892	0.839	-	-	1.737	1.687
Sr	-	-	-	-	-	0.005	0.006	-	-	-	-
Ba	-	-	-	-	-	-	-	0.111	0.019	-	-
K	-	-	-	-	-	-	-	0.880	0.984	0.050	0.065
Na	-	-	-	-	-	0.013	0.028	0.003	0.004	0.014	-

n.a = not analyzed; n.d = not detected; \* Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio calculated from stoichiometry; ‡ total also includes 0.21 wt.% Ta<sub>2</sub>O<sub>5</sub> (0.001 apfu Ta); <sup>#</sup> total also includes 0.74 wt.% Pr<sub>2</sub>O<sub>3</sub> (0.007 apfu Pr). 1 Monticellite; 2-5 zoned crystal with a magnesiochromite core (2), spinel intermediate zone (3), and magnetite rim (4-5); 6-7 perovskite; 8-9 phlogopite (core and rim, respectively); 10-11 suolunite.